Holocene Carbon and Nitrogen Accumulation Rates and Contemporary Carbon Export in Discharge

A Study from a Boreal Fen Catchment

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Cover: Winter, spring, summer, and autumn at Degerö Stormyr.
(photo: M. Blackburn (winter and spring), M. Gazovic (summer and autumn))

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Past carbon and nitrogen accumulation rates and contemporary carbon export in discharge – a study from a boreal fen catchment

Abstract

The contemporary role of mires in land-atmosphere exchange of carbon dioxide (CO_2) is the subject of intense scientific debate. Investigating patterns and mechanisms of variations in past carbon (C) accumulation rates as well as contemporary C fluxes of peatlands facilitates predictions of future mire C sink strength under a changing climate. Nitrogen (N) is an important macro-nutrient and thereby strongly coupled to the C accumulation rate. Thus, I have investigated Holocene C and N accumulation rates and their potential controls, and the annual and seasonal stream C export during the Holocene at the oligotrophic fen Degerö Stormyr in northern Sweden.

The mean (±SD) long-term apparent rates of C and N accumulation (LORCA and LORNA) were estimated to 13.7±5.5 g C m^{-2} yr^{-1} and 0.28±0.14 g N m^{-2} yr^{-1}, respectively. These rates were relatively low compared to those of other northern peatlands. Variations in C and N accumulation rates exhibited similar temporal patterns largely coinciding with major changes in botanical remains, and mainly primary production controlled the accumulation rates. The botanical composition had a major impact on the degree of decomposition, with indications of enrichment of recalcitrant compounds in highly degraded peat, as well as differences in ^{13}C-^{12}C composition of litter at the onset of decomposition. There were also indications of preferential plant uptake of ^{14}N at higher N availability.

Stream total C export was primarily driven by discharge, with average annual C export estimated to 12.2 g m^{-2} yr^{-1} over twelve years. This flux typically corresponded to 25-37% of the mean annual net uptake of CO_2 (NEE). However, during a year with a dry summer and wet autumn the discharge C export corresponded to as much as 90%, highlighting the importance of seasonality. The highest TOC export was exhibited during summer when accounting for differences in discharge, underlining the importance of timing of precipitation for the seasonal C export. Seasonal variations in C quality ($SUVA_{254}$) indicate different within mire sources of TOC during the year.

In this thesis I conclude the importance of primary production for C and N accumulation rates, and highlight the importance of seasonality for stream C export from mires.

Keywords: peat, mire, carbon accumulation, nitrogen accumulation, $\delta^{13}C$, $\delta^{15}N$, TOC, DIC, CH_4, stream carbon export

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Dedication

Till Lars, Tina, Samuel och David.

I had a screw loose, but now I lost it.
Mark Blackburn

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Larsson, A. Segerström, U. Laudon, H. and Nilsson, M.B. Holocene carbon and nitrogen accumulation rates in a boreal oligotrophic fen (submitted manuscript).

II Leach, J. Larsson, A. Nilsson, M.B. and Laudon, H. Twelve-year interannual and seasonal variability of stream carbon export from a boreal peatland catchment (manuscript).

The contribution of Anna Larsson to the papers included in this thesis was as follows:

I Contributing to idea and hypothesis, main responsible person for planning and performing field work, laboratory and data analysis, data interpretation, and writing of the manuscript.

II Contributing to idea and hypothesis, data interpretation, and writing of the manuscript.

Abbreviations

C	Carbon
CH_4	Methane
CO_2	Carbon Dioxide
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
GHG	Greenhouse Gas
IPCC	Intergovernmental Panel on Climate Change
LOI	Loss On Ignition
LORCA	Long-term Apparent Rate of Carbon Accumulation
LORNA	Long-term Apparent Rate of Nitrogen Accumulation
N	Nitrogen
TOC	Total Organic Carbon

1 Introduction

Northern peatlands store about one third of the global soil carbon (C) pool (Post *et al.*, 1982; Loisel *et al.*, 2014), although they cover only 3% of the land surface of the Earth (Maltby & Immirzi, 1993). The substantial amount of C stored in northern peatlands is of high importance if fluxes of C to and from these landforms change under a changing climate, affecting the C sink strength of mires and potentially resulting in increased concentrations of greenhouse gases (GHGs) in the atmosphere. According to the Intergovernmental Panel on Climate Change (IPCC) the climate in northern latitudes, including northern Europe (IPCC, 2013; Stocker *et al.*, 2013), will be warmer and wetter under a future changing climate. A warmer climate increases the potential for increased gross primary production (GPP) as well as decay, which could result in changed C fluxes to the atmosphere. Wetter conditions tend to lead to lower ecosystem respiration and increased GPP, than under drier conditions. However, lack of field data limits the possibility to quantify global change impacts on peatlands, which could potentially result in further effects on the climate (Frolking *et al.*, 2011). Long term rate of C accumulation (LORCA) and C in discharge constitute important components of the total C balance of peatlands (Turunen et al., 2002; Roulet et al., 2007; Nilsson et al., 2008; Koehler et al., 2011; Dinsmore et al., 2013; Loisel et al., 2014). Investigating patterns and mechanisms of variations in past C accumulation, as well as how contemporary C fluxes from peatlands vary, facilitates predictions on future C fluxes under a changing climate.

Nitrogen (N) is an important macro-nutrient and is coupled to the C accumulation rate as plant growth in peatlands may be limited by N availability (Aerts *et al.*, 1992; Limpens *et al.*, 2011). An altered N supply could cause changes in the dominating plant species (Wiedermann *et al.*, 2007; Eriksson *et al.*, 2010), and thereby the productivity and C accumulation rate, and hence it is important to understand the link between C and N in peatlands. The stock of N in peatlands is estimated to 9.7 Gt (Loisel *et al.*, 2014), making up about

10% of the global soil N pool of 95 Gt (Post *et al.*, 1985). Relatively few studies have reported N concentrations over depth profiles in peatlands (Loisel et al., 2014), and even less have reported C and N accumulation rates over depth profiles. The faith of mire N stocks under a changing climate is not well known (Loisel *et al.*, 2014), and therefore, fundamental research in this area is important.

1.1 Objectives

The main goals of this thesis were to determine the long-term apparent C and N accumulation rates (LORCA and LORNA, respectively) of a boreal mire, and aquatic losses of C from the mire catchment. In Paper I LORCA and LORNA of the oligotrophic fen Degerö Stormyr in northern Sweden were investigated and significant variations in C and N accumulation rates were interrelated with variables such as Loss On Ignition (LOI), C:N ratio, stable C and N isotopes, plant macrofossil composition of the peat, and degree of decomposition of bulk peat. This was done to examine controls of long-term C and N accumulation rates.

In Paper II a twelve year record of total organic carbon (TOC), dissolved inorganic carbon (DIC) and methane C (CH_4-C) in discharge from the Degerö Stormyr mire catchment was analyzed. This was done through exploration of associations between stream C export and hydroclimate conditions, carbon concentration, and TOC quality to further improve our understanding of inter-annual and seasonal variation of aquatic C export.

1.2 Mires as landforms

Mires are peat forming landforms with high ground water table. Peat accumulation takes place in mires when the primary production of plants is larger than the decay of organic material. Peat formation is controlled by external as well as internal forces, such as climate and local topography and edaphic conditions (Ivanov 1981; Korhola 1994; Belyea & Baird 2006). Peat has accumulated in northern peatlands since the end of the last glaciation, a time period called the Holocene.

There are two major forms of mires: minerogenous fens where the ground water table is in contact with the surrounding catchment, and ombrogenous bogs where the ground water table is independent of the surrounding catchment (Charman, 2002). Fens are potentially more rich in nutrients and less acidic than bogs due to the connectivity to the surrounding catchment, but the nutrient level is dependent on the character of the bedrock and soil type in the area

(Immirzi *et al.*, 1992). In Scandinavia the bedrock and soil is mostly poor and acidic (Wastenson *et al.*, 1994), resulting in comparably poor fens.

Mires are often comprised of two layers (*Figure 1*) – the shallow layer with a variable ground water table, and the deeper layer that is constantly under water (Ingram, 1978). In the shallow layer, termed acrotelm, the decay rate is relatively high compared to the deeper catotelm (Ingram, 1978; Clymo, 1984). Hence, a large proportion of the sequestered C is released in the acrotelm, and the proportion that is left in the peat is incorporated into the catotelm.

1.3 Carbon and mires

Historically, mires have acted as sinks to C, the stored peat in itself making up the evidence. The long-term apparent C accumulation rate (LORCA) is the average accumulation rate since the start of peat build-up, and hence the result of all C fluxes over an extended period of time. The C losses from mires are the product of production, consumption and transport of dissolved carbon (c.f. Koprivnjak and Moore, 1992). Carbon dioxide (CO_2) is sequestered by plants (*Figure 1*) and is then either incorporated into plant biomass or emitted back to the atmosphere. Organic material produced by plants can be incorporated into peat or decomposed and ultimately released to the atmosphere (see section 1.3.1), or transported from the mire in discharge (see section 1.3.2). The different gaseous and aqueous C fluxes (*Figure 1*) contribute to the annual and seasonal C balance to different degrees depending on biotic and abiotic conditions.

1.3.1 Carbon fluxes between mire and atmosphere

The net flux of CO_2, i.e. the difference between CO_2 uptake and CO_2 loss, is termed net ecosystem exchange (NEE). Carbon is also released to the atmosphere in the form of CH_4 (*Figure 1*), which is released primarily from the wetter part of peatlands. Over a period of 100 years CH_4 is 34 times more potent as a GHG than CO_2 (Myhre *et al.*, 2013) making its contribution to global change significant. Atmospheric deposition of C containing compounds is generally low (Dillon & Molot, 1997; Willey *et al.*, 2000) and makes only a small contribution to the C balance (c.f. Koprivnjak and Moore, 1992).

1.3.2 Carbon fluxes in water

In minerogenous fens, as opposed to ombrogenous bogs, carbon is imported with water from the surrounding catchment (*Figure 1*). The import is generally small compared to the C balance of the peatland. The aqueous losses of C (*Figure 1*) are however significant, made up by total organic carbon (TOC), including particulate (POC) and dissolved (DOC) species, dissolved inorganic carbon (DIC), and CH_4.

The annual variations in C export in the northern latitudes is driven by discharge (Clark *et al.*, 2007), with wet years resulting in high fluxes of C and the contrary for dry years. In regions with snow rich winters a significant proportion of the annual export of C occurs during the snow melt (c.f. Finlay et al., 2006; Ågren et al., 2007). The concentration of C species in discharge from mires decrease at high flows, such as freshet and rain events, due to dilution (c.f. Dinsmore et al., 2013; Wallin et al., 2010; Ågren et al., 2012), though increased DOC concentrations has been reported at higher discharge as well (Dinsmore *et al.*, 2013).

The high hydraulic conductivity of the acrotelm compared to the catotelm, results in high lateral movement of water in the acrotelm, but there is also evidence indicating vertical movement in the catotelm to be important. Studies of water movement within mires (Charman *et al.*, 1994; Siegel *et al.*, 1995; Waddington & Roulet, 1997), and variations in dissolved C concentrations (Nilsson & Bohlin, 1993) and age of gaseous C with depth in mires (Charman *et al.*, 1994), indicate that the source within mires to stream C varies depending on e.g. season, precipitation and evapotranspiration patterns. Seasonally changing C sources to DOC in discharge can be indicated using specific ultraviolet absorbance at 254 nm divided by DOC concentration ($SUVA_{254}$; c.f. Ågren et al., 2008). $SUVA_{254}$ is a measure of DOC quality, and is strongly and positively correlated to the aromaticity of DOC (Weishaar *et al.*, 2003).

1.4 Nitrogen and mires

The long-term apparent N accumulation rate (LORNA) is the average N accumulation rate since mire initiation and the result of all N fluxes since the onset of peat formation.

1.4.1 Nitrogen fluxes between mire and atmosphere

Atmospheric N is added to mires through atmospheric deposition and N fixation (*Figure 2*). The atmospheric deposition includes inorganic additions of NO_x and NH_y as well as organic N, such as amino acids and organic nitrates (Neff *et al.*, 2002; Limpens *et al.*, 2006). N fixation is performed by a number of different bacteria and other organisms, in a number of different environments, though minerotrophic nutrient rich conditions seem to be the most favorable (Dickinson, 1983; Limpens *et al.*, 2006).

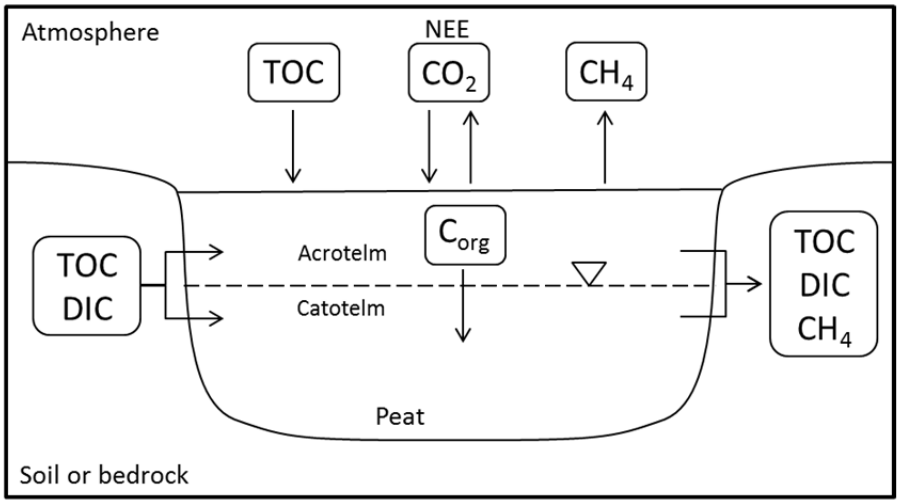

Figure 1. Schematic picture of C fluxes within a mire and between a mire (fen) and the surroundings. The dashed line indicates the boundary between acrotelm and catotelm, and the triangle denotes the permanent water table level. TOC is total organic carbon, NEE is net ecosystem exchange of carbon dioxide (CO_2), CH_4 is methane, DIC is dissolved inorganic carbon, and C_{org} is organic carbon.

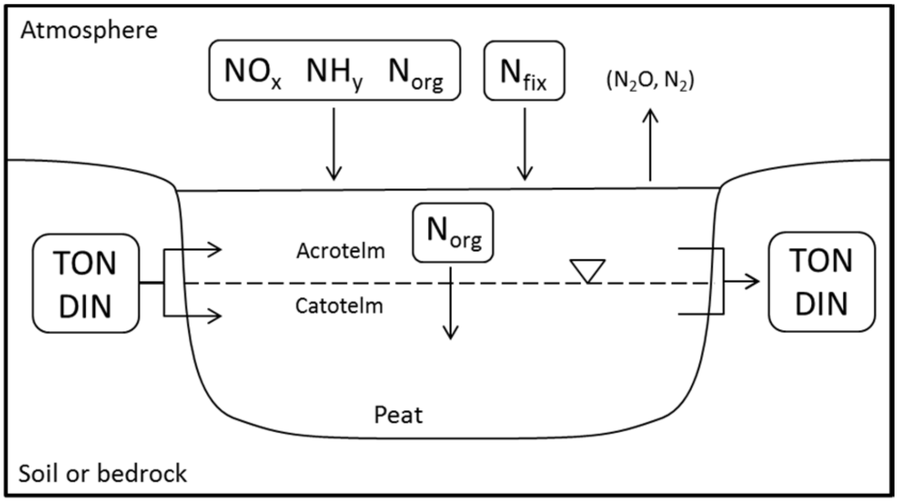

Figure 2. Schematic picture of N fluxes within a peatland and between a mire (fen) and the surroundings. The dashed line indicates the boundary between acrotelm and catotelm, and the triangle denotes the permanent water table level. NO_x and NO_y are inorganic N species, N_{org} is organic N species, TON is total organic N, and DIN is dissolved inorganic N.

Nitrogen is possibly lost to the atmosphere through denitrification (reduction of NO_3^- to gaseous N_2O or N_2; Limpens et al., 2006). Difficulties measuring denitrification probably contributed to scarcity of data on denitrification rates (Wray & Bayley, 2007), but in poor bogs and fens the rates should be small or quantitatively unimportant due to NO_3^- uptake by plants and microbes (Urban *et al.*, 1988). Due to the limited denitrification, N_2O and N_2 losses from mires should be small (Urban & Verry, 2011).

1.4.2 Nitrogen fluxes in water

In addition to atmospheric N deposition and fixation, N is added to fens through inflow from the surrounding catchment (*Figure 2*). The main losses of N from peatlands are through runoff. The dominating species in discharge from mires are primarily TON, but inorganic ammonium is of quantitative importance as well.

1.5 Stable isotopes

Isotopes can be used to trace biological processes, and isotopes commonly used to do this are $\delta^{13}C$ and $\delta^{15}N$. The $\delta^{13}C$ and $\delta^{15}N$ signatures of bulk peat are the results of fractionation during C fixation (photosynthesis), N fixation by microbes, microbial processes such as decomposition (Limpens *et al.*, 2006), and possibly plant and mycorrhizal N uptake, similarly to fractionation in other ecosystems (Högberg *et al.*, 1996, 1999; Nadelhoffer *et al.*, 1996). It is, however, often complicated to interpret underlying reasons for variations in the isotopic signature of different matrices, since many different processes of mixing and fractionation may underlie these signatures. In general terms, the heavier isotopes tend to react slower in kinetic reactions and concentrate where chemical bonds are the strongest in exchange reactions. At abundance of an element the heavier isotope tend to be depleted in the product of a reaction, and i.e. discriminated against (Fry, 2006).

2 Methods

2.1 Site description

The study site, the Degerö Stormyr catchment (2.7 km^2, 64°11’N and 19°33’E, 270 meters above sea level, *Figure 3*) is situated ca 70 km from the Gulf of Bothnia in northern Sweden, and within the Kulbäcksliden research park. The areal coverage of the catchment is 70% mire and 30% till covered by coniferous forest. The studied oligotrophic fen has an area of 1.9 km^2 and lies within a mixed mire system covering 6.5 km^2. The system consists of a number of interconnected mires with islands and ridges of till. The soils in the area are till, peat or gyttja (organic-rich lake sediments) underlain by gneiss bedrock (Malmström, 1923).

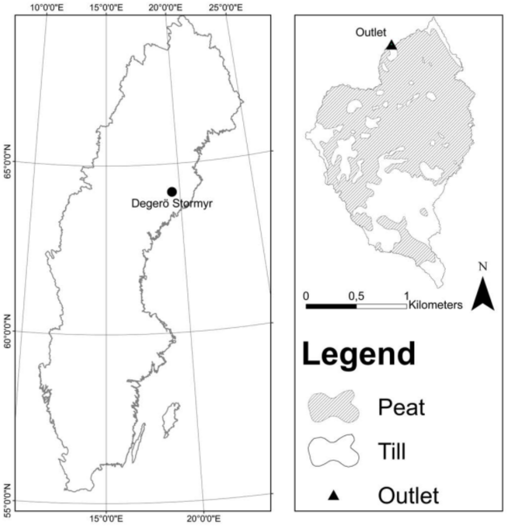

Figure 3. Location and outline of the Degerö Stormyr catchment. Soil types are indicated by hatched (peat) and blank (till) areas.

The climate at the site is defined as cold temperate humid type and the 1981-2010 mean annual temperature is +1.8°C, and the mean January and July temperatures are -9.5°C and +14.7°C, respectively. The mean annual precipitation during the same period was 614 mm (Laudon *et al.*, 2013), of which about 35% falls as snow (Löfvenius *et al.*, 2003). The climate data were recorded 10 km from the mire at the reference climate station Svartberget.

In general the vascular plant community of the peatland is dominated by *Eriophorum vaginatum* L., *Trichophorum cespitosum* L. Hartm., *Vaccinium oxycoccos* L., *Andromeda polifolia* L., and *Rubus chamaemorus* L. The bottom layer in the hollows is dominated by *Sphagnum majus* C. Jens. and *Sphagnum balticum* C. Jens. with *Sphagnum lindbergii* Schimp. occuring sparsely. The field layer in the hollows is very sparsely developed and dominated by *E. vaginatum*, *A. polifolia*, and *V. oxycoccus*, with *Carex magellanica* Lam., *Scheuchzeria palustris,* and *T. cespitosum* occurring even more sparsely. The bottom layer of the carpets is dominated by *S. majus*, while the lawns are dominated by *S. balticum,* and *S. lindbergii*. On the hummocks *Sphagnum fuscum* Schimp. Klinggr. and *Sphagnum rubellum* Wils. are the most common mosses.

The forested part of the catchment is a mixed coniferous forest (*Pinus sylvestris* L. and *Picea abies* L. H. Karst) with minor contribution by birch (*Betula pubescens* Ehrh.). The forest floor vegetation is dominated by dwarf shrubs, typically *Vaccinium vitis-idea* L. and *Vaccinium myrtillus* L., and mosses (e.g. *Hylocomium splendens* Hedw. Schimp. and *Pleurozium schreberi* Brid. Mitt).

2.2 Sampling and analysis

2.2.1 C and N accumulation (Paper I)

Figure 4. Sampling of deep peat. (Photo: A. Larsson)

Peat cores were retrieved from a hollow in late March 2009 (*Figure 4*), between 60 and 374 cm depth. A Russian peat corer (Jowsey, 1966) with 50 cm long, 5 cm diameter collector was used. The cores were taken without overlap. The peat cores were divided into slices of two centimeters thickness. Bulk density was determined for 94 slices, of which 10 was split to allow for ^{14}C dating on one half. LOI was determined roughly every 12 cm from 37 slices, with higher frequency where LOI was variable. The C and N contents and stable C and N isotopes were determined on 25 bulk samples evenly spread out along the peat cores. Analysis of degree of decomposition, macro fossil, and algae and animal remains were performed on 26 slices by the Institute of Horticulture, Russian Academy of Agricultural Sciences, Vereya, Russia. Methods used are further described in Paper I and a summarizing table of analyses made is found in the supplementary information of Paper I (Table S1).


Figure 5. Sphagnum leaves used for ^{14}C dating. (Photo: A. Larsson)

To retrieve the age of peat from different depths 21 samples were ^{14}C dated using Accelerator Mass Spectrometry (AMS) at the Ångström Laboratory, Uppsala, Sweden. The dated macrofossil material was mostly *Sphagnum* spp. leaves and stems, but a few macrofossils of other mosses and a coniferous seed were dated as well (*Table 1*). The macrofossils were picked using forceps from under a microscope (*Figure 5*). Fifteen samples from 13 depths were used to model the age-depth relationship (*Figure 6*; software: clam 1.0; Blaauw, 2010; http://chrono.qub.ac.uk/blaauw/clam.html; calibration curve IntCal09, smooth spline with spar 0.4; programming language R; version 3.0.2, R Development Core Team, 2010). Samples with inconsistent ^{14}C ages compared to the nearby samples were excluded. Details regarding excluded samples and methods used are found in Paper I. The modelled ages, together with depth, were used to calculate the vertical peat growth rate. Carbon and N accumulation rates were calculated according to:

$$A_X = r \times \rho \times X \qquad \text{Equation 1}$$

where r is the vertical peat growth rate (mm yr^{-1}), ρ is the organic matter bulk density dry mass (g cm^{-3}), and X denotes C or N content as a relative proportion (0-1) of the bulk density dry mass. Averages over 5700 years were calculated to obtain LORCA and LORNA. Regression analysis was used to test correlation between C content and δ^{13}C signature, as well as the C:N ratio and δ^{15}N signature. Significant differences were considered when $p < 0.05$.

Table 1. *Depth, ^{14}C age, calibrated ^{14}C age from the Ångström Laboratory, calibrated ^{14}C age retrieved from clam 1.0, $\delta^{13}C$ from ^{14}C analysis, and macrofossil material of dated samples.*

Sample code	Lab code[a]	Depth interval (cm)	^{14}C age (BP[b])		Ångström 2SD cal age range (BP)	clam 2SD cal age range (BP*)	$\delta^{13}C$ (‰ VPDB)	Material
DS1	Ua-38650	59-61	779	±44	780 – 660	777 - 664	-27,8	*Sphagnum* spp. leaves, moss stems
DS4	Ua-38651	94-96	1173	±36	1180 – 970	1217 - 979	-27,4	*Sphagnum* spp. leaves, moss stems
DS7	Ua-38652	129-131	1773	±55	1830 – 1550	1823 - 1554	-28,5	*Sphagnum* spp. leaves, moss leaves and stems
DS10	Ua-38653	163-165	2159	±47	2320 – 2000	2312 - 2007	-29,8	*Sphagnum* spp. leaves, moss stems
DS35	Ua-40076	181-183	2433	±30	2700 – 2350	2699 - 2354	-29	*Sphagnum* spp. leaves, moss stems
DS13	Ua-38654	198-200	3338	±63	3730 – 3400	3806 - 3406	-27,6	*Sphagnum* spp. leaves, moss stems
DS36	Ua-40077	219-221	3652	±31	4090 – 3880	4083 - 3890	-25,2	*Sphagnum* spp. leaves, moss stems
DS16	Ua-38655	240-242	4550	±106	5600 – 4850	5571 - 4877	-28,1	*Sphagnum* spp. leaves
DS19	Ua-38656	268-270	4538	±64	5450 – 4970	5446 - 4973	-27,1	*Sphagnum* spp. leaves, moss leaves and stems
DS37	Ua-40078	283-285	4398	±31	5220 – 4860	5210 - 4866	-29	*Sphagnum* spp. stems and leaves, moss leaves
DS30RB1	Ua-40072	301-303	5285	±31	6190 – 5940	6181 - 5948	-29,4	Bulk sample, roots and bark removed
DS30RB2	Ua-40073	301-303	5240	±30	6180 – 5920	6175 - 5920	-29,2	Bulk sample, roots and bark removed
DS22[c]	Ua-38657	303-305	3476	±91	3980 - 3480	–	-27,8	*Sphagnum* spp. leaves and stems, unknown material
DS38RB1	Ua-40079	318-320	6501	±32	7480 - 7320	7476 - 7325	-29,3	Bulk sample, roots and bark removed
DS38RB2	Ua-40080	318-320	6513	±32	7490 - 7320	7487 - 7328	-29,2	Bulk sample, roots and bark removed
DS25	Ua-38658	337-339	7360	±56	8330 - 8030	8321 - 8032	-23,7	*Sphagnum* spp. leaves and stems, moss leaves, pine seed
DS39RB1[c]	Ua-40081	353-355	6854	±33	7760 - 7610	–	-28,9	Bulk sample, roots and bark removed
DS39RB2[c]	Ua-40082	353-355	6936	±33	7840 - 7680	–	-29	Bulk sample, roots and bark removed
DS34RB1[c]	Ua-40074	370-372	6728	±32	7660 - 7510	–	-29,2	Bulk sample, roots and bark removed
DS34RB2[c]	Ua-40075	370-372	6732	±34	7670 - 7510	–	-28,9	Bulk sample, roots and bark removed
DS28[c]	Ua-38659	372-374	6237	±257	7650 - 6450	–	-28,7	*Sphagnum* spp. leaves, moss leaves and stems, pollen

a: Lab code from the Ångström laboratory, Lägerhyddsvägen 1, 752 37 Uppsala, Sweden.

b: Before Present, in reference to year 1950 AD.

c: Ages of samples are younger than previous layers and therefore the samples were not used when modelling the depth-age relationship.

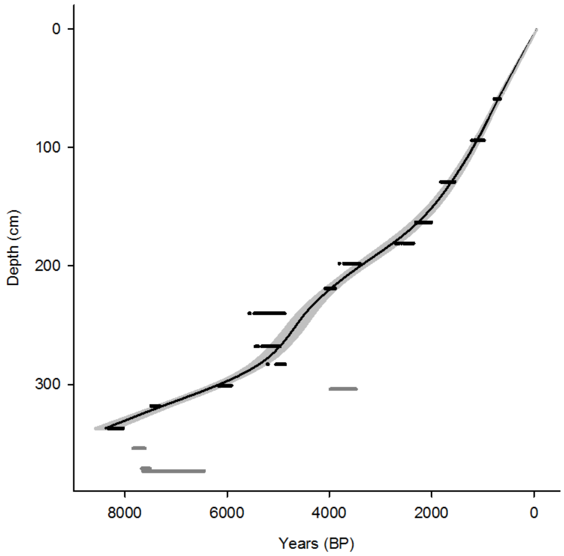

Figure 6. Calibrated age-depth relationship (Blaauw, 2010; calibration curve IntCal09, smooth spline with spar 0.4) with the shaded area indicating 2SD confidence interval. The black and gray horizontal blocks show highest posterior density ranges. The gray blocks are not included in the model, due to inconsistencies in ages compared to nearby samples. BP (before present) refers to 1950 A.D.

2.2.2 Aquatic C losses (Paper II)

Water samples for TOC, DIC, and CH_4-C analysis were collected every second week during spring, summer, and autumn with a higher frequency of 1-3 times per week during the spring flood. At winter baseflow samples were collected once a month. The samples were retrieved from two sites: 1) the upwelling site where the stream originates, and 2) 250 meters further down the stream where catchment discharge was measured; the downstream site was sampled somewhat more frequently than the upwelling site (341 occasions compared to 309). Water for TOC analysis was taken as grab samples without headspace in high-density polyethylene (HDPE) bottles. In 2004 and 2011-2014 the samples were filtered before analysis. In boreal Scandinavia DOC is a reasonable estimate of TOC (Ivarsson & Jansson, 1994; Mattsson *et al.*, 2005), and two studies in the local area (at Degerö Stormyr and at the Krycklan catchment 10 km from Degerö Stormyr; Nilsson et al., 2008 and Laudon et al., 2011) confirm this. Water for DIC analysis was sampled directly in the stream and analyzed using a headspace method on a gas chromatograph equipped with a methanizer and a flame ionization detector (GC-FID). The specific ultraviolet absorbance at 254 nm divided by the DOC concentration ($SUVA_{254}$) was used to analyze the quality of TOC. Stream water concentrations of DIC and CH_4-C were calculated from headspace $p\mathrm{CO}_2$ and $p\mathrm{CH}_4$ using equations for carbonate equilibrium and Henry's law, according to the methods in Wallin *et al.* (2010, 2014). Details on methods used are found in Paper II.

Modelling and uncertainty

Discharge was estimated by applying stage-discharge rating curves to hourly water level measurements at a v-notch weir (2003-2007) or a flume (2008-2014; *Figure 7*). For periods when stage measurements were missing, a long term discharge record for a reference site in the Krycklan catchment was used together with the MOVE.2 streamflow record extension approach (Hirsch, 1982). Details on discharge estimations are found in Paper II.

Figure 1. Spring flood at the flume where water level measurements were performed 2008-2014. (Photo: P. Blomkvist)

The export of TOC, DIC and CH_4-C were calculated by multiplying daily discharge (L s^{-1}) and daily concentrations (mg L^{-1}) of the C species. Daily C concentrations were retrieved by interpolation of data from consecutive sampling occasions. Dissolved inorganic carbon and CH_4-C concentrations were higher at the upwelling site, due to degassing over the course of the stream. Hence, when available, data from the upwelling site was used for modelling DIC and CH_4-C export. For occasions when samples were available from the downstream site only, DIC was estimated using a linear regression model. At corresponding data gaps for CH_4-C the long-term mean CH_4-C concentration was used, since there was no linear relationship between concentrations by the upwelling and the downstream site. Total organic carbon concentrations were similar at the upwelling and downstream site, and hence data from the more frequently sampled downstream site was used for the analysis.

A standard probable error propagation method (Bevington & Robinson, 2003) was used to account for uncertainties in discharge and C concentrations. Specifically, uncertainties due to discharge estimations, interpolation of C concentrations between sampling occasions, modelling of DIC and CH_4-C concentrations at the upwelling site, and sample storage were accounted for. Calculations and uncertainties are further described in Paper II.

3 Results and discussion

3.1 Long term C and N accumulation rates (Paper I)

The LORCA of the Degerö Stormyr fen was estimated to 13.7±5.5(SD) g C m^{-2} yr^{-1}. This is low in comparison to other northern mires (Turunen *et al.*, 2002; Franzén *et al.*, 2012; Loisel *et al.*, 2014). The low value could be due to that the average of northern peatlands include results from both bogs and fens. In Finland fens generally have lower LORCA than bogs (Turunen *et al.*, 2002), and if this applies to all northern peatlands, the comparably low LORCA from Degerö Stormyr would be explicable.

The estimated long term rate of N accumulation (LORNA) of Degerö Stormyr was 0.28±0.14(SD) g m^{-2} yr^{-1} (5700-700 before present (BP) in reference to year 1950 AD). This is close to, or lower than LORNA of northern peatlands in general (Loisel et al., 2014; 6000-0 BP and Wang et al., 2015; 10 000-0 BP, respectively). Loisel et al. (2014) had an overrepresentation of *Sphagnum* spp. dominated peatlands, which contributed to their low LORNA compared to Wang et al. (2015). The time periods compared also contributed to the difference, since the LORNA during the latter part of the Holocene was lower than during the first part (Loisel et al., 2014). Impact of these factors was evident in the LORNA of Degerö Stormyr, where the peat was dominated by *Sphagnum* and the LORNA represented the latter part of the Holocene. Thus, a comparably low LORNA would be expected.

Variations in C and N accumulation rates at Degerö Stormyr largely coincided with changes in the dominating plants species (*Figures 8*a and *b* and *9b-j*). The variations were largely connected to the primary production of the plants, since the degree of decomposition and vertical peat accumulation rate were not necessarily manifested in the C and N accumulation rates (*Figures 8a, b, e* and *9k*). There were, however, variations attributed to degree of decomposition (see below).

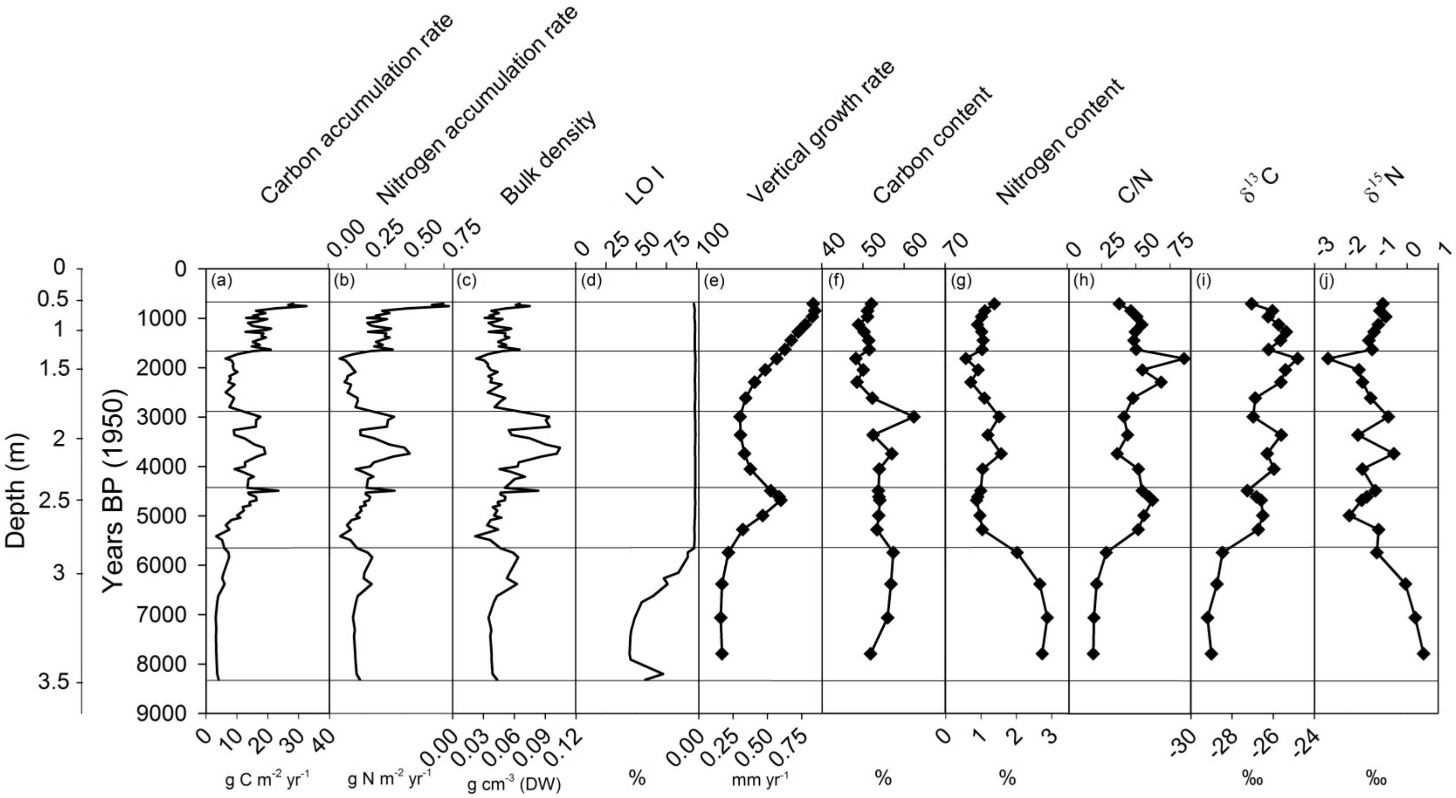

Figure 8. (a) Carbon accumulation rate in g C m^{-2} yr^{-1}, (b) N accumulation rate in g N m^{-2} yr^{-1}, (c) organic matter bulk density in g cm^{-3}, (d) LOI as a percentage, (e) vertical growth rate in mm yr^{-1}, (f) C content as a percentage, (g) N content as a percentage, (h) C:N ratio, (i) stable $\delta^{13}C$ isotopes in permille, and (j) stable N isotopes in permille. The diagram is divided into five time periods based on the variations in C and N accumulation rate and macroscopic plant remains, indicated by the horizontal lines. The age scale BP refers to 1950 AD.

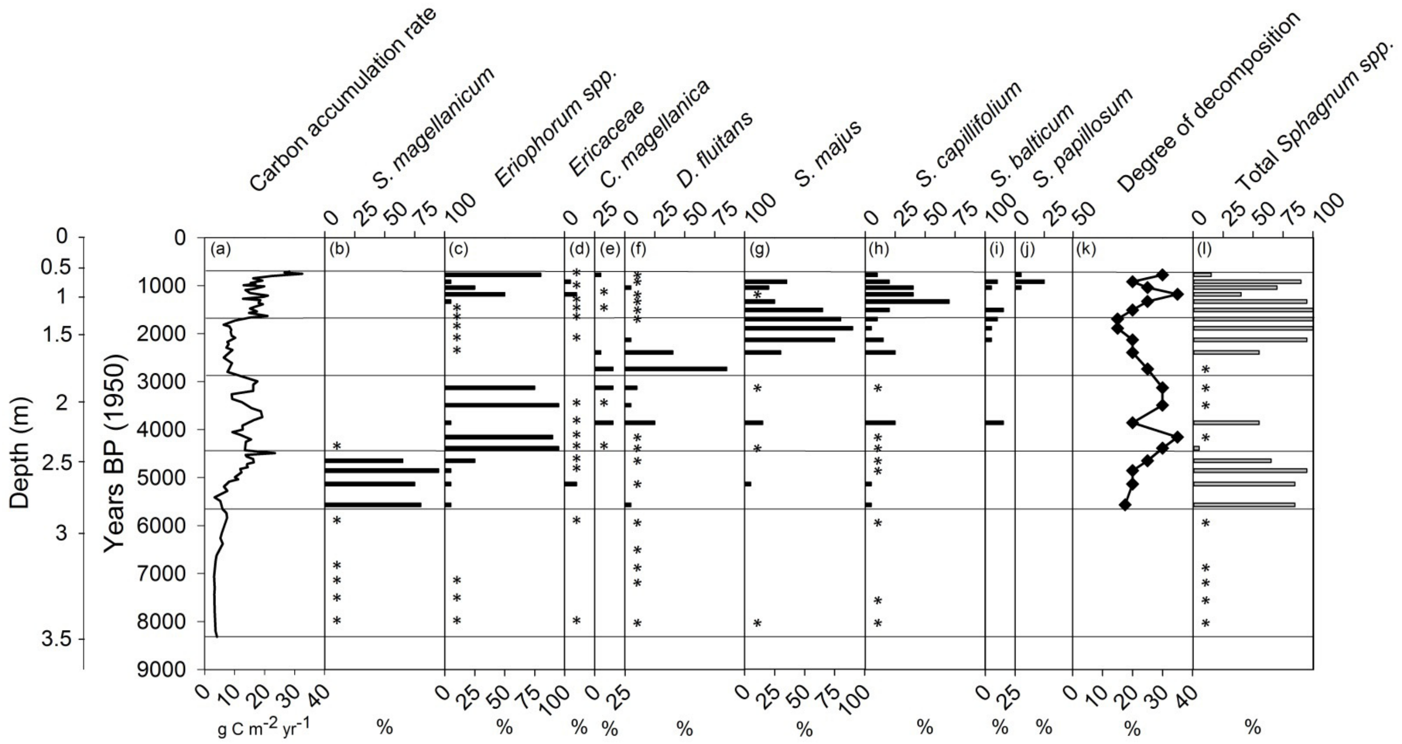

Figure 9. (a) Carbon accumulation rate in g C m^{-2} yr^{-1}, (b)-(j) relative occurrence of plant macrofossils as a percentage, (k) degree of decomposition as a percentage, and (l) relative occurrence of total *Sphagnum* spp. macrofossils as a percentage. The diagram is divided into five time periods based on the variations in C and N accumulation rate and macroscopic plant remains, indicated by the horizontal lines**.** The age scale BP refers to 1950 AD.

There were positive correlations between C and N accumulation rates that differed depending on the dominating plant species of the peat (*Sphagnum* spp.: $p < 0.001$, R^2adj = 0.93 and *Eriophorum* spp.: $p < 0.001$, R^2adj = 0.88, respectively; *Figure 10*). The co-variation indicated that the same processes explain the variations. Periods when the peat was dominated by *Eriophorum*, however, tended to exhibit a higher N accumulation rate, especially at the higher end of the C accumulation rate. This could be explained by the higher degree of decomposition in peat dominated by *Eriophorum* than *Sphagnum* (*Figure 9k*). During decomposition, C is respired from the peat and N is retained to a higher degree (Kuhry & Vitt, 1996). This effect should be more evident at higher degrees of decomposition, since a higher proportion of C would have been respired. Stable N isotope signatures (*Figure 12*) of the periods with the highest C and N accumulation rates (4400-2900 BP and 1700-800 BP) indicate that the N availability was largest during these periods, which could be one reason for the high accumulation rates.

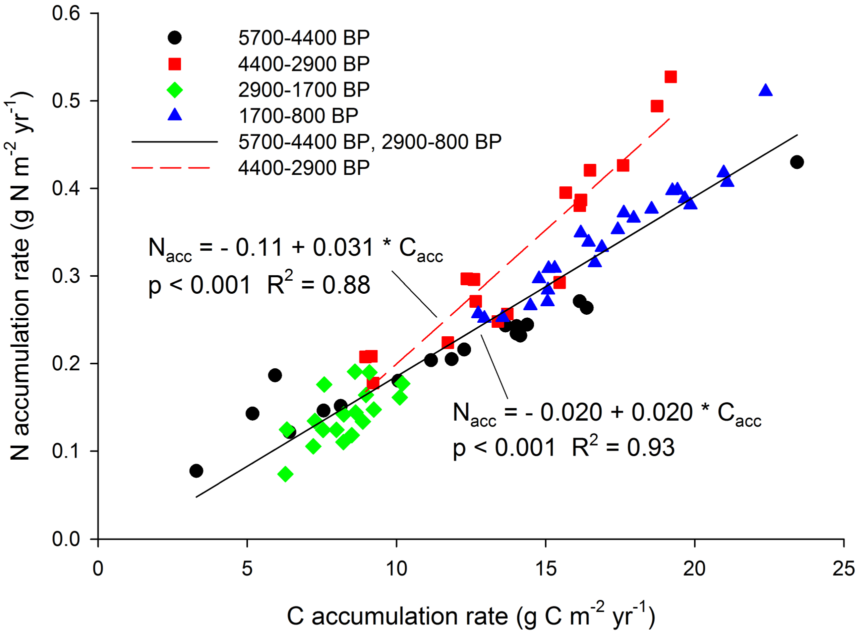

Figure 10. Relationships between C (g C m^{-2} yr^{-1}) and N (g C m^{-2} yr^{-1}) accumulation rates. The periods dominated by *Sphagnum* spp. and *Eriophorum* spp. respectively are described by the equations $N_{acc\mathit{Sph}} = -0.020 + 0.020 * C_{acc}$ ($p < 0.001$ and R^2adj = 0.93) and $N_{acc\mathit{Eri}} = -0.11 + 0.031 * C_{acc}$ ($p < 0.001$ and R^2adj = 0.88). The solid line represents *Sphagnum* spp. dominated periods, with the following key to the symbols: filled circles 5700-4400 (*S. magellanicum*); diamonds 2900-1700 (*S. majus*); and triangles 1700-700 (*S. capillifolium* and *S. majus*). The dashed line and squares represent the *Eriophorum* spp. dominated period 4400-2900 BP.

3.1.1 Indications of decomposition

There were negative correlations between C content and $\delta^{13}C$ signature of bulk peat that were dependent on the dominating plant species (*Sphagnum* spp. dominated peat: $p < 0.001$, R^2adj = 0.69, and *Eriophorum* spp. dominated peat: $p = 0.007$, R^2adj = 0.98; *Figure 11*). The underlying cause was probably increasing C concentrations during decomposition due to a relative decrease of low C density compounds, e.g. carbohydrates (Benner *et al.*, 1987) and increase of recalcitrant high C density compounds, such as phenols, lipids, and waxes (Bohlin *et al.*, 1989; Nordén *et al.*, 1992). The latter compounds are depleted in the ^{13}C isotope compared to carbohydrates (Schulten & Gleixner, 1999), which would give rise to ^{13}C depletion in the bulk peat during decomposition. The different slopes exhibited by the different species was probably due to different $\delta^{13}C$ signatures in the original plant litter, as well as different decomposability of the litter.

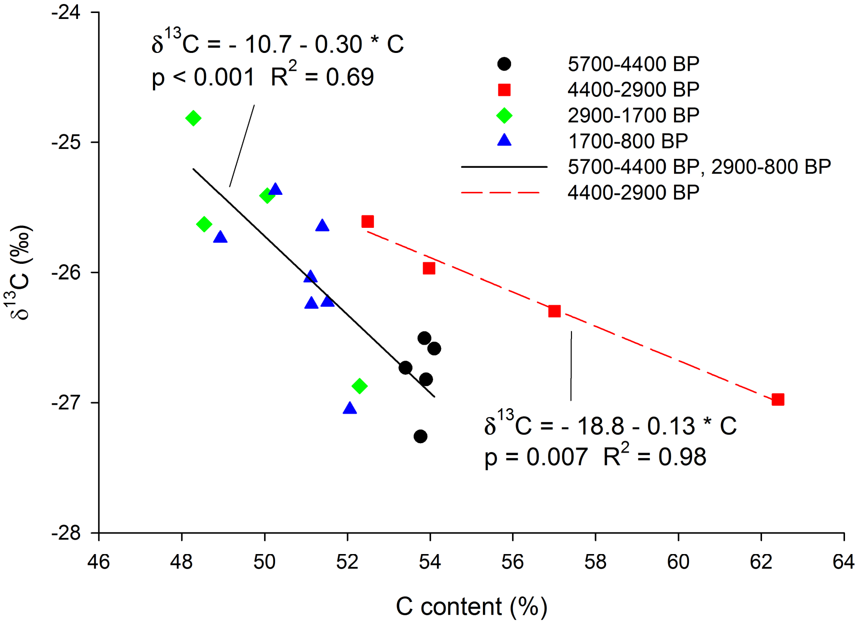

Figure 11. Significant regressions between C content (%) and $\delta^{13}C$ (‰) for *Sphagnum* and *Eriophorum* dominated bulk peat. The relationships are described by the linear regressions $\delta^{13}C_{Sph} = -10.7 - 0.30 * C$ ($p < 0.001$, R^2adj = 0.69, n = 16), and $\delta^{13}C_{Eri} = -18.8 - 0.13 * C$ ($p = 0.007$ R^2adj = 0.98, n = 4). The solid line represents peat dominated by the following *Sphagnum* species: filled circles *S. magellanicum* (5700- 4400 BP), diamonds *S. majus* (2900-1700 BP), and triangles *S. capillifolium* and *S. majus* (1700-700 BP). The dashed line and squares represent *Eriophorum* dominated peat.

Enrichment of $\delta^{15}N$ with decreasing C:N ratio ($p < 0.001$ and R^2adj = 0.60; *Figure 12*) was evident for bulk peat. This could be explained by decomposition with co-occurring preferential plant uptake of the lighter ^{14}N isotope. During decomposition the C:N ratio decreases due to respiration of C and retention of N (Post *et al.*, 1985), and at N uptake plants have been found to favor the lighter N isotope (Högberg *et al.*, 1996; Nadelhoffer *et al.*, 1996; Lindahl *et al.*, 2007). At times of high decomposition rates, more N could be available to plants, causing more pronounced fractionation and ^{15}N enrichment in the peat. An important difference in our study compared to other studies ascribing ^{15}N fractionation to plant uptake, is the investigated soil depth. The other studies only investigated surface soil in tundra (Nadelhoffer et al., 1996) and boreal forest (Högberg et al., 1996; Lindahl et al., 2007). However, we investigated deep peat (60-370 cm), i.e. all peat in our study belong to the catotelm and has undergone more or less the same processes, but to different degrees. That is probably why we see a connection between the $\delta^{15}N$ signature and a proxy for decomposition (i.e. the C:N ratio (Post et al., 1985)), but not depth.

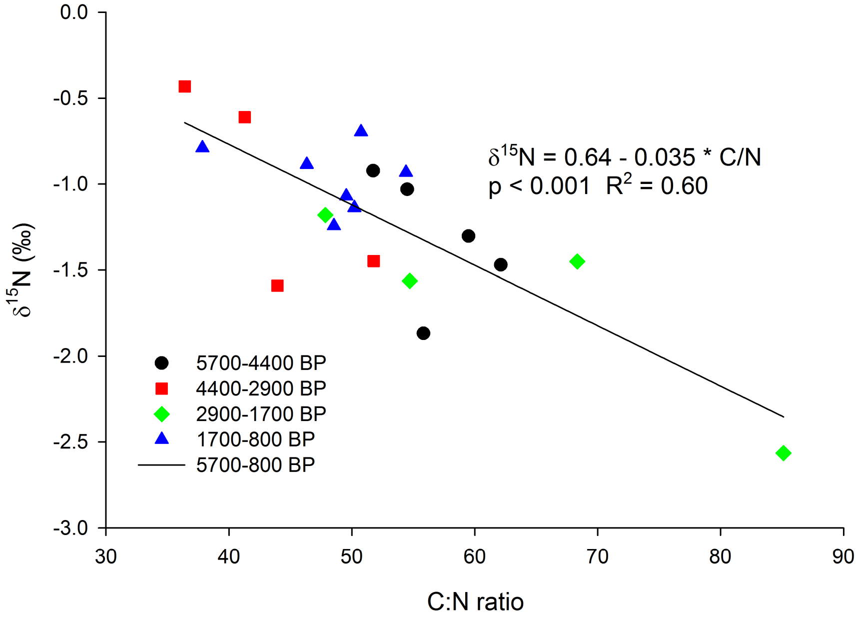

Figure 12. Significant regression between C:N ratio and $\delta^{15}N$ (‰). The relationship is described by the regression $\delta^{15}N = 0.64 - 0.035 * C/N$ ($p < 0.001$, R^2adj = 0.60). Filled circles represent *S. magellanicum* dominated peat 5700-4400 BP, squares represent *Eriophorum* dominated peat 4400-2900 BP, diamonds represent *S. majus* dominated peat 2900-1700 BP, and triangles represent *S. capillifolium* and *S. majus* dominated peat 1700-700 BP. Removing the point with large influence results in the regression $\delta^{15}N = 0.32 - 0.029 * C/N$ with $p = 0.006$ and R^2adj = 0.33

3.2 Stream carbon export (Paper II)

The stream C export constitutes an important flux of C in the net ecosystem carbon balance (NECB) of mires (c.f. Dinsmore et al., 2010; Nilsson et al., 2008; Roulet et al., 2007). Dissolved organic carbon in streams is also crucial for aquatic life (c.f. Jansson et al., 1996; Miller et al., 2006; Stepanauskas et al., 2000), and hence changes in concentrations may impact biota downstream mires. There are other studies reporting DOC measurements from over ten years of measurements (e.g. Pumpanen *et al.*, 2014) or includes all major C fluxes (TOC, DIC, and CH_4-C) over a few years and compare them to NEE (e.g. Nilsson *et al.*, 2008; Dinsmore *et al.*, 2013). This study however, is unique since it includes all major C fluxes (TOC, DIC, and CH_4-C) over twelve years of measurements (Paper II).

Furthermore, in this study stream water was sampled in a stream close to its origin in an upwelling, allowing for sampling before the supersaturation of CO_2 and CH_4 caused degassing of stream water. Otherwise, evasion is required to be accounted for, as was done by Dinsmore *et al.* (2013) and Wallin *et al.* (2013).

3.2.1 Total and seasonal stream carbon export

In agreement with Clark et al. (2007) the stream C export from Degerö Stormyr was driven by precipitation (*Figure 13*), that was closely related to runoff (not shown). The average stream C export over the 12 year study was 12.2 g C m^{-2} yr^{-1} with a range from 6 to 18 g C m^{-2} yr^{-1} (*Figure 14*). The annual C export is lower than export from other mires (Billett *et al.*, 2004; Roulet *et al.*, 2007; Dinsmore *et al.*, 2013; Wallin *et al.*, 2015), but relative to the amount of precipitation, it is in the same order of magnitude. Total organic carbon dominated the export with an average of 72% of total export. Dissolved inorganic C as the second largest stream C flux contributed with 25%. Methane-C, however, comprised only 3%, though its high global warming potential made the contribution substantial in a climate change conext. The proportion of DIC and CH_4-C are higher than in discharge at the Auchencorth Moss, Scotland (Billett *et al.*, 2004; Dinsmore *et al.*, 2013). This is probably due to that in this study water was sampled close to the upwelling where the stream originated, with limited degassing of stream water before sampling.

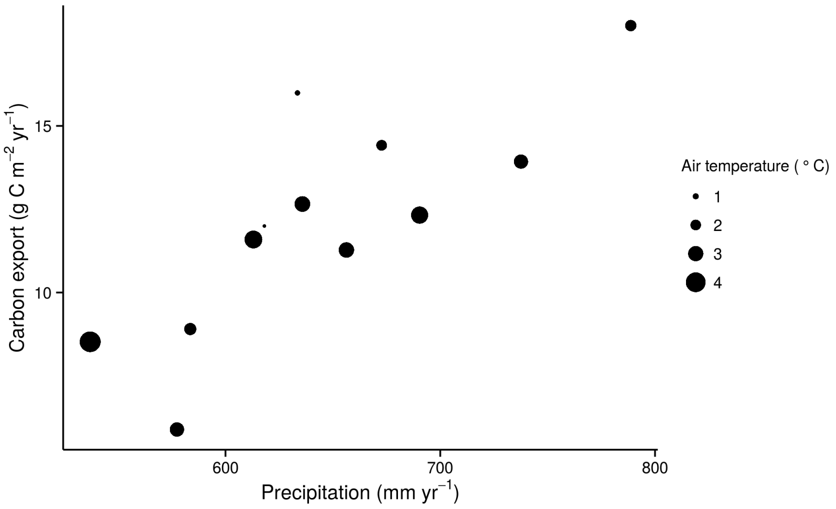

Figure 13. Annual C export (g C m^{-2} yr^{-1}) versus precipitation (mm). The size of the symbols indicates the average air temperature (°C) per year.

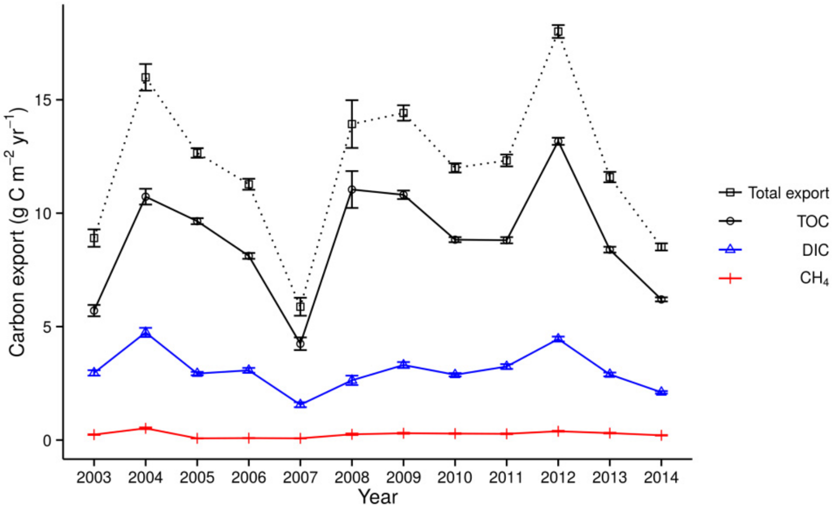

Figure 14. Annual total stream C export (Total export), total organic carbon export (TOC), dissolved inorganic carbon (DIC) and CH_4-C export (CH_4) 2003-2014 in the unit of g C m^{-2} yr^{-1}. Error bars represent ± 1 standard deviation.

The spring season was a major contributor the total annual C exports, with 30-55% of the export 2003-2014 (*Figure 15*). The contribution from summer and autumn seasons were highly variable, with 1-45% and 9-53%, respectively. The proportions of C export during different seasons were correlated to the relative contribution of seasonal discharge to total discharge during different years. This highlights the importance of timing of runoff events for seasonal variations in C export of mires.

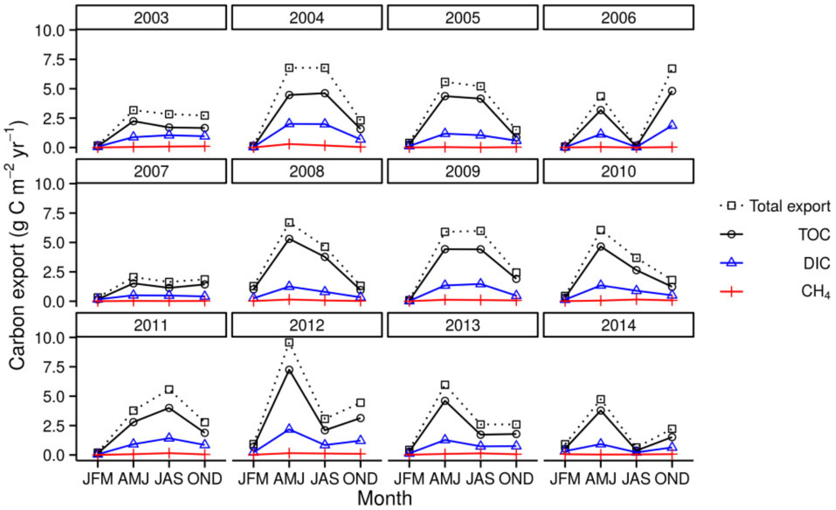

Figure 15. Seasonal C export of all C species added together (Total export), total organic carbon export (TOC), dissolved inorganic carbon (DIC), and CH_4-C export (CH_4) in g C m^{-2} yr^{-1}.

The importance of timing of runoff events is also evident when comparing the annual stream C exports to net ecosystem exchange (NEE). The NEE during the years 2001-2012 was calculated for the Degerö Stormyr mire by Peichl et al. (2014). The stream C export in our study typically made up 25-37% of NEE (2003-2012; i.e. the overlapping years in our study and Peichl et al. 2014; *Figure 16*), which is similar to other studies (Roulet *et al.*, 2007; Dinsmore *et al.*, 2010), but exceed the corresponding 12% from a subarctic peatland (Olefeldt *et al.*, 2012). During 2006, however, the stream C export made up between 63 and 90% of NEE (*Figure 16*). This year, an exceptionally dry summer and a wet autumn caused inhibition of summer photosynthesis (Peichl *et al.*, 2014) and high autumn C export (*Figure 15*), further accentuating the importance of timing of runoff events for seasonal C export.

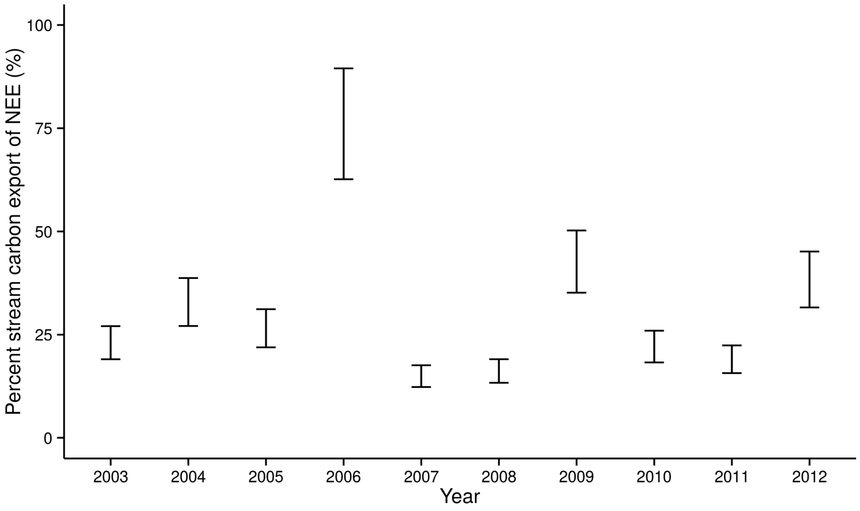

Figure 16. Annual percent stream C export relative to NEE.

3.3 Stream carbon concentration and quality

In this study, relationships between discharge, stream C export, concentrations and quality ($SUVA_{254}$) were investigated to hypothesize on controls on stream C export. The relationship between C species concentration and discharge was different for TOC compared to DIC and CH_4-C during all seasons except spring (*Figure 17*). Dissolved inorganic C and CH_4-C concentrations exhibited decreasing values under increasing discharge, while TOC displayed no such pattern, except for the spring period. One reason for the decreasing C species concentrations could be dilution by low concentration event water. The discharge dependence of DIC and CH_4-C concentrations could also be due to DIC and CH_4-C concentration gradients with peat depth, together with varying depth of the ground water table. A study showed higher CH_4 gas concentrations with depth in northern Swedish mires (Nilsson & Bohlin, 1993), however no correlation for CO_2 with depth was evident. Instead, CO_2 was positively correlated to *Sphagnum* remains. In paper I the botanical composition of peat in Degerö Stormyr shows an overall dominance of *Sphagnum*, indicating that most peat of Degerö Stormyr could sustain high concentrations of DIC. Due to supersaturation of DIC and CH_4 in mire water and shorter distance to the peat surface in the superficial layers, it is reasonable to assume degassing takes place to a higher degree in shallow layers, and hence a concentrations gradient could be induced, causing the concentration patterns in stream water exhibited for DIC and CH_4-C with varying discharge.

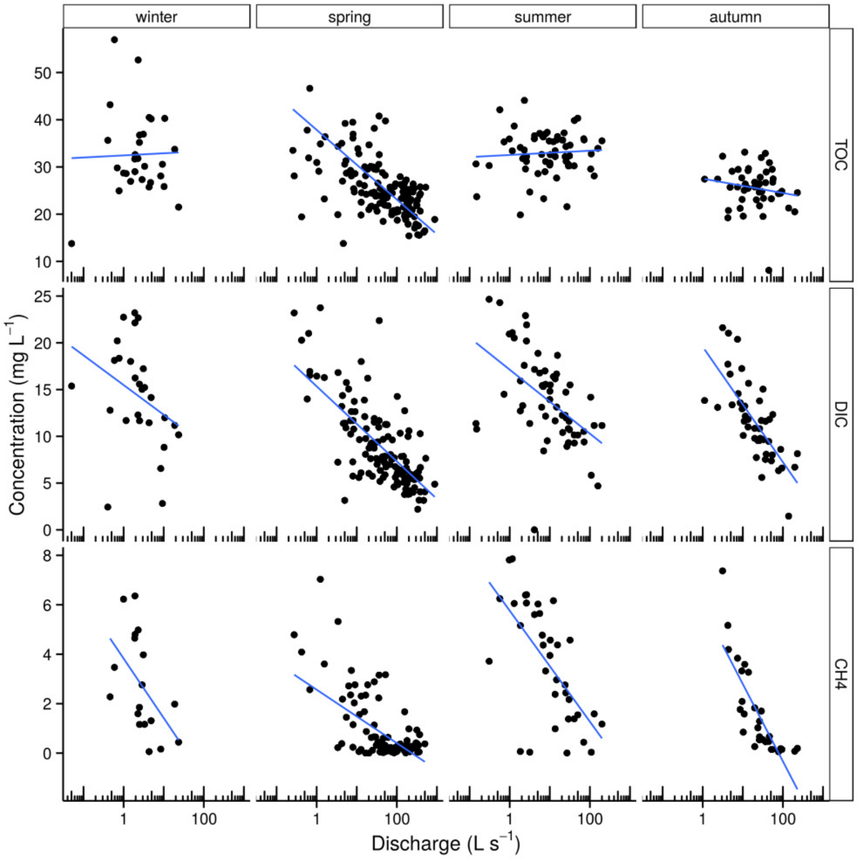

Figure 17. Carbon concentration (mg L^{-1}) versus discharge (L s^{-1}) for total organic C export (TOC), dissolved inorganic C (DIC) and CH_4-C export (CH_4) during different seasons.

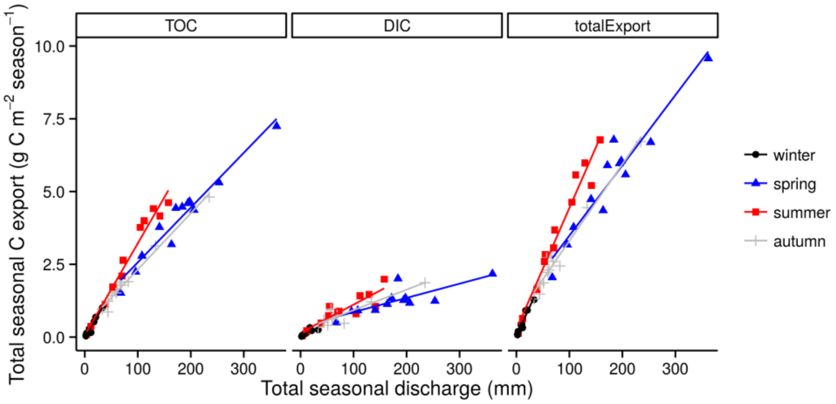

Figure 18. Seasonal export of total organic carbon export (TOC), dissolved inorganic carbon (DIC) and total export of C (g C m^{-2} seasons-^{2}) versus total seasonal discharge (mm).

The export of TOC, and to a lesser degree DIC, was greater during summer compared to the other seasons after accounting for differences in discharge (*Figure 18*). This implies higher TOC (and DIC) availability during summer compared to the other seasons. This is also evident in the overall lower TOC concentrations during autumn compared to summer (Figure 17).

Organic carbon quality ($SUVA_{254}$) displayed a seasonal pattern, with an increase during the first part of the year with a peak during spring and thereafter a decrease until the end of the year (*Figure 19*). During summer $SUVA_{254}$ exhibited moderate discharge dependence (not shown), indicating TOC originating in shallower less decomposed peat layers (Ågren *et al.*, 2008) at high flows. Lower average $SUVA_{254}$ during autumn compared to summer indicated TOC likely being sourced from more superficial peat layers.

Alternatively, the seasonal $SUVA_{254}$ pattern could be associated with production of TOC and travel times for water and TOC to the outlet. For example, the low autumn $SUVA_{254}$ could be explained by summer TOC, low in aromatic carbon, traveling through the peat and reaching the outlet in the autumn.

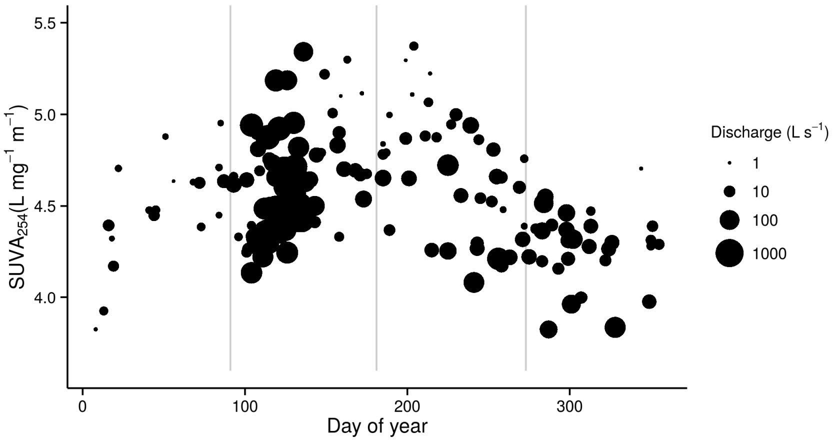

Figure 19. Total organic carbon quality $SUVA_{254}$ (L mg^{-1} m^{-1}) versus day of year. Point sizes are scaled to the logarithm base 10 of discharge (L s^{-1}). The grey vertical lines indicate season classification.

3.3.1 Climate change implications

Climate change projections for northern Europe predict increased precipitation and temperature, with the highest temperature increase during winter and highest precipitation increase during summer (Stocker *et al.*, 2013; scenario

RCP4.5). Altered climate conditions may change processes controlling the carbon balance of northern peatland catchments (Frolking *et al.*, 2011).

Modelled stream flow response to a future changing climate (Teutschbein *et al.*, 2015) indicates that the overall streamflow will increase, the magnitude of spring flood peak flow will decrease, and winter discharge will increase. Hence, C export will likely increase, since streamflow is the primary control of discharge C export in the Degerö Stormyr mire catchment. The seasonal timing of increased streamflow might, however, be important for the magnitude of the increase. An increase in streamflow during summer potentially leads to relatively higher export compared to spring and autumn, since the TOC availability was higher during summer compared to the other seasons (*Figure 18*). The importance of spring to the annual C export might also decrease with a decreasing intensity of spring flood, and the winter contribution probably increases with higher winter flows. Greater export of C, and changes in magnitude and timing of flows, potentially has implications for carbon balance of mires. Furthermore, it may affect downstream aquatic ecosystems (Dangles *et al.*, 2004).

4 Conclusions

In this thesis I determined Holocene LORCA and LORNA, and interrelated variations in C and N accumulation rates with different variables to examine controls on accumulation rates in the boreal fen Degerö Stormyr (Paper I). Annual and seasonal contemporary stream C export in the same mire catchment was determined over 12 years, and associations between stream C export and hydroclimate conditions, carbon concentration, and TOC quality were explored (Paper II).

Primary production was identified as the main control of Holocene C and N accumulation rates (Paper I). This implies that climate change favoring primary production could result in higher C and N accumulation rates, and lower accumulations rates under climatic conditions limiting primary production. However, decomposition also affected the C and N accumulation rates, underlining that accumulation rates result from the balance between production and decomposition rates. Major changes in accumulation rates were concomitant with changes in dominating plant species, indicating that the effect of a changing climate on the botanical composition of mires will be crucial for future C and N accumulation rates.

Degree of decomposition in catotelm peat was also strongly related to plant species, with *Sphagnum* dominated peat exhibiting lower degrees and *Eriophorum* dominated peat exhibiting higher degrees of decomposition. The linear N accumulation rate to C accumulation rate relationships further underlined the important role of species composition. These results indicate that shifts in botanical composition could affect the degree of decomposition in the peat, and thereby magnitudes of GHG emissions and C export in discharge.

The major driver of stream C export at Degerö Stormyr was runoff (Paper II). Hence, predicted climate change in the local area, with higher runoff, will likely increase the annual C export of all C species. The magnitude of this increase might however differ depending on the timing of runoff events during the year. The overall effect on NECB depends partly on the effects of climate change on stream C export, but also NEE and CH_4 emissions.

The results from this thesis indicate that primary production is the main driver of C and N accumulation rates. Furthermore, the results underline the importance of runoff events for the seasonal stream C export, and that the annual C export from the Degerö Stormyr catchment likely will increase under the predicted climate change.

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