Quantity and composition of waterborne carbon transport in subarctic catchments containing peatlands and permafrost

David Olefeldt

Department of Geography, McGill University, Montreal.

Submitted January 2011.

A thesis submitted to McGill University in partial fulfillment
of the requirement of the degree of Doctor of Philosophy

"You could not step twice into the same river,
for other waters are ever flowing on to you."

Heraclitus (535 BC – 475 BC) quoted by Plato

CONTENTS

PREFACE

ACKNOWLEDGMENTS

The research in this thesis was supported by a NSERC Discovery Grant awarded to my supervisor Nigel Roulet. It was further supported by the Global Environment and Climate Change Centre (GEC^3), the Sweden-America foundation and Sixten Gemzéus stiftelse.

I would like to start by thanking my supervisor Prof. Nigel Roulet for his advice and support, both academic and non-academic. Many thanks also to the other members of my committee, Prof. Tim Moore, Dr. Wayne Pollard and Dr. Bernhard Lehner. I have also benefitted from some very productive collaborations: Dr. Reiner Giesler at Umeå University has provided me with access to analytical instrument while at Abisko research station and given good research advice when needed, Dr. Andreas Persson at Lund University has provided the GIS wizardry and been of great collegial support, Prof. Torben Christensen at Lund University was responsible for getting me into peatland research in the first place and also introduced me to the work at Stordalen, Dr. Onil Bergeron at McGill University was indispensable for setting up and maintaining the micro-meteorological tower along with the post-processing of its data, Prof. Patrick Crill at Stockholm University shared resources, data and help from field assistant for my work in Abisko and Mike Dalva at McGill University helped with the logistics of sending equipment to Sweden and assisted with the analysis. Further technical and analytical help was given by Dr. Charlotte Roehm, Dr. Jan Karlsson, Michelle Collins, Dr. Kristina Bäckstrand and the staff at Abisko research station. The field work would not have been possible without diligent assistance by Sophine Johnsson, Stephanie Daneau, Jackie Grom and Ann Lalancette, and I owe you many thanks. The support from fellow graduate students in Abisko and at McGill has also been vital, both academically and personally, including but not limited to: Meaghan Murphy, Julia Christensen, Young-Il Kim, Jiangwua Wu, Angela Kross, Derrick Lai, Julie Turgeon, Alec

Blair, Nils Ohlanders, Rik Van Bogaert, Frida Keuper, Eva Köller, Stef Bokhorst, Michał Heliasz, Catherine Preece, Marika Makkonen and Gregoire Freschet – and I wish you all good luck in your continued work.

Of course, this thesis would not have been completed – probably not even attempted – without the support and assistance of my lovely wife Erin.

CONTRIBUTIONS OF AUTHORS

Chapters 3 to 6 inclusive are written as manuscripts in a format that is suitable for eventual publication in peer-reviewed scientific journals. All these chapters are co-authored with my supervisor Nigel T. Roulet, who has aided in planning the research, provided advice and discussion on the analysis of data and the presentation of the arguments in the manuscripts and contributed financially to the completion of the research.

For all of the manuscripts presented in this paper the scientific questions, the objectives, the research plan and its execution along with the analysis and interpretation of the results were my contributions. As with most research in the biogeosciences I benefitted from the assistance and collaboration of other scientists beyond that of my primary supervisory and these additional contributions are acknowledged by junior co-authorships on the manuscripts that constitute Chapters 4 and 5. The specific contribution of these co-authors is as follows:

Chapter 4. "Carbon accumulation of a high latitude permafrost peatland" by David Olefeldt, Nigel T Roulet, Onil Bergeron, Patrick Crill, Kristina Bäckstrand and Torben Christensen (To be submitted). Onil Bergeron helped install and program the micrometeorological tower and aided the post-processing of the data. Onil contributed to writing parts of the method section and provided editorial comments on the other sections of the manuscript. Patrick Crill and Kristina Bäckstrand carried out the research on total hydrocarbon fluxes in Stordalen, and provided me with the raw data on these fluxes so they could be included in the calculation of the NECB. Torben Christensen is the scientific leader for carbon studies in the Stordalen peatland complex and this research has its origins back to an invitation to Nigel Roulet to come to Abisko to see the research on subarctic peatlands. Crill and Christensen are currently reviewing the manuscript but none of their comments have been incorporated as of the submission of my thesis.

Chapter 5. “Total waterborne carbon export and DOC composition from ten nested subarctic peatland catchments” by David Olefeldt, Nigel T Roulet, Reiner Giesler and Andreas Persson (To be submitted). Reiner Giesler aided in the analysis of water samples and contributed intellectually to the interpretation of data and the eventual organization of the manuscript that appears in the thesis. Andreas Persson created and performed the analysis of the digital elevation map to provide the estimates of the catchment areas, and provided input to the relevant sections in the description of the methods.

ABSTRACT

Both quantity and composition of waterborne transport of dissolved organic carbon (DOC) from peatlands has been hypothesized to be affected by permafrost thaw. Changes in DOC can impact the carbon (C) balance of peatlands directly, but also the carbon balances and metabolism of downstream aquatic environments. In this study I have investigated the DOC export from different peatland types in the Stordalen catchment of northern Sweden (68.20N, 19.03E). The research was performed at various spatial and temporal scales in order to assess the importance of peatland permafrost thaw for both peatland and catchment DOC export. In the Stordalen catchment, peatland permafrost thaw leads to the conversion of palsas (a rain-fed peatland type with a permafrost core) into bogs dominated by *Sphagnum* mosses or into fens of varying nutrient status depending on their hydrological setting.

The palsas were found to have low DOC export rates, at between 2.5 and 3.5 g C m^{-2} yr^{-1}, and its composition characterized by several bulk DOC indices was of poor substrate quality for microbial degradation. The DOC export from the bogs was not found to differ in quantity to that of the palsas, but its DOC composition had lower aromaticity and a larger fraction derived from microbial sources. Snowmelt runoff occurred early on the palsa and bog, and mass flux at this time of years was responsible for >70% of the annual DOC export – causing the palsas and bogs to significantly affect catchment DOC export patterns during early snowmelt runoff, despite covering <4% of the catchments. Partly due to the restricted DOC export, the Stordalen palsa/bog complex was found to be net annual C sinks despite its low ecosystem productivity.

In contrast, the fens were found to export 2 to 4 times as much DOC as the palsas and bogs, with a majority of the DOC export occurring outside the snowmelt runoff period. Several pieces of evidence show that fens not only act as catchment sources of DOC, but through selective degradation they transform DOC that reach the fens from upstream sources, causing the fens to regulate catchment DOC

composition and concentrations during summer and fall low runoff periods despite covering only a small fraction of the catchment area.

The impact on peatland DOC export from permafrost thaw is primarily dependent on the hydrological setting after thaw in Stordalen, where a conversion of palsas into fens has the greatest potential for the alteration of catchment DOC export patterns.

RÉSUMÉ

L'hypothèse a été émise que la quantité et la composition du carbone organique dissous (COD) des tourbières, transporté par l'eau, est affecté par le dégel du pergélisol. Les changements de COD peuvent influer sur l'équilibre du carbone (C) directement, mais aussi les bilans de C et le métabolisme des milieux aquatiques en aval. Dans cette étude, j'ai étudié l'exportation de COD provenant de différents types de tourbières dans le bassin versant Stordalen au nord de la Suède (68.20N, 19.03E). La recherche a été réalisée à différentes échelles spatiales et temporelles afin d'évaluer l'importance du dégel du pergélisol des tourbières sur la tourbière elle-même et sur l'exportation du COD dans le bassin versant. Dans le bassin versant Stordalen, le dégel du pergélisol des tourbières a conduit à la conversion des palses (un type de tourbière pluviale avec un noyau de pergélisol) vers des tourbières dominées par les sphaignes ou en tourbières de carex avec des statuts d'éléments nutritifs variés en fonction de leur contexte hydrologique. Les palses se sont avérés avoir un faible taux d'exportation de COD, entre 2,5 et 3,5 gC m^{-2} an^{-1}, et sa composition se caractérise par plusieurs indices de COD qui étaient de mauvaise qualité de substrat pour la dégradation microbienne. L'exportation du COD dans les tourbières n'a pas montré de différences quant à la quantité par rapport à celles de la palse, mais sa composition avait une plus faible aromaticité et une fraction plus importante provenant de sources microbiennes. La fonte des neiges s'est produite tôt dans la palse et les tourbières, et le flux de COD à ce moment de l'année a été responsable de plus de 70% de l'exportation annuelle de COD – provoquant la palse et les tourbières de modifier sensiblement l'exportation du COD du bassin versant malgré que ces dernières ne couvrent que moins de 4% du bassin versant. En raison notamment de l'exportation restreinte de COD, le complexe palse/bassin versant Stordalen a été déterminé être un puit net annuel de C en dépit de sa faible productivité de son écosystème.

En revanche, les tourbières à carex on montré une exportation de 2 à 4 fois plus élevée que le COD des palse et des tourbières à sphaigne, avec une majorité de

l'exportation du COD survenant en dehors de la période de fonte des neiges. Plusieurs preuves ont montrés que les tourbières à carex n'agissaient pas uniquement en tant que source de captage de COD, mais par la dégradation sélective, elles transforment le COD qui atteint les tourbières à carex à partir de sources en amont, ce qui provoque les tourbières à carex de modifier la composition du COD et les concentrations du bassin versant, en été et en automne, période de faible hydraulicité, malgré que ces dernières ne couvrent qu'une petite fraction du bassin versant.

L'impact de l'exportation de COD des tourbières durant le dégel du pergélisol a été montré dépendant des conditions hydrologiques après le dégel, durant laquelle une conversion en tourbières à carex montre un plus grand potentiel pour la modification des patrons de transport de COD.

1. INTRODUCTION

The main objective of my doctoral studies is to understand the controls of waterborne carbon (C) transport in subarctic catchments, with special consideration on how permafrost thaw in peatlands affect the transport and composition of dissolved organic carbon (DOC). These aims are achieved by using a combination of techniques applied at various temporal and spatial scales, including hydrological mass balances, characterization of DOC chemical composition, hydrological mixing models and micrometeorological methods.

Potentially important feedback mechanisms between climate change and peatland C balances have caused peatland C biogeochemistry to be a 'hot scientific topic' in earth system science. Waterborne transport of C from terrestrial ecosystems and downstream through catchments represent significant but often poorly understood C exchanges, with importance for both the C balances of terrestrial ecosystems and the metabolism of aquatic ecosystems linked to the potential evasion of C back to the atmosphere.

Estimated net C balances of terrestrial ecosystems can have significant errors if the waterborne C losses are not accounted for. A large fraction of northern peatlands are affected by permafrost and ongoing climate change is causing widespread permafrost thaw in peatlands, particularly in the southern limit of the extent of permafrost. Given the projections for climate change over the next 100 years the loss of permafrost is expected to continue and to be extensive. Loss of permafrost in peatlands often represents an abrupt change in vegetation and hydrology, and consequently affects peatland C biogeochemistry, fluxes and balance. Few studies have assessed the impact of peatland permafrost thaw on waterborne C losses.

Terrestrial waterborne losses also represent a C input to downstream rivers and lakes and thus intimately link terrestrial and aquatic C biogeochemistry. Northern freshwater aquatic ecosystems are heterotrophic, i.e. their microbial metabolism is driven in excess of C fixed within their boundaries by the input of terrestrially

derived DOC. Peatlands have been identified as significant sources of DOC to downstream ecosystems. In addition, DOC exported from peatlands has a different composition than DOC from other terrestrial ecosystems, and its composition may influence how readily available the DOC is for microbial degradation. Peatlands may not only be sources of DOC, but peatlands that receive water inputs and hence DOC from upstream sources – e.g. fens, may also act as significant catchment sites for retention and transformation of DOC. Loss of permafrost in peatlands may alter the hydrological setting and vegetation composition and thus alter the quantity and composition of DOC that reaches downstream ecosystems, with implications for both aquatic C biogeochemistry and peatland C balances.

In order to advance the understanding of the interactions between peatlands, hydrology, C biogeochemistry and permafrost thaw, I have studied waterborne C transport at different spatial and temporal scales within a subarctic catchment in northern Sweden. The spatial resolutions range from that of individual peatland types to entire catchments while the temporal resolutions range from hourly to inter-annual. The specific objectives for my research (and the chapters in which they are addressed) include:

(1) The estimation of the mass transport of DOC from the constituent peatland types within a subarctic peatland complex, including characterization of the composition of DOC delivered to downstream ecosystems from each peatland type in order to assess the possible implications of continued permafrost thaw on peatland complex waterborne C export (Chapter 3).

(2) The comparison of the magnitude of the DOC export from the parts of a peatland complex that contain permafrost with the atmospheric C exchange, leading to estimation and partitioning of the net ecosystem carbon balance (NECB) that can be contrasted with NECBs that have been observed for non-permafrost peatlands (Chapter 4).

(3) The assessment of the importance of peatlands to a broader catchment's waterborne C export and DOC composition, including an attempt to determine how this importance varies with inter-annual and intra-annual hydrological variability (Chapter 5).

(4) To distinguish different catchment water sources and study how they mix to create the observed stream chemistry at catchment outflows, investigating time scales that vary from individual storm runoff events to seasonal flow patterns, with the aim to identify and separate the influence and importance of permafrost and non-permafrost peatlands for DOC transport in mixed catchments (Chapter 6).

The research in this thesis was carried out in the Stordalen catchment (Fig. 1.1 to 1.3) in northern Sweden (68.20N, 19.03E). The Stordalen peatland complex has been a research site for ecological and biogeochemical studies since it was established as one of the Arctic ecosystems sites of the International Biological Program in the early 1970s (Sonesson, 1980). In the last decade this interest has intensified with more direct measurements of the peatland complex atmospheric exchange of carbon dioxide (CO_2) and methane (CH_4) (Bäckstrand et al., 2010; Johansson et al., 2006b; Malmer and Wallén, 1996). There have also been studies on the C dynamics of aquatic ecosystems (Karlsson et al., 2010; Kokfelt et al., 2009; Roehm et al., 2009) and upland birch forests (Christensen et al., 2007) in the larger Stordalen catchment. The peatlands in this region are currently thawing, coinciding with increased annual temperatures and winter precipitation over the last few decades (Åkerman and Johansson, 2008). Peatland permafrost thaw in Stordalen has led to a conversion of palsas into either a *Sphagnum* moss dominated bog type peatland or a fen peatland type of variable nutrient status depending on the magnitude of the water flow-through.

Figure 1.1. Photo of the Stordalen catchment. The Stordalen peatland complex is located in the foreground, with the main stream draining the catchment seen on the right hand side. Both fen and palsa parts of the peatland can be distinguished. Photo by Nils Åkerman.

Figure 1.2. Sites for discharge measurements and water sampling at the Stordalen peatland complex, with the palsa catchment outflow on the left and the north fen outflow on the right.

Figure 1.3. Instrumentation and fieldwork in Stordalen catchment. Stream sampling site installed with auto-sampler, water table sensor, electrical conductivity and temperature sensors (Top left). Emptying the auto-sampler after storm event (Top right). Installing the micrometeorological tower at Stordalen (Bottom left). Measuring discharge during peak snowmelt runoff (Bottom right).

2. LITERATURE REVIEW

This literature review examines the role of waterborne C export in high latitude catchments where peatlands are a common ecosystem. The review will start with an introduction to DOC, focusing on its composition and sources along with its role in ecosystem C cycling. This will be followed by a section that describes the C balance of northern peatlands, and shows why peatland DOC export is important to both the C balance of the peatlands and the catchment scale C balance. In the last section I further explore the transport of DOC in northern catchments, comparing the influence of different landscape units, e.g. forested ecosystems, peatlands and aquatic ecosystems and look into the possible impacts on DOC export that peatland permafrost thaw might have. I will show gaps in knowledge with regards to the changes in DOC transport that follows peatland permafrost thaw. In the literature review I present a general synthesis and leave details relevant to each chapter to the specific chapter introductions.

2.1 DISSOLVED ORGANIC CARBON

2.1.1 DOC SOURCES AND COMPOSITION

DOC in aquatic ecosystems is predominately allochtonous, i.e. originating from terrestrial soils (Billett et al., 2006; Elder et al., 2000; Guo and Macdonald, 2006). Sources of DOC include vegetation, litter, soil leachates, plant root exudates and microbial enzymes and biomass (Fenner et al., 2004; Kalbitz et al., 2003a). Several processes can affect DOC compounds while on-route to and within aquatic ecosystems, including sorption processes in mineral soils (Kaiser and Zech, 1998), photodegradation (Bertilsson and Tranvik, 2000) and microbial degradation, transformation and mineralization (Kalbitz et al., 2003b). The DOC pool is thus composed of compounds along a continuum from slightly modified plant-derived carbohydrates over highly altered lignin-derived compounds to products of microbial re-synthesis (Guggenberger and Zech, 1994). Due to its diverse chemical composition, DOC is operationally defined on the basis of molecular size, with the threshold usually set at 0.45 μm. Larger compounds are classified as particulate organic carbon (POC).

In soil solutions and aquatic environments, DOC is commonly dominated by high molecular weight compounds, fulvic and humic acids in particular, but also includes low molecular weight compounds such as aliphatic and aromatic organic acids, peptides, amino acids, mono- and disaccharides, amino sugars, phenolics and siderophores (van Hees et al., 2005). Because it is practically impossible to identify and quantify all the individual compounds that constitute the DOC pool, characterization of DOC is often done based on bulk characteristics such as polarity (hydrophilic/hydrophobic), acidity (acids/neutrals), functional group content, stoichiometry (e.g. C/N ratio), aromaticity and origin (terrestrial/aquatic) (Guggenberger et al., 1994; Kalbitz et al., 2000; Marschner and Kalbitz, 2003; McKnight et al., 2001; Weishaar et al., 2003).

2.1.2 DOC IMPORTANCE IN AQUATIC AND TERRESTRIAL ECOSYSTEMS

DOC is of importance for many biogeochemical processes both in terrestrial and in aquatic environments. For example, in terrestrial ecosystems DOC is important for macronutrient availability (Kalbitz et al., 2000; Michalzik et al., 2001), solubility of metals and organic compounds, rates of weathering (Raulund-Rasmussen et al., 1998), soil acidity and soil formation – podsolization in particular (Lundström et al., 2000). In aquatic environments DOC is important for light and UV attenuation (Schindler et al., 1997), pH buffering (Buffam et al., 2007), the transport of metals and organic micro-pollutants (Kalbitz and Wennrich, 1998) and represents a major issue in the treatment of water (Volk et al., 2000).

Of central importance for the research in this thesis, DOC also plays a role in the C cycling and C balance of both terrestrial and aquatic ecosystems. In soils DOC represents a small C pool (typically <10-30 g C m^{-2} in the upper 1 m of soil in forests), but since it is readily available for microbial mineralization, particularly the low molecular weight compounds, DOC mineralization can be responsible for >50% of soil respiration (van Hees et al., 2005) – i.e. it is a critical component in C turnover. Waterborne export of soil DOC into downstream aquatic ecosystems also constitutes a C flux that can be of significance for the C budget of terrestrial

ecosystems, particularly when the waterborne C transport also includes POC and dissolved inorganic carbon (DIC) (Dawson et al., 2002; Striegl et al., 2007).

Terrestrial DOC entering aquatic environments can either be removed from the water column through sedimentation (von Wachenfeldt and Tranvik, 2008) or be mineralized by microbes (Karlsson et al., 2010) or through photodegradation (Bertilsson and Tranvik, 2000). Even DOC that is not removed and thus transported further downstream is often altered from its original composition by microbial degradation (Berggren et al., 2009a) and photodegradation (Anesio and Graneli, 2003). Both microbial degradation (Kalbitz et al., 2003a) and photodegradation (Molot and Dillon, 1997) of DOC in lakes are done preferentially on different fractions of the DOC pool. DOC that is incorporated into microbial biomass in lakes can also be channeled to higher trophic levels by the grazing on bacterial biomass (Berggren et al., 2010).

The C balance of aquatic ecosystems in the boreal, subarctic and arctic is strongly dependent on DOC from terrestrial ecosystems, as respiration is generally greater than the autotrophic C uptake (Tranvik et al., 2009). The influence of terrestrial DOC on CO_2 emissions from lakes has been found to be stronger than that exerted by annual temperature over a large regional scale (Sobek et al., 2005). It is estimated that between 30 and 80% of DOC exported from boreal terrestrial ecosystems is mineralized or sedimented in the aquatic environments and does not reach the oceans (Algesten et al., 2004). Because the C fluxes of aquatic ecosystems, including both atmospheric exchange and waterborne C transport, are not insignificant at a landscape scale and are intimately linked to the terrestrial ecosystems, it has been suggested that the most suitable unit for the analysis of the C balance might not be the 'ecosystem' but rather the catchment (Cole et al., 2007; Jonsson et al., 2007; Kling et al., 1991; Tranvik et al., 2009).

2.1.3 DOC LABILITY AND DOC COMPOSITION INDICES

Some compounds in the DOC pool are more or less readily available for microbial uptake and mineralization due to intrinsic qualities of their chemical structures (Kalbitz et al., 2003a; Marschner and Kalbitz, 2003; McDowell et al., 2006). For example it has been shown that certain fractions of DOC, primarily low molecular weight compounds and hydrophilic compounds are preferentially utilized for microbial degradation and therefore have a significantly higher turnover rate than the bulk DOC pool and is disproportionally responsible for soil respiration and microbial growth rates in relation to their concentrations (Berggren et al., 2010; van Hees et al., 2005). Continuous removal of labile DOC fractions can also be part of the reason why the DOC pool in soils is dominated by recalcitrant hydrophobic DOC (Wickland et al., 2007). In accordance, laboratory incubations of DOC solutions from various terrestrial and aquatic sources have shown that reduction of DOC concentrations is rapid during the initial two days of the incubation, after which the continued degradation of DOC is very slow (Roehm et al., 2009). The biodegradable fraction of DOC, defined as the fraction of the DOC pool that is involved in microbial degradation (mineralization, incorporation into microbial biomass or transformation into new DOC compounds) over a defined period of time (usually between 15 to 90 days), varies significantly (5-90%) with the DOC source or sampling location in a catchment (Kalbitz et al., 2003a; McDowell et al., 2006; Roehm et al., 2009).

Several indices of DOC bulk composition have been developed with the aim to use simple analytical techniques to attain information on source and lability of a DOC sample. Several of these indices use UV absorbance or fluorescence as a basis, measurements that require very little sample preparation and are easily obtained, thus enabling relative rapid analysis of largenumber of samples. Specific UV absorbance (SUVA) is a commonly used measurement that gives an estimate of DOC per cent aromaticity (Weishaar et al., 2003), and is defined as the absorbance (usually at 254 nm, - i.e. $SUVA_{254}$) per unit concentration of DOC. Another index based on absorbance is the ratio between absorbance at 250 and 365 nm (referred to as either E2/E3 or a_{250}/a_{365}), and it has been found to be well

correlated with the averaged molecular weight of the DOC sample (Peuravuori and Pihlaja, 1997). The fluorescence index (FI), which is defined as the ratio of the intensities of emission at 450 and 500 nm while excited with light at 370 nm, has been indentified to give an indication whether the DOC sample is made up of primarily terrestrially or microbially derived material (McKnight et al., 2001). Another index based on fluorescence is the humification index (HIX) which gives an indication of how far the humification of fluorescing compounds has progressed – which is related to decreased H/C ratios and a shifted emission spectra towards higher wavelengths (Zsolnay et al., 1999). In general, because terrestrially derived humic and fulvic acids are considered to be highly recalcitrant, it is expected that increased SUVA, HIX and decreased a_{250}/a_{365} and FI would be linked to decreased DOC lability.

While indices of DOC composition have been successfully used both to differentiate between DOC sources (Fellman et al., 2008; Wickland et al., 2007) as well as relate stream DOC composition with catchment ecosystem composition (Ågren et al., 2008b; Hood et al., 2006), the link to biodegradability is not unequivocal. The biodegradability of DOC derived from soil leachates has in several cases been found to correlated with both $SUVA_{254}$ and a_{250}/a_{365} (Kalbitz et al., 2003a; Marschner and Kalbitz, 2003), but the unexplained variation remains significant and for DOC samples from catchment outflows the link to biodegradability has been even weaker or even opposite to what would be expected (Holmes et al., 2008; Roehm et al., 2009). A decoupling between DOC composition indices and lability at the catchment scale could be due to processes that influence the lability of the non-aromatic fraction of DOC. It is, for example, known that selective absorption in mineral soils causes groundwater DOC to be high in non-aromatic but simultaneously dominated by aged and recalcitrant DOC (Holmes et al., 2008; Neff et al., 2006; Spencer et al., 2009), and that photodegradation selectively degrades aromatic DOC into non-aromatic DOC of unknown lability (Bertilsson and Tranvik, 2000; Stedmon and Markager, 2005).

Thus while DOC composition indices alone might not be enough to accurately predict the fate of terrestrial DOC that is exported into aquatic environments, they can be useful for identifying sources of aquatic DOC, and evaluating the influence of different ecosystems on catchment DOC dynamics. Peatlands have several characteristics that enable them to affect catchment DOC patterns (both composition and fluxes) to a higher degree than expected based on their area of coverage.

2.2 NORTHERN PEATLANDS

2.2.1 CARBON STORAGE AND PEATLAND CLASSIFICATION

Northern peatlands are ecosystems that have an organic soil layer that is >30cm deep and are located primarily between 50°N and 70°N, covering ~2.5% of the global land surface (Gorham, 1991). The defining characteristic of northern peatlands is their C accumulation over long timescales – i.e. their long term net primary production exceeds the total C losses. This is primarily due to restricted decomposition in cool, acidic, waterlogged conditions and a predominance of plants such as *Sphagnum* moss that are a poor substrate for decomposition. Estimates of the total C storage in northern peatlands are uncertain (range 270 to 600 Pg), primarily due to uncertainties of the average depth of peat deposits, in particular those located in Russia (Gorham, 1991; Tarnocai et al., 2009; Turunen et al., 2002). A significant fraction of the northern peatland C storage is found in the circumpolar permafrost region (including continuous, discontinuous, sporadic and isolated permafrost regions) where peatlands cover approximately 20% of the land surface (Tarnocai et al., 2009).

Classification of peatlands into bogs and fens is often the first categorization of peatlands, with bogs identified through ombrotrophic (rain fed) water supply, high acidity (pH < 5), low nutrient availability and a dominance of *Sphagnum* mosses and ericaceous vegetation while fens are identified by minerotrophic (stream or spring fed) conditions, lower acidity (pH > 6), higher nutrient availability and an absence of *Sphagnum* mosses (Wheeler and Proctor, 2000). However, the distinction is not always clear between fens and bogs and it is often more useful to

consider the classification of peatlands as a continuum from nutrient rich fens to very nutrient poor bogs, with an overlap where nutrient poor but minerotrophic peatlands have vegetation assemblages that resembles those of purely ombrotrophic bogs. Further classification of peatlands is often based on vegetation composition, which is determined by site fertility and climatic factors (Masing et al., 2010; Wheeler and Proctor, 2000). Several types of peatlands are found in permafrost regions, including several different types of palsa peatlands (Kuhry, 2008; Masing et al., 2010; Seppälä, 1988). It has been established that long term C accumulation rates differ greatly among peatlands, with the variation depending on peatland age and physical location but is also related to peatland type, with generally higher accumulation rates in non-permafrost bogs than in fens or palsas (Robinson, 2006; Sannel and Kuhry, 2009; Turunen et al., 2002).

Palsa peatlands are characterized by having accumulated segregated ice, often at the interface between peat and underlying mineral substrate (e.g. silt) that acts to elevate the peat surface of the palsa above the surrounding peatland forcing ombrotrophic conditions. While palsas in Eurasia are non-treed and dominated by *Sphagnum* mosses, dwarf shrubs, cloudberry, cottongrass and lichens (Malmer et al., 2005; Masing et al., 2010), in North America palsas (often referred to as peat plateaus) are usually treed in the discontinuous zone of permafrost but more similar in vegetation composition to Eurasian palsas in more northern and colder areas (Halsey et al., 1997a; Wright et al., 2009). Palsas are generally located towards the southern limit of widespread permafrost and in the last few decades these regions have experienced considerable warming causing partial thawing of the permafrost and a deepening of the active layer (Åkerman and Johansson, 2008; Camill, 2005; Payette et al., 2004). Climate models that include permafrost functions project this trend will continue (Lawrence et al., 2008). Permafrost thaw in palsas leads to altered hydrological settings and vegetation composition, which both can affect the C balance of the peatland (Camill et al., 2001; Malmer et al., 2005).

2.2.2 THE CARBON BALANCE OF PEATLANDS

Because of their large storage of C and its sensitivities to environmental variables, alterations of the NECB of northern peatlands has been identified as a potentially important feedback to climate change (Limpens et al., 2008; McGuire et al., 2009; Schuur et al., 2008). In particular, the C balance of peatlands that are, or will be undergoing permafrost thaw, are of interest because permafrost thaw represents a non-linear forcing which may cause a large mass of C to become accessible to hydrological and microbial processes. The NECB is defined as the sum of net ecosystem productivity (NEP – i.e. the atmospheric CO_2 exchange), waterborne C fluxes (including DOC), and the atmospheric exchange of non-CO_2 C compounds (primarily CH_4 emissions) (Chapin et al., 2006).

The largest C fluxes of the NECB for peatlands are the CO_2 uptake through photosynthesis (gross primary production, GPP) and release through autotrophic and heterotrophic respiration (jointly referred to as ecosystem respiration, ER). In comparison to other ecosystems, peatlands exhibit relatively low annual rates of GPP, but because ER is further suppressed it is often found that peatland measurements of NEP (the sum of GPP and ER) indicate an atmospheric CO_2 uptake in the range 20 to 60 g C m^{-2} yr^{-1} (Limpens et al., 2008). The two most common methods used to measure NEP are through permanently installed chambers or by eddy covariance (EC) techniques – all of which have advantages and disadvantages. While EC provides measurements of NEP for an area of several hundred m^2, and therefore average the spatial heterogeneity, it leaves gaps in the data coverage for periods of insufficient turbulent mixing (Barr et al., 2006). Chamber measurements provide NEP information for a very small area (<1 m^2), hence upscaling is necessary to estimates ecosystem NEP and this can be problematic in heterogeneous ecosystems, such as peatlands (Fox et al., 2008; Laine et al., 2006). Annual peatland NEP has been found to be a function of broad scale geographical location and physical setting (Limpens et al., 2008), while inter-annual variation is primarily dependent on hydrological conditions (Lindroth et al., 2007). Mosses and sedges however, have been found to differ in their response to water table fluctuations, with greater annual GPP and ER from moss

dominated bogs and lower fluxes from sedge dominated fens during years with relatively high water table (Sulman et al., 2010).

Peatlands also exchange CH_4 with the atmosphere, and are known as relative large sources at the landscape level, estimated to represent between 3 and 9% of the net land/ocean CH_4 emissions (Fletcher et al., 2004; McGuire et al., 2010). Exchange of CH_4 is important for the peatland C balance, but also of interest with regards to climate change feedbacks due to its property as a potent greenhouse gas (Friborg et al., 2003; Frolking et al., 2006). Microbial CH_4 production in peatlands, occurring in anaerobic peat layers, has been linked to the availability of DOC compounds derived from recent photosynthetic activity (Ström et al., 2003). Increased CH_4 emission rates have been linked to high water tables (thus suppressing CH_4 consumption in the overlying aerobic peat layer), increased temperatures and certain vegetation compositions, in particular the presence of sedges with aerenchymous roots (Christensen et al., 2003; Ström et al., 2005). Annual CH_4 emissions from peatlands have been found to vary between <1 g C m^{-2} yr^{-1} in dry bogs to over 30 g C m^{-2} yr^{-1} in fens (Bäckstrand et al., 2010; Suyker et al., 1996).

The last C flux that is commonly important to the total C balance of peatlands is the waterborne C export, which can be further divided into export of DOC, POC and DIC (which includes dissolved CO_2 and HCO_3^- derived from soil respiration or bedrock weathering), but is often dominated by the DOC component. Jointly they have been found to range up to 50 g C m^{-2} yr^{-1}, but with central values between 10 and 20 g C m^{-2} yr^{-1} (Dawson et al., 2004; Dinsmore et al., 2010). As such, they can represent up to 30% of the long term average NEP uptake (Dinsmore et al., 2010; Nilsson et al., 2008; Roulet et al., 2007), highlighting the importance of measuring the waterborne C export and DOC export in particular, in order to fully characterize the C balance of a peatland.

2.2.3 Peatland DOC export

Export of DOC from peatlands is determined by the production and removal of DOC in soil water and the water budget of the peatland that determines its runoff

patterns. Runoff from peatlands is dependent on the slope of the water table and the storage of water in the peatland, which in turn is further dependent on the balance between precipitation inputs and evapotranspiration losses. The water budget of fens also involves surface water from upstream sources and possible groundwater interactions. Peatlands act conservatively with regards to evapotranspiration – i.e. evapotranspiration from peatlands is lower than what would be expected from open water surfaces, though the extent of resistance to evapotranspiration is a function of the dominant vegetation type (Humphreys et al., 2006). Vascular plants in peatlands exert stomatal control on transpiration despite unlimited access to water (Admiral and Lafleur, 2007), while surfaces dominated by *Sphagnum* moss decrease evaporation rates rapidly once the water table is a few centimeters below the peat surface (Lafleur and Roulet, 1992). Peatlands often have a large store of water due to the water holding capacity of peat and the absence of significant hydraulic gradients in peatlands. During summers it is common for the water table to be lower as evapotranspiration often exceeds precipitation, particularly in more continental settings. In this situation runoff is reduced since saturated conditions with free water are restricted to depths where the hydraulic conductivity is quite low (Clymo, 2004). Change in storage among years can be very important in determining the total annual runoff for deep bogs (Kellner and Halldin, 2002). Snowmelt and storm events play a disproportionate role in the total runoff, and therefore also in the total DOC export, highlighting the importance of increased frequency of sampling during these periods to accurately estimate DOC export (Clark et al., 2007).

Peatlands generally exhibit high concentrations of DOC in pore water, ranging between 30 and 60 mg C l^{-1} (Elder et al., 2000; Fraser et al., 2001; Moore, 2003). Anoxic conditions of peatlands promote anaerobic decomposition which to a greater degree leads to production of DOC rather than full mineralization into CO_2 (Fenner et al., 2005), while low pH and generally low nutrient availability in peatlands act to slow the degradation of DOC (Moore and Dalva, 2001). High concentration of DOC in peatlands is promoted by long residence times of soil water which allow for build-up of DOC compounds. This effect, however, is

restricted to an initial phase, until DOC concentrations reach an equilibrium concentration (Blodau et al., 2004). Soil water in peatlands is generally not in contact with a mineral soil and this means that DOC export from peatlands can reach aquatic ecosystems without being absorbed, a process that is known to significantly decrease DOC export from forested ecosystems (Peichl et al., 2007). DOC concentrations at peatland catchment outflows often decrease during periods of high runoff (Jager et al., 2009), a result that has been interpreted as a dilution following a depletion of DOC reserves in the peat soil water rather than a shift in the flow pathways that the runoff follows (Worrall et al., 2002).

Evidence shows that a large proportion of the exported DOC from peatlands is of recent origin, despite the predominately old C present in peat storage (Billett et al., 2007). Photosynthesizing *Sphagnum* moss has been found to produce a significant amount of DOC (Fenner et al., 2004) that is surprisingly labile (Wickland et al., 2007) when compared to the recalcitrant DOC composition of water at the outflow of peatland catchments (Ågren et al., 2008b). This indicates that DOC produced by *Sphagnum* moss both has a highly labile fraction, as well as a highly recalcitrant fraction that becomes more important as the DOC is transported downstream.

While the magnitude of DOC export has been found to be influenced by air temperature (Evans et al., 2005), sulfur and nitrogen deposition (Chapman et al., 2005), inter-annual effects of winter conditions (Ågren et al., 2010) and drought conditions (Freeman et al., 2001), increased atmospheric CO_2 concentrations (Fenner et al., 2007) and vegetation composition, the primary control on DOC export from peatlands is generally considered to be the magnitude of runoff (Jager et al., 2009; Pastor et al., 2003; Worrall et al., 2008). The magnitude of peatland DOC export has been found in the range between 1.5 and 40 g C m^{-2} yr^{-1} (Fraser et al., 2001), export rates that are generally higher than those of catchments that do not contain peatlands.

2.3 DOC EXPORT FROM NORTHERN PEATLAND CATCHMENTS

Peatlands cover approximately 20% of the land surface at high latitudes (Tarnocai et al., 2009), and often contain permafrost. Assessing peatland influence on catchment DOC export and composition can be done in many different ways – e.g. through correlation studies between catchments or through processes studies within individual catchments. Correlation studies have shown that increased peatland coverage of catchments is significantly linked to increased DOC concentrations and also increased DOC export (Creed et al., 2008; Kortelainen et al., 2006; Laudon et al., 2004), but has also revealed that the unexplained variance can be large (Johnston et al., 2008; Mattsson et al., 2005). By studying individual catchments it is possible to learn more about processes that affect DOC transport, thus providing information that can be used to better understand how DOC export can be affected by permafrost thaw for example.

2.3.1 NORTHERN CATCHMENTS; HYDROLOGICAL REGIMES, RUNOFF GENERATION, DOC EXPORT AND RETENTION

Rivers draining northern catchments typically exhibit a nival streamflow regime – i.e. their annual runoff is dominated by snowmelt (Woo et al., 2008). Variations of the nival streamflow regime are produced when the catchments are strongly influenced by glacial runoff (proglacial regime), lake storage (prolacustrine regime) or significant summer precipitation (pluvial regime). Northern catchments exhibit relatively high runoff ratios (often ~0.6 in comparison with the global average of 0.36 (McNamara et al., 1998)), due to restricted evapotranspiration and reduced storage potential during snowmelt by seasonal frost or permafrost.

Several conceptual models of runoff generation have been used in northern catchments, and have implications also for the understanding of DOC transport. Catchments can be considered to be made up of hydrological units, e.g. lakes, bogs or forested areas, which have less variability with regards to hydrological variables within each unit than between units. The variable source area concept is useful for understanding runoff generation and DOC export from individual hydrological units and states that runoff generation is not spatially

static but varies with the level of the water table within each unit (Carey and Woo, 2001; Quinton and Marsh, 1999). In hillslope areas the highest water table positions are found close to the stream channels, leading to more frequent flushing of organic rich riparian soils that provides runoff with high DOC concentrations (Kohler et al., 2009; Pacific et al., 2010). The largest proportion of contributing areas is exhibited during snowmelt that in combination with restricted shallow organic flow paths due to seasonal frost table or permafrost conditions leads to high stream DOC concentrations – often higher than expected from the relationship between runoff and stream DOC concentration that is found during summers (Finlay et al., 2006). Forested catchments, in particular, also exhibit transport of DOC with higher lability during snowmelt compared to during the summer (Ågren et al., 2008a; Holmes et al., 2008). Rapid changes in stream chemistry during snowmelt and storm events have been identified as important for the annual fluxes, requiring increased sampling frequency during such periods (Clark et al., 2007; Inamdar et al., 2009; Saraceno et al., 2009) Hydrograph mixing models and other methods have recently been applied to quantify the different sources (e.g. wetlands, riparian zones, shallow forest soils or groundwater) that contribute DOC to stream flow by using DOC composition as an indicator of the DOC source (Fellman et al., 2009; Hood et al., 2006; Spencer et al., 2009; White et al., 2008).

In contrast to the variable source area concept, the unit threshold concept deals with how hydrological units are connected and how they interact to create a hydrological response at the catchment outlet (Laudon et al., 2007; Spence and Woo, 2006). Each hydrological unit can here be conceptualized as a bucket that conveys runoff to its downstream neighbor only when inputs from precipitation/upstream neighbors surpass its storage capacity (Woo and Mielko, 2007) – this is now referred to as “fill and spill”. The breaking of these connections is common during summer in northern catchments as evapotranspiration often is greater than precipitation leading to an increase in storage capacity on the landscape. Due to great differences in storage capacity, severance and reconnection of landscape elements do not necessarily follow an up

or down stream sequence. This behavior leads to very different discharge responses to similar magnitude precipitation events depending on antecedent conditions. It also follows that even if DOC is exported from terrestrial units, e.g. peatlands, these units might not be connected to the catchment outflow and thus may not contribute to catchment DOC export – i.e. their spill may go to storage in a downstream element that has excess storage capacity. Severed runoff connections between catchment units, involving lakes in particular (Woo and Guan, 2006), can be part of the reason why catchment lake coverage (Mattsson et al., 2005) and catchment size (Ågren et al., 2007) has been found to be linked to decreased catchment DOC export, especially when coupled with processes of DOC removal in lakes as discussed above.

2.3.2 Peatland permafrost thaw and catchment DOC export

Permafrost loss along with altered precipitation and increased temperatures have been identified as the major perturbation to catchment DOC export and lake C processing over the coming decades (Tranvik et al., 2009). However, the response to permafrost thaw is expected to vary across catchments due to their different characteristics (land cover, soil type and topography and permafrost characteristics) and the net result is currently uncertain (Frey and McClelland, 2009; McGuire et al., 2009).

For non-peatland ecosystems the most important alteration to DOC export is likely to be due to increased interaction with mineral soils as the active layer deepens. As more runoff passes through a mineral soil, substantial amounts of DOC is absorbed, thus reducing DOC export and altering the composition of the exported DOC through selective sorption processes (Balcarczyk et al., 2009; Kawahigashi et al., 2004; Prokushkin et al., 2007). This mechanism has been invoked to explain the apparent reduction of DOC export from the Yukon River over the last decades, which also has been coupled with increased DIC export as would be expected from an increased groundwater influence (Striegl et al., 2005; Walvoord and Striegl, 2007).

Because runoff from peatlands generally does not interact with mineral soils even when thawed, it has been proposed that DOC export from peatlands will increase when the thawed peat becomes available for hydrological transport (Frey and Smith, 2005). Studies of lake sediments have also indicated that palsa thaw causes increased lake sedimentation rates (Kokfelt et al., 2010). Further, it has been shown that the radiocarbon age of POC in catchments that are currently undergoing thaw is predominately older C, indicating that the POC is derived from riverside erosion of old peat (Guo and Macdonald, 2006). However, POC export is a smaller flux than DOC export and DOC in catchments with thawing peatlands is mostly modern – i.e. derived from recent plant photosynthetic activity rather than from peat deposits (Striegl et al., 2007). Experimental leaching of thawed organic soils shows that <1% of the soil organic C can be readily leached as DOC (Guo et al., 2007). These observations imply that changes to DOC export from peatlands that experience thaw could be more closely linked to changes in vegetation composition rather than due to the increased hydrological access to stored peat.

Part of the uncertainty in the understanding of the impact of thaw on DOC export from peatlands comes from the multiple hydrological end-points that are possible after thaw. Peatland permafrost thaw has both been found to lead to fen conditions with a large interaction with catchment runoff (Malmer et al., 2005) and to hydrologically isolated collapse scars (Camill et al., 2001). Because these hydrological settings lead to both different vegetation successions and DOC transport potential, they will not respond similarly with respect to DOC export and its composition.

2.4 Conclusions from literature review

Export of DOC from northern peatlands is of importance for the peatland C balance, as it generally represents a larger flux relative to the atmospheric C exchange in comparison to other ecosystems. Peatland DOC export is also important for the catchment aquatic C balance, due to its relatively large DOC export. Quantity, but also composition of DOC affects aquatic C cycling, with

possible implications for catchment C balance and DOC export. Different types of peatlands can have very differing patterns of DOC export and its composition, depending on hydrology and vegetation composition.

Loss of permafrost in northern peatlands has been associated with potentially important feedback mechanisms with regards to climate change, but the focus has primarily been on the atmospheric fluxes of CO_2 and CH_4. It is possible that permafrost degradation also can affect peatland DOC export, but there are gaps in knowledge on the direction of change and through which processes. It is important to consider both DOC quantity and composition when evaluating the impact of permafrost on peatland DOC export since both can have cascading effects on the C balance at the catchment scale.

CONTEXT OF CHAPTER 3 WITHIN THESIS

This following study of DOC export in Stordalen catchment investigates differences between different peatland types that are present in Stordalen peatland complex. The Stordalen peatland complex contains palsa parts that contain permafrost that is currently thawing and being converted into either non-permafrost bog type peatlands dominated by *Sphagnum* moss or into flow-through fens. By studying these peatland type ecosystems that permafrost thaw leads to, I can generate hypotheses on the implications of continued permafrost degradation of subarctic peatlands. This study also links to subsequent studies in this thesis by enabling a full C budget for the palsa part to be constructed as well as providing information that can be used at the catchment level to understand the influence of peatlands and permafrost degradation on DOC transport.

3. EFFECTS OF PERMAFROST AND PERMAFROST THAW ON COMPOSITION AND TRANSPORT OF DISSOLVED ORGANIC CARBON FROM A SUBARCTIC PEATLAND COMPLEX.

3.1 ABSTRACT

By changing the hydrological regime and ecosystem structure and function, loss of permafrost can alter the export and composition of DOC from subarctic peatlands. We studied DOC transport from four peatland parts within the Stordalen peatland complex in northern Sweden: a palsa and a bog that both have permafrost and two flow-through fens without permafrost. A DOC mass balance was estimated for each peatland part, and DOC composition was assessed using several indices. The palsa and the bog had net DOC export of 3.2 and 3.5 g C m^{-2} yr^{-1} respectively and their annually flow-weighted average DOC composition was found to have higher aromaticity, molecular weight, relative terrestrial origin of fulvic acids and C/N ratio than DOC exported from non-peatland parts of the catchment. Net exports of DOC from the fens were larger at 10.5 and 7.5 g C m^{-2} yr^{-1}, with greater export from the fen that had greater annual flow-through. DOC composition shifted significantly from fen inflows to outflows, increasing aromaticity, molecular weight and C/N ratios. Thus the fens were strong net sources of DOC to the downstream catchment, but the shift in DOC composition from inflows to outflows also implies that the fens act as locations for degradation and transformation of DOC from upstream sources. We expect DOC export from the Stordalen peatland complex to increase with continued permafrost thaw, but the influence of thaw on DOC composition is difficult to infer.

3.2 INTRODUCTION

An understanding of export of DOC from northern peatlands is important for assessing peatland NECB (Roulet et al., 2007) and the impacts of climate change on arctic C biogeochemistry (McGuire et al., 2009). Peatland runoff supplies downstream aquatic ecosystems with relatively more DOC than other terrestrial ecosystems (Kortelainen et al., 2006) and hence influences C cycling in these predominately heterotrophic ecosystems. Loss of permafrost from northern

peatlands is likely to be a significant factor affecting peatland DOC export and composition, with implications for both the peatland and catchment C cycling.

Northern peatlands in the permafrost region are estimated to store 280 Pg C: half of this store is in the discontinuous, sporadic or isolated permafrost zones (Tarnocai et al., 2009). Permafrost thaw over the latter part of the 20th century in peatlands in both North America (Camill, 2005) and Eurasia (Åkerman and Johansson, 2008) has been attributed to higher temperatures and increased snowfall. With increased permafrost thaw projected for the next century (Lawrence et al., 2008), a portion of the peatland C storage may become microbiologically and hydrologically available.

A large proportion of DOC exported from terrestrial northern ecosystems is either respired or added to sediments in streams and lakes before reaching the ocean (Cole et al., 2007). The spatial and temporal variability of DOC losses in aquatic ecosystems is poorly understood (McGuire et al., 2009), but the composition of the DOC is one important factor (Berggren et al., 2009b). Bioavailability of DOC has been found to correlate with aromaticity, molecular weight, carbon to nitrogen (C/N) ratio and the origin of the DOC – e.g. microbial or terrestrial (Berggren et al., 2009a; Fellman et al., 2008; McKnight et al., 2001; Peuravuori and Pihlaja, 1997).

Northern peatlands can undergo significant and widespread changes in vegetation, hydrology and ecosystem productivity due to climate change and permafrost thaw (Malmer et al., 2005). Mechanisms that cause a change in DOC export and composition due to permafrost degradation in peatlands have been proposed (Striegl et al., 2007; Wickland et al., 2007), but there is still considerable uncertainty (Frey and McClelland, 2009). Our objectives were to examine the DOC export and composition over the annual cycle from several different parts of a northern peatland complex in order to better understand the impact of continued permafrost thaw.

3.3 SITE DESCRIPTION

Stordalen (351 m above sea level) is a 15 ha peatland complex located 10 km east of Abisko in northern Sweden (68.20N, 19.03E). It is situated in the lower elevations of a 15 km^2 catchment that drains into Lake Torneträsk. The catchment contains several peatlands similar to Stordalen, but upstream of the peatlands the catchment is dominated by mountain birch forest and alpine heath above the tree line.

The average annual temperature 1913-2009 measured at the nearby Abisko Scientific Research Station is -0.5 °C, but recent warming has increased the average annual temperature for 1980-2009 to 0.0 °C. Annual total precipitation has increased from 306 mm for the period 1913-2009 to 336 mm in 1980-2009 (NORDKLIM, data available at http://www.smhi.se/hfa_coord/nordklim). The permanent snow cover period has decreased from 5.8 months to 4.9 months per year over the last 50 years, along with an increase in the maximum birch forest snow depth from 59 to 70 cm (Malmer et al., 2005).

The Stordalen peatland complex, for the purpose of our study, is classified into three peatland types; palsa, bog and fen. Classification is based on hydrology but clearly identified by vegetation composition, and is compatible with earlier classifications at Stordalen by Sonesson and Kvillner (1980) and Malmer et al. (2005). Over the last 35 years there has been pronounced shifts in vegetation due to thawing of the permafrost. On the palsa there has been an increase in maximum active layer depth from 0.6 to 0.8 m (Christensen et al., 2004), and a relative shift in dominance from bryophytes to lichens (Malmer et al., 2005). At the same time 1 ha, or 10% of the palsa area has been converted to bog and fen (Malmer et al., 2005).

The palsa parts are ombrotrophic and raised 0.5-2.0 m above its surroundings due to ice lenses in the permafrost of the underlying silt layers. The permafrost underlying the palsa and also the bog is estimated to be between 10 and 20 m thick (Åkerman and Johansson, 2008). The palsa is dominated by dwarf shrubs e.g. *Empetrum hermaphroditum*, along with a moderate abundance of *Eriophorum*

vaginatum, and a surface cover of mosses, *Sphagnum fuscum* and *Dicranum elongatum,* or lichens, *Cetaria* spp. and *Cladonia* spp. The peat is relatively thin on the palsa, between 0.4-0.6 m. Only the upper 0.25 m is ombrogenic *Sphagnum* peat and ^{14}C dating suggests that the transition from fen to palsa occurred between 800 and 300 years BP (Malmer and Wallén, 1996). The active layer thickness follows the surface topography: thinnest in hummocks and thicker in depressions (Rydén and Kostov, 1980). Drainage follows the frost table, filling first the internal depressions and then draining out of the palsa via narrow channels, similar to that described for Canadian treed palsa plateaus (Wright et al., 2009).

The bog is also underlain by permafrost, but wetter conditions cause a thicker active layer that reaches into the silt, hence frost heave is minimized and the water table is generally closer to the surface than in the palsa. Vegetation is dominated by *Sphagnum balticum* and *E. vaginatum*. The peat layer is generally thicker than on the palsa, ranging from 0.5 m up to 3 m in some locations (Rydén et al., 1980). The central bog in Stordalen receives runoff from the surrounding palsa, and in turn drains into the southern fen (Fig. 3.1).

The fens do not have permafrost. The fens receive a large water supply from a lake to the east of the peatland complex, and convey it into a stream on the west side of the peatland complex (Fig. 3.1). The catchment upstream of the eastern lake contains no significant peatlands and drains 1.7 km^2, i.e. a catchment size approximately 40 times greater than the joint area of the fens. Higher nutrient availability and water levels in the fens support *Carex rostrata* and *Eriophorum augustifolium* close to the fen inflows, mixed with increasing abundance of *E. vaginatum* and *Sphagnum riparium* closer to the outflows or away from the main flow paths. The water table is at or above the peat surface in the fens.

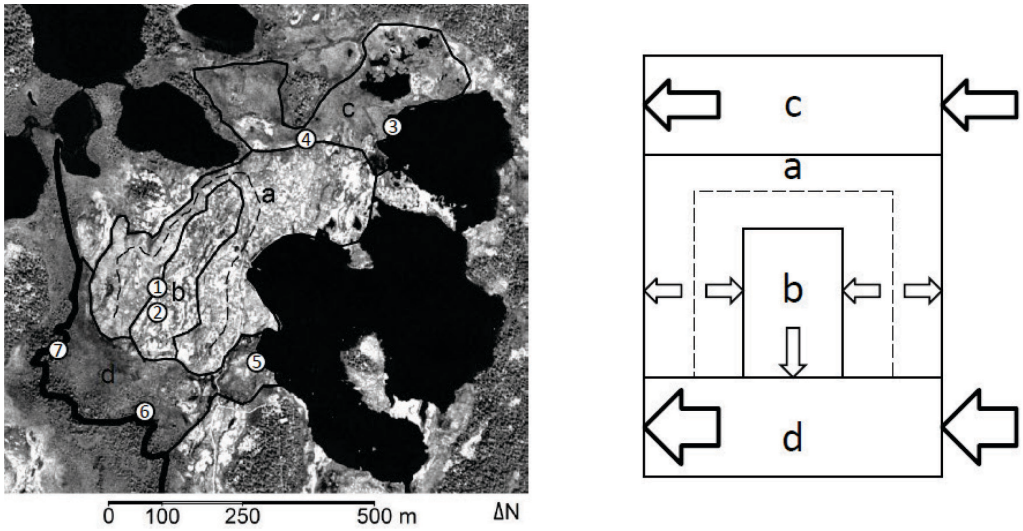

Figure 3.1. Aerial photograph (taken in July 2000, available at Abisko Scientific Research Station) of the Stordalen peatland complex (68.20N, 19.03E), with peatland types and sampling locations indicated. The hydrological connections are shown conceptually in the box diagram on the right. Dashed lines, on both diagrams, indicate the hydrological divides on the palsa, and arrows indicate the hydrological connections. The peatland types are: a. palsa, b. bog, and fens divided into c. north fen and d. south fen. Sampling points are indicated by circles: 1. palsa catchment outflow, 2. bog catchment outflow, 3. north fen inflow, 4. north fen outflow, 5. south fen inflow, 6. south fen east outflow, 7. south fen west outflow.

3.4 METHODS

This study monitored hydrology and DOC of one palsa catchment, one composite palsa/bog catchment (hence forth referred to as the bog catchment) and two separate fens, referred to as the north fen and the south fen (Fig. 3.1). The studied bog catchment (3.34 ha) contained ~45% palsa peatland type in addition to the bog peatland type and nested the monitored palsa catchment (0.39 ha). The palsa catchment outflow was gauged by installing a thin metal plated 20° V-notch weir (Fig. 3.1 – site 1). The bog catchment was sampled at a flume box located at a narrowing of the surface flow paths close to the transition into the south fen (Fig. 3.1 – site 2). It was however not possible to directly quantify the mass flow of water at the bog catchment outflow because of the diffuse nature of the water movement. Specific runoff from the palsa catchment was thus used to estimate the runoff for the bog catchment, since the bog catchment nests the palsa catchment.

Both inflows and outflows of the two fens were sampled for water chemistry, but it was only possible to directly measure discharge at the outflows. The outflow of the north fen (1.34 ha) (Fig. 3.1 – site 4) was sampled using a flume box, while the south fen (3.72 ha) had two outflow sites that were sampled using a small 45° V-notch weir (Fig. 3.1 – site 6) and a flume box (Fig. 3.1 –site 7). Discharge reported for the south fen is the sum of its outflows, and all reported water chemistry for individual sampling occasions is a flow-weighted average of the outflows. Discharge at the fen inflows were estimated as the residuals after solving the water budget of the fens, taking outflows, precipitation, evapotranspiration and change in storage into account. Precipitation was measured at Stordalen by a tipping bucket. Hourly fen evapotranspiration was estimated by the Penman-Monteith equation with parameters (aerodynamic and canopy resistance) appropriate to wet northern fens (Wessel and Rouse, 1994) and using hourly data (net radiation, air temperature, wind speed and relative humidity) from a micrometeorological tower located centrally on the palsa/bog part of Stordalen peatland. Change in fen water storage was calculated from the water level changes in the fens. The south fen water budget also took into account the inflow of water from the palsa/bog bog area (5.71 ha) that drains into the south fen, with its specific runoff estimated from the palsa catchment runoff.

Water level at the weirs, flume boxes and of the eastern lake was recorded hourly with Odyssey capacitance probes (resolution <1 mm). The probes were verified by manual stage measurements on each occasion the sites were sampled for water chemistry. Flume box discharge was calculated by the velocity-area method and was measured by an Aqua Data Sensa Electromagnetic Current Meter – RC2 (± 0.01 m s^{-1} resolution). Discharge over the weirs was calculated using information from LMNO Engineering, Research and Software, Ltd (http://lmnoeng.com), and verified by manual calibration. Rating curves were constructed using 2nd order polynomial functions (north fen outflow: n=11, r^2=0.99; south fen west outflow: n=30, r^2=0.95; south fen east outflow: n=16, r^2=0.87; palsa: n=10, r^2=0.99, all significant at $p<0.001$). We used the confidence bounds (95%) of the rating curves at the estimated average discharge rate of the

week of peak snowmelt in 2008 to estimate the uncertainty of our discharge measurements, yielding runoff uncertainties of 7% for the north fen outflow, 7% for the south fen west outflow, 15% for the south fen east outflow and 10% for the palsa.

Snow surveys were conducted on the palsa and bog prior to the commencement of melt in 2008 and 2009 in order to estimate the water storage in snow prior to snowmelt. Snow depth was measured on a grid of 100 by 200 m, n = 100, and a subset of those points were analysed for snow water equivalent, n = 15. The thickness of the thawed active layer was measured every 3 to 7 days in 9 sites on the palsa and 12 sites on the bog between late April and mid-October of 2008 and 2009.

Sampling frequency for water chemistry was dependent on hydrological conditions: every 1 or 2 days during snowmelt and other high flow events and every 3 to 6 days during lower flows. All sites were sampled in 2008, while in 2007 only the fens were sampled and in 2009 only the palsa catchment was sampled. Sampling started before snowmelt in early April and ended in late September in 2007 and mid October in 2008 and 2009. Each site was sampled between 40 and 63 times each year. Samples were filtered through 0.45 μm glass fibre filters, acidified to a pH of 2 with 0.5 M HCl and kept in 25 ml vials in a dark refrigerator at 5°C. Absorbance at 250, 254 and 365 nm was measured on a Shimadzu UV-160A with a 1 cm quartz cuvette on same day as the water samples were collected. A Shimadzu TOC-V CPH analyzer was used for DOC and total nitrogen (TN) analysis, with analysis done within 3 weeks of sample collection. Fluorescence intensity at 450 and 500 nm with a 370 nm excitation was measured on a Perkin Elmer LS55 within 3 weeks of collection. POC was analyzed through loss on ignition at 375 °C for 16 hours, after filtering 1 l of sample water through 0.45 glass fibre filter (Ball, 1964). Each sampling site was analysed for POC seven times in 2008, evenly distributed over the season. Water temperature was measured at an hourly frequency with HOBO temperature loggers installed at all sampling sites.

Daily DOC fluxes were estimated by multiplying average daily discharge rates with DOC concentrations, using linearly interpolated DOC concentrations for days between sampling occasions. From daily DOC fluxes we estimated the seasonal (April-October) and monthly DOC fluxes, along with flow-weighted average concentrations. Because the peatland freezes in late October, the seasonal export rates (April-October) can be assumed to represent the annual waterborne C fluxes of the peatland. Due to low sampling frequency and no apparent relationship between POC concentration and hydrology or season at any sampling site, annual POC export was estimated using the arithmetic mean POC concentration and total runoff. Fen net DOC and POC export was estimated as the difference between fen inflows and outflows, while also taking into account the estimated inputs from the palsa/bog area that drains into the south fen.

Uncertainties of annual DOC and POC fluxes were estimated using Monte Carlo simulations with 10 000 realizations for each estimate. Waterborne C flux uncertainties are a composite of the uncertainties of the annually flow-weighted average DOC concentration, the total annual discharge and area of catchment or fen. Uncertainty of the flow-weighted average DOC concentration is assumed to be primarily due to the interpolation, as replicate sample analysis of DOC samples had high precision. We assume a conservative 7.5% (SD) uncertainty of the flow-weighted DOC concentrations (similar to that estimated by Nilsson et al. (2008)). Uncertainty of the annual average POC concentration was estimated through the SD of measurements at each sampling site and varied between 15 and 30%. The uncertainty of the total annual runoff is due to the rating curve confidence bounds as discussed above, and additionally we assume a 5% uncertainty of catchment and fen areas. The uncertainty of the net waterborne C fluxes from the fens is based on the flow-weighted average difference in DOC/POC concentrations between fen inflows and outflow.

Composition of DOC was assessed using four indices. Specific UV absorbance ($SUVA_{254}$) is defined as the UV absorbance at 254 nm normalized for the DOC concentration (l mg^{-1} C m^{-1}) and increases linearly with measured DOC

aromaticity (Weishaar et al., 2003). Reported values of $SUVA_{254}$ range between 0.5 and 6 l mg^{-1} C m^{-1}, equivalent to a range of per cent aromaticity between 5 and 45%. The UV absorbance ratio between 250 and 365 nm (a_{250}/a_{365}), is inversely related to the DOC weight-averaged molecular weight (Lou and Xie, 2006; Peuravuori and Pihlaja, 1997), with reported values in the range 3 to 8. Fluorescence index (FI) is a measure of terrestrial or microbial origin of DOC fulvic acids (McKnight et al., 2001), and is calculated as the ratio between emittance intensity at 450 to 500 nm at 370 nm excitation. Reported values of FI are in the range 1.2-1.9, with higher values indicating a microbial source and lower values a terrestrial. The reported C/N ratio was assumed to be equal to the measured DOC/TN ratio, an assumption that was tested by analysing a sub-set of samples for dissolved inorganic nitrogen (DIN). Analysis of DIN on 5 samples from each sampling site with a Foss FIAstar 5000 detected only minor concentrations of NO_3^- (all samples <0.01 mg N l^{-1}) and NH_4 (all samples <0.005 mg N l^{-1}), supporting our assumption that only dissolved organic nitrogen significantly contributes to the TN.

3.5 RESULTS

3.5.1 CLIMATE

All years in the study were warmer than both the 1913-2009 and 1980-2009 average, with 2007 and 2008 more than a standard deviation warmer than the 1913-2009 average (Table 3.1). Differences in annual temperatures between the Abisko Research Station and Stordalen peatland complex were small, while summer precipitation at Stordalen peatland complex was greater during all three years. Precipitation measured at Abisko Research Station for the 2007 hydrological year (1st Nov- 30th Oct) was above the 1913-2009 average, mainly due to winter (November to May) precipitation that was more than one standard deviation above the average. This led to a larger spring flood in 2007. Precipitation in both 2008 and 2009 were below the 1913-2009 average, with the measured 2009 June to October precipitation at Stordalen peatland complex >50 mm less than in either 2007 or 2008. Inputs of DOC from precipitation were

estimated at between 0.3 and 0.5 g C m^{-2} yr^{-1}, based on an average DOC concentration in snowpack and rainfall of 1.8 mg C l^{-1}.

Table 3.1 Precipitation and temperature for the years of the study, compared to long term means[a]

	Nov 2006 – Oct 2007	Nov 2007 – Oct 2008	Nov 2008 – Oct 2009	1913-2009 Mean
Annual precipitation (mm)	349	274	269	306
Nov-May precip. (mm)	170	152	143	139
June-Oct precip. (mm)	179 (209)	122 (183)	126 (133)	177
Temperature (°C)	0.9 (0.8)	0.7 (0.6)	0.3 (0.3)	-0.5

[a]Observations are made at the Abisko Scientific Research station 10 km west of the Stordalen peatland complex. Annual temperature and summer precipitation were also measured directly at Stordalen and is reported in brackets. Precipitation from November to May represents snow storage and precipitation from June to October is primarily rainfall.

3.5.2 Palsa and bog catchments runoff and DOC patterns

Runoff from the palsa and bog catchments was 101 and 123 mm in 2008 and 2009 respectively (Table 3.2). In 2009 there was no runoff recorded after June 18, while 24% of the annual total runoff in 2008 occurred after the end of June. Runoff during the week of peak snowmelt runoff was 54 mm in 2008 and 63 mm in 2009, or >50% of the annual total in both years. The runoff during the melt period was greater than the estimated snow water equivalent measured prior to snowmelt: this was 47 mm in 2008 and 33 mm in 2009.

Total net DOC export from the palsa catchment (taking precipitation inputs into account) was 3.2 and 2.5 g C m^{-2} yr^{-1} in 2008 and 2009, and 3.5 g C m^{-2} yr^{-1} in 2008 from the bog catchment (Table 3.2). The palsa and bog catchment outflow DOC concentrations varied between a factor of 5 and 9 over a full season (Fig. 3.2 and Table 3.3). Measured DOC concentrations were negatively correlated with runoff (Fig. 3.3). Paired t-tests show that the palsa catchment had significantly lower DOC concentrations than the bog during April and May ($n=16$, $p<0.05$) but higher concentrations during September and October ($n=11$, $p<0.01$). Export of DOC from April to June in 2008 was 65% of the annual DOC export from the palsa and 74% of the total for the bog, while in 2009 all DOC export from the

palsa occurred before Jun 18th. DOC concentrations continued to rise in palsa pore water after runoff had ceased during the 2008 summer, reaching 95 mg C l^{-1} (Fig. 3.2). Water sampled at the bog outflow flume-box during the summer when runoff had ceased reached 140 mg C l^{-1}. Concentrations of POC were much lower than DOC over the entire 2008 season, with all samples < 2 mg C l^{-1} (Table 3.3) resulting in a POC export <0.1 g C m^{-2} yr^{-1} (Table 3.2).

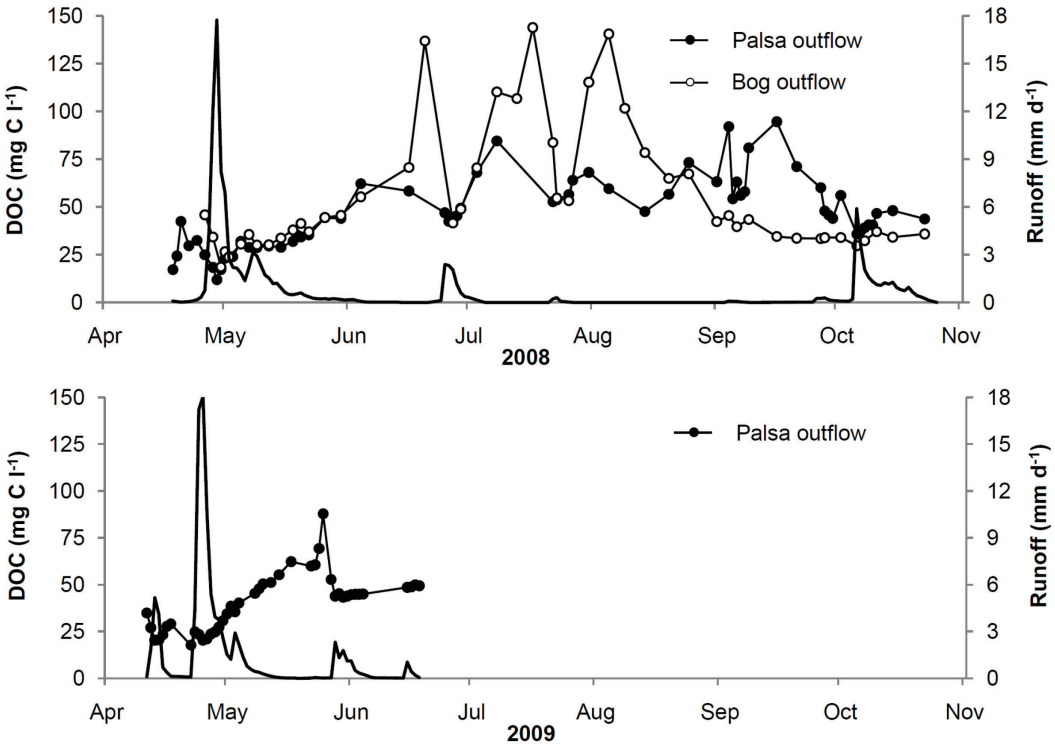

Figure 3.2. Hydrograph and DOC concentrations for the palsa and bog catchment outflows. No runoff occurred from the palsa after June 18th in 2009.

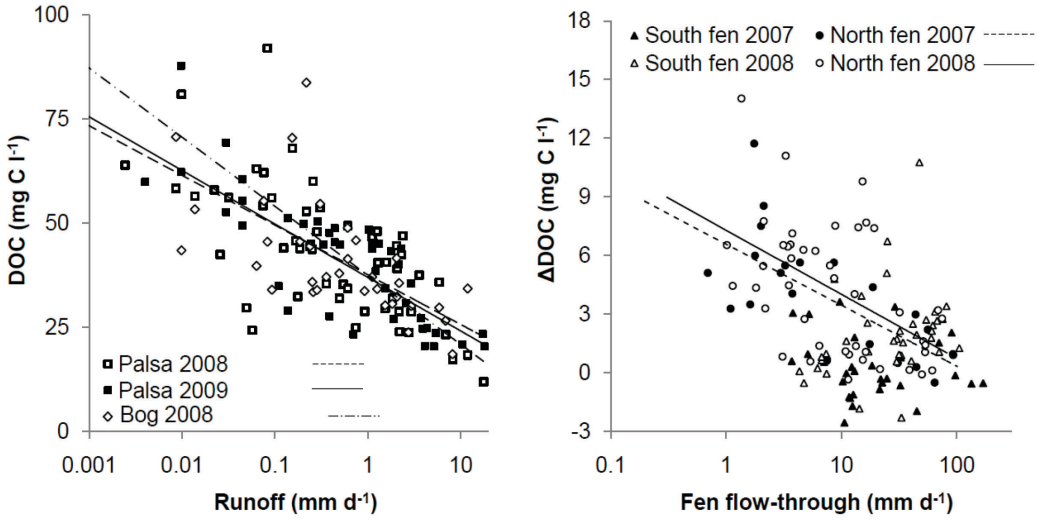

Figure 3.3. Relationship between DOC concentrations and rate of runoff or fen flow-through (defined as the fen area specific discharge rate at fen outflows). Values of DOC concentrations used for the palsa and bog were from their outflows while the values for the fens are the differences between in- and outflow concentrations. The correlations are significant ($p<0.01$) for the palsa (2008, $r^2=0.41$; 2009, $r^2=0.57$), the bog (2008, $r^2=0.41$) and the north fen (2007, $r^2=0.47$; 2008, $r^2=0.26$). The relationships for the south fen were not significant.

Flow-weighted averages of DOC composition indices showed that the palsa had higher $SUVA_{254}$ and lower FI and a_{250}/a_{365} than the bog (Table 3.4). Paired t-tests showed that this difference was significant in all months in 2008 ($p<0.05$), with the exception of April (Fig. 3.3). A difference may have existed but our concurrent sample size for April was too small (n=3) to constrain a t-test. The difference between $SUVA_{254}$ of the palsa and the bog increased with less runoff ($r^2=0.50$, $p<0.01$) and higher water temperatures ($r^2=0.41$, $p<0.01$). An upward shift in $SUVA_{254}$, occurred during snowmelt for both the palsa and bog (Fig. 3.4). This step change in DOC composition occurred both in 2008 and 2009 once the active layer depth had reached 5 to10 cm (Fig. 3.5). This trend could also been seen in decreased values of a_{250}/a_{365} and FI (not shown), indicating a shift away from non-aromatic microbial DOC of low molecular weight with increased active layer thickness.

Table 3.2. Hydrological and waterborne C fluxes for the studied peatland parts of Stordalen peatland complex between April and October of selected years. All water and C fluxes are normalized to their catchment (palsa and bog catchments) or areal extent (fens). Negative fluxes indicate peatland losses, and positive fluxes are gains.

	Specific water flux (mm)[a]	**Average DOC conc.** (mg l^{-1})[a]	**Specific DOC flux** (g m^{-2}) ±2SD	**Average POC conc.** (mg l^{-1})[a]	**Specific POC flux** (g m^{-2}) ±2SD
2007 Precipitation	290	1.8	0.5 ±0.5	0	0
2008 Precipitation	228	1.8	0.4 ±0.4	0	0
2009 Precipitation	181	1.8	0.3 ±0.3	0	0
2007 Fen evapotranspiration	-280	0	0	0	0
2008 Fen evapotranspiration	-255	0	0	0	0
North fen 2007					
Outflow	-2790	9.6	-26.8 ±6.7	-	-
Lake inflow	2631[b]	7.7	20.1 ±5.1	-	-
Net storage	-51	-	**-6.1 ±1.9**	-	-
North fen 2008					
Fen outflow	-2282	10.5	-23.9 ±5.9	0.5	-1.1 ±0.6
Fen inflow from lake	2137[b]	7.5	16.0 ±4.0	0.6	1.3 ±0.5
Net storage	-102	-	**-7.5 ±2.4**	-	**0.1 ±0.4**
South fen 2008					
Fen outflow	-5882	10.2	-60.2 ±15.1	0.6	-3.6 ±1.6
Palsa/bog part inflow	188[c]	31.4[c]	5.9 ±1.4	0.8	0.1 ±0.0
Fen inflow from lake	5339[b]	8.1	43.4 ±10.5	0.5	2.8 ±0.8
Net storage	-83	-	**-10.5 ±4.6**	-	**-0.6 ±0.7**
Palsa catchment 2008					
Palsa outflow	123	29.1	-3.6 ±0.9	0.7	-0.06 ±0.04
Net export	-	-	**-3.2 ±1.1**	-	**-0.06 ±0.04**
Palsa catchment 2009					
Palsa outflow	101	27.2	-2.8 ±0.7	-	-
Net export	-	-	**-2.5 ±0.9**	-	-
Bog catchment 2008					
Bog outflow	123[d]	31.4	-3.9 ±0.9	0.8	-0.08 ±0.03
Net Export	-	-	**-3.5 ±1.1**	-	**-0.08 ±0.03**

[a]See text for uncertainty bounds for water fluxes and flow-weighted average DOC concentrations that were used to calculate the SD of the waterborne C fluxes through Monte Carlo analysis.

[b]Lake inflows calculated as the residual of the fen water balances, including fen outflow, precipitation, evapotranspiration, change in storage and for the south fen also the input from the palsa/bog part that drains into the fen.

[c]Palsa/bog part discharge to the south fen estimated from the specific runoff from the palsa catchment, and then rescaled to the area of the south fen. Palsa/bog part DOC concentration assumed to be equal to the sampled bog catchment.

[d]Bog catchment runoff assumed to be equal to the palsa catchment runoff since they are nested.

Table 3.3. Flow-weighted means and ranges of measured DOC composition indices at sampling locations within the Stordalen peatland complex.

Site and Year	DOC conc. (mg C l^{-1})		POC conc. (mg C l^{-1})		$SUVA_{254}$ (l mg^{-1} C m^{-1})		FI		C/N		a_{250}/a_{365}	
	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range
North fen												
2007 inflow	7.72	4.3 - 15.0	-	-	1.71	1.02 - 3.28	-	-	29.2	16.0 - 42.8	-	-
2007 outflow	9.60	5.4 - 26.8	-	-	2.02	1.37 - 3.61	-	-	32.3	20.2 - 47.1	-	-
2007 net Δ	1.88	-0.5 - 11.7	-	-	0.29	-1.03 - 2.04	-	-	3.1	-3.4 - 20.3	-	-
2008 inflow	7.48	5.0 - 10.8	0.56	0.33 - 0.96	1.65	1.25 - 2.20	1.71	1.59 - 1.79	28.7	15.4 - 36.0	5.35	4.68 - 6.55
2008 outflow	10.50	6.1 - 22.4	0.47	0.21 - 0.91	2.18	1.33 - 2.95	1.63	1.50 - 1.73	33.5	22.3 - 46.5	4.70	4.19 - 5.29
2008 net Δ	2.99	-0.3 - 11.1	-	-	0.53	0.00 - 1.40	-0.08	-0.19 - 0.01	4.8	-5.1 - 20.7	-0.66	-1.85 - -0.01
South fen												
2008 inflow	8.12	3.9 - 11.1	0.51	0.39 - 0.68	1.98	1.47 - 2.56	1.66	1.55 - 1.77	32.3	21.8 - 49.5	5.28	4.59 - 7.50
2008 outflow	10.65	6.2 - 29.7	0.63	0.29 - 1.21	2.17	1.35 - 3.02	1.59	1.53 - 1.65	37.6	25.4 - 55.4	4.56	3.78 - 5.07
2008 net Δ	2.53	-2.4 - 24.4	-	-	0.19	-0.27 - 1.05	-0.07	-0.22 - 0.03	5.3	-15.3 - 33.6	-0.71	-1.76 - 0.05
Palsa												
2008 outflow	29.10	11.9 - 81.0	0.69	0.29 - 1.68	3.12	1.59 - 4.41	1.43	1.36 - 1.52	55.5	39.6 - 73.9	4.60	3.82 - 5.53
2009 outflow	27.20	17.7 - 87.9	-	-	2.76	2.03 - 3.41	-	-	70.0	42.5 - 93.7	3.40	3.03 - 4.65
Bog												
2008 outflow	31.40	18.5 - 83.7	0.83	0.47 - 1.47	2.61	1.44 - 3.82	1.49	1.40 - 1.55	57.8	34.8 - 83.1	4.88	3.64 - 6.52

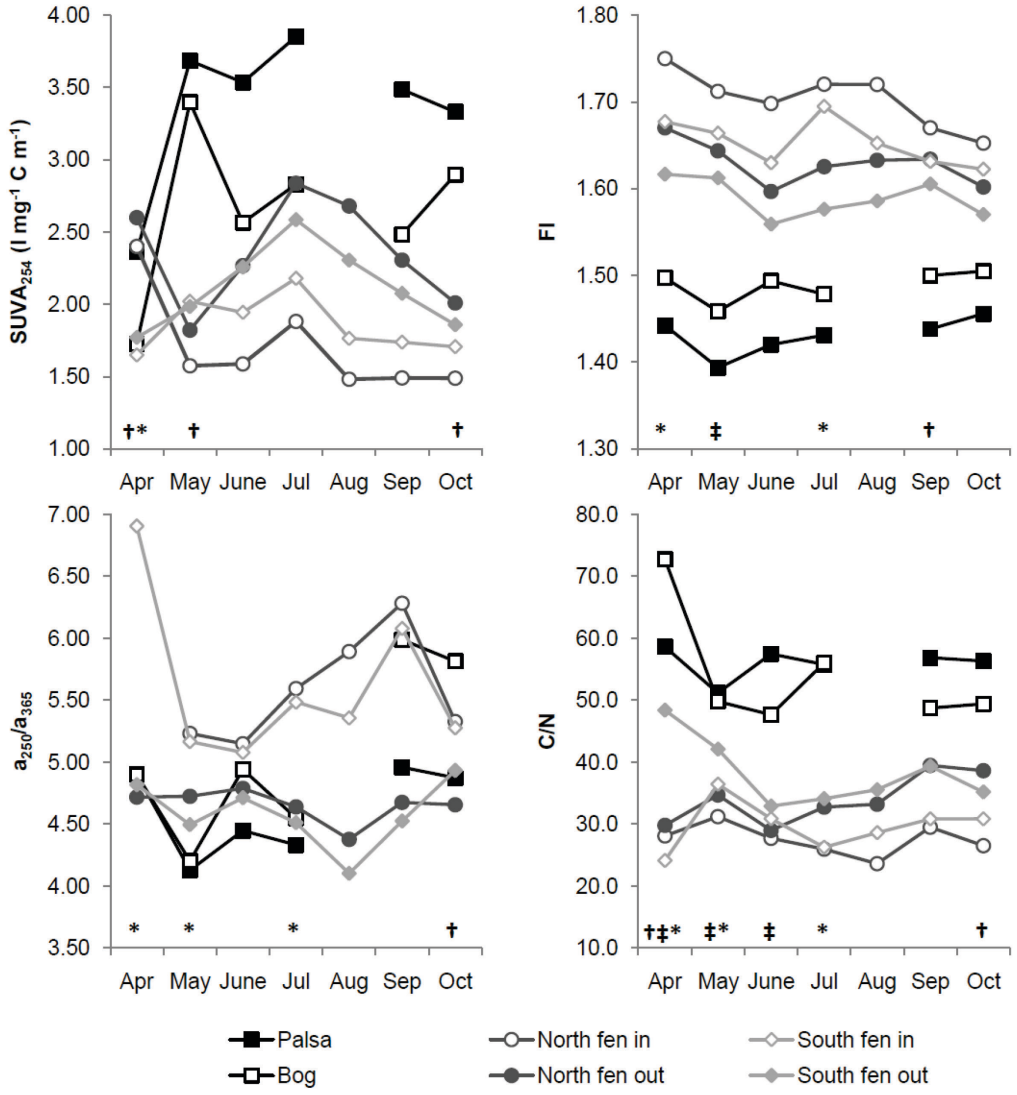

Figure 3.4 Monthly flow-weighted averages of DOC composition indices for the different sampling points in Stordalen peatland complex in 2008. There are no data from the palsa and bog during August since there was no runoff. Note the symbols above the x-axis for significant differences between monthly averages (pair wise t-tests, $p>0.05$). † No significant difference between south fen inflow and outflow, ‡ No significant difference between north fen inflow and outflow, * No significant difference between the palsa and bog outflows.

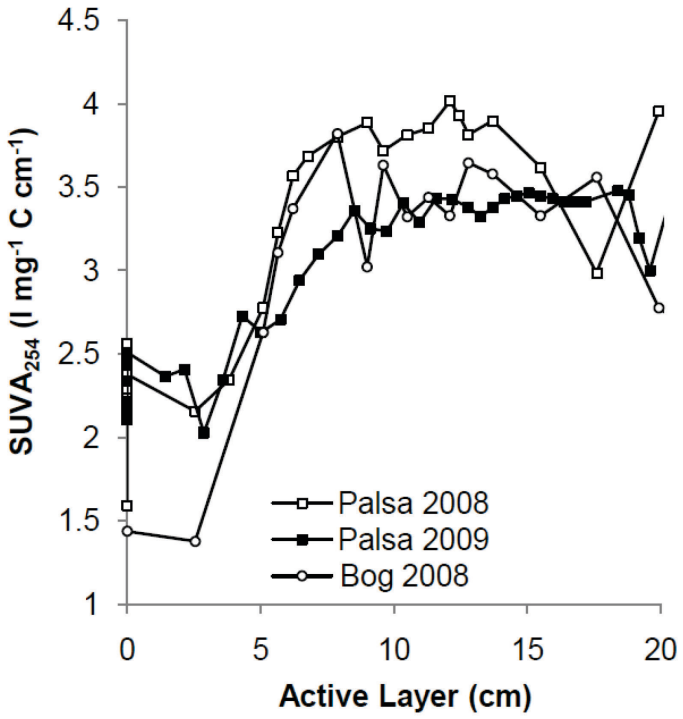

Figure 3.5. Shift in $SUVA_{254}$ in water samples from the palsa and bog catchments runoff, with the deepening of the active layer. The active layer started developing on the 27th of April in 2008 and on the 21st of April in 2009. Snowmelt runoff ended on both years by the end of May, which coincided with the active layer reaching a thickness of 20 cm on the 4th of June in 2008 and on the 26th of May in 2009.

3.5.3 FEN FLOW-THROUGH AND DOC PATTERNS

The south and north fen convey runoff from a 1.7 km^2 catchment, with >80% of this catchment runoff passing through the south fen. Precipitation, evapotranspiration, change in fen storage between April and October and runoff from the palsa/bog portion that drains into the south fen were all small fluxes in comparison to the measured total fen outflow magnitudes (Table 3.2). In 2008, none of these minor water fluxes exceeded 4 or 10% of the south and north fen outflow magnitudes respectively. The discharge at the fen inflows were estimated as the residual of the water budget, and showed that both the north and south fen total inflow was estimated to be 97% of the outflow total discharge – a difference that is within the uncertainty bounds. Because the fen water budgets were so dominated by surface water fluxes we define the fen flow-through rates as the discharge per fen area as measured at the fen outflows.

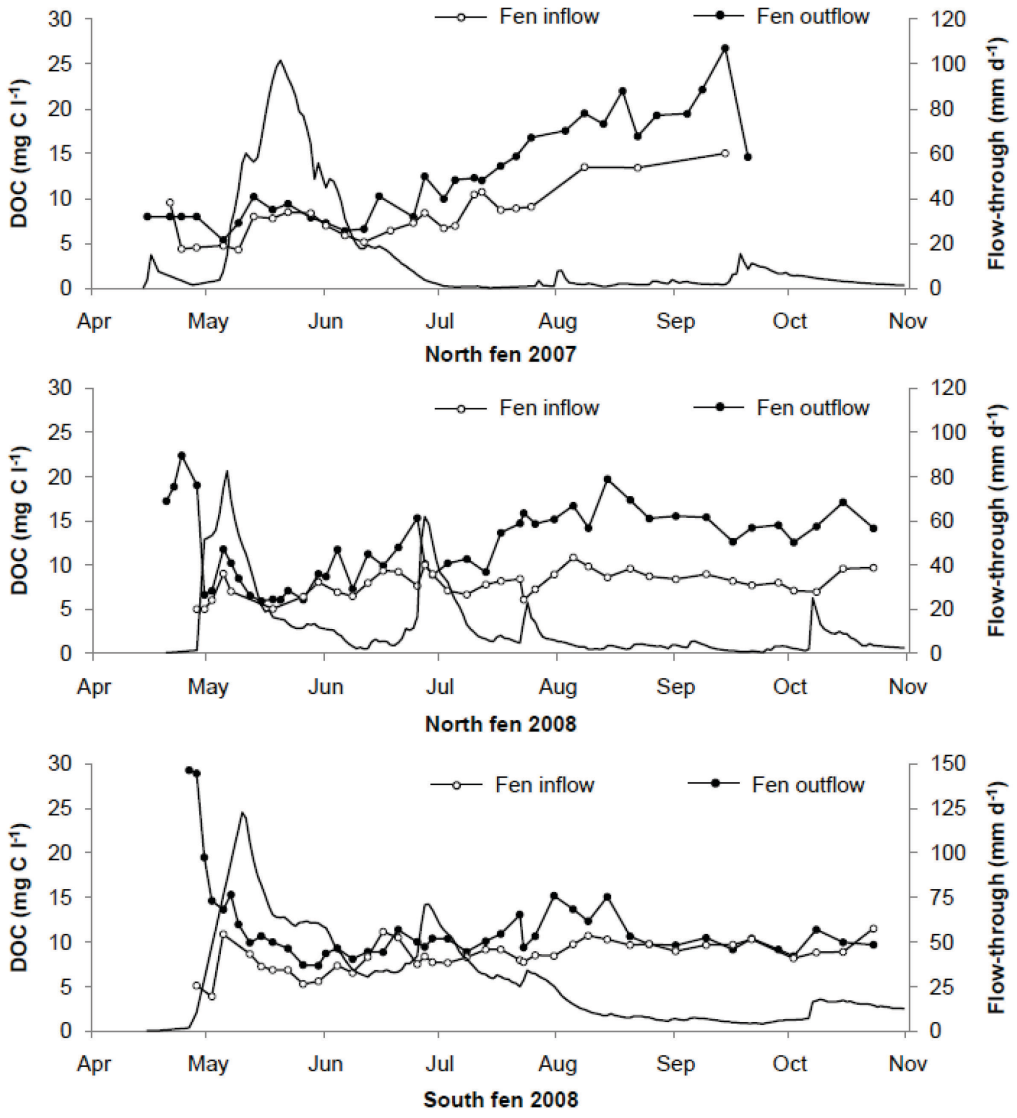

Figure 3.6. Fen flow-throughs and DOC concentrations for the north and south fen.

The net DOC export from the north fen was 6.1 and 7.5 g C m^{-2} yr^{-2} in 2007 and 2008 and 10.5 g C m^{-2} yr^{-1} from the south fen in 2008 (Table 3.2). The seasonal patterns of DOC concentration at the fen outflows were consistent both between the north and south fen and between years, with high DOC concentrations prior to snowmelt, minimum concentrations during snowmelt and progressively increasing concentrations over the summer (Fig. 3.6). Paired t-tests show that the north fen outflow DOC concentrations were higher than inflow concentrations in

all months of 2008 and 2009, (n size varied from 4 to 16 depending on the month, $p<0.01$). Concentrations in the south fen outflow were significantly higher than in its inflow during Apr-May and Jul-Aug of 2008 ($n=5$-13, $p<0.05$). These four months accounted for 86% of the estimated annual net DOC export from the south fen. There was a significant correlation between the difference in fen in- and outflow DOC concentration and flow-through for the north fen (2007: $r^2=0.47$, $p<0.01$. 2008: $r^2=0.26$, $p<0.01$) (Fig. 3.3) but not for the south fen. Average POC concentrations in fen in and outflows ranged between 0.47 and 0.65 mg C l^{-1}, and the sampling proved insufficient in determining whether the fens were sinks or sources of POC (Table 3.2).

Fen inflows had lower flow-weighted average $SUVA_{254}$ and C/N ratios and higher FI and a_{250}/a_{365} ratios than their respective outflows (Table 3.3). This difference in DOC composition between fen in and outflows was significant during most months in 2008 (Fig. 3.4). The difference between $SUVA_{254}$ in inflows and outflows increased with warmer water temperatures and less runoff (Fig. 3.7).

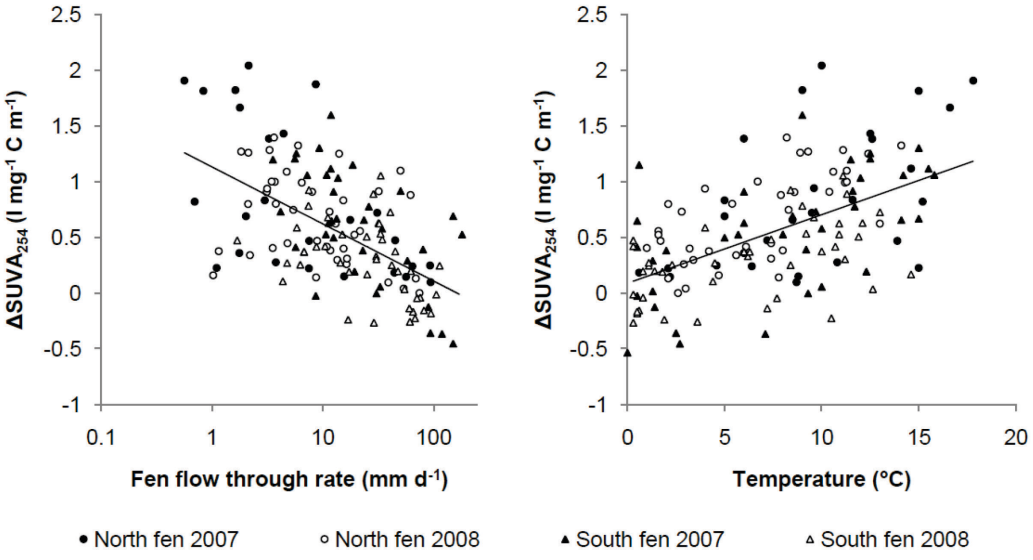

Figure 3.7. Fen flow-through rate and water temperature of fen outflows versus the difference in $SUVA_{254}$ between fen inflows and outflows. Using data from both fens and both years yield significant ($p<0.01$) correlation with both runoff ($r^2=0.33$, $n=148$) and water temperature ($r^2=0.32$, $n=148$).

3.6 DISCUSSION

3.6.1 PALSA AND BOG

Compared to the literature values of peatland DOC export (Billett et al., 2004; Koehler et al., 2009; Nilsson et al., 2008) the palsa and bog had lower DOC export than average estimates for peatlands: 2.8 ± 0.7 (2 SD) and 3.9 ±0.9 g C m^{-2} yr^{-1} (palsa and bog, respectively) compared with ~15 g C m^{-2} yr^{-1}. DOC export was limited by runoff, since our flow-weighted DOC concentrations of 27-32 mg C l^{-1} were in the range of 25-40 mg C l^{-1} observed by others (Fraser et al., 2001; Kohler et al., 2009; Nilsson et al., 2008). Runoff from the palsa and bog catchments were only 100-120 mm yr^{-1}, while the runoff from the catchment at large was 180-270 mm yr^{-1} for the same period. Permafrost conditions have raised the palsa above the surroundings, leading to reduced snow accumulation and snowmelt magnitude compared to other catchment elements. The runoff magnitude during summers is also reduced compared to the greater catchment, due to increased water storage capacity once the active layer deepens, favoring evapotranspiration rather than runoff.

Differences in DOC export from the palsa between 2008 and 2009 were related to differences in runoff. Total runoff from the palsa was 21% greater in 2008 than in 2009, and the DOC export was similarly greater (+29%), mainly due to a late fall runoff event that represented 35% of the annual DOC export. In 2009, no export occurred after mid June. The 2008 fall runoff event was 24% of the annual runoff, showing how runoff after snowmelt can be disproportionally important for annual DOC export. In a related study the DOC export was compared to the net ecosystem productivity (NEP, the atmospheric CO_2 exchange) measured by eddy co-variance techniques and it was found that the DOC export over two years only represented 6% of NEP which is a lower importance for the peatland C balance than reported from several non-permafrost bogs (see chapter 4).

Exported DOC from the palsa and bog catchments had higher $SUVA_{254}$, C/N ratios and lower FI and a_{250}/a_{365} than the birch forest dominated catchment at large (represented by measurements at the fen inflows). High aromaticity, primarily

derived from terrestrial fulvic acids, with relatively high C/N ratio and large molecular size of the DOC as implied from the indices of DOC composition indicate that DOC exported from the palsa and bog would be a poor substrate for downstream microbial degradation (Berggren et al., 2009a; Fellman et al., 2008; McKnight et al., 2001; Peuravuori and Pihlaja, 1997). Recalcitrant DOC composition is consistent with DOC derived from aged peat (Roehm et al., 2009), but could also be due to in-situ selective DOC degradation prior to export. Long residence time of peat water has been shown to increase the CO_2 released from peat (Pastor et al., 2003) and increase DOC aromaticity (Berggren et al., 2009a).

A shift in DOC composition occurred during snowmelt for both the palsa and bog catchments, with $SUVA_{254}$ indicating a shift towards more aromatic DOC. This shift was not related to the rate of runoff but rather concurrent with a thawing of the active layer below 5 cm and also coincided with the accumulated snowmelt runoff equaling the pre-snowmelt snow water equivalent. It is thus likely that the shift in DOC composition during snowmelt is associated with a shift in DOC source, from DOC derived from decomposing surface litter to DOC derived from the peat itself.

The palsa catchment had consistently and significantly higher $SUVA_{254}$ than the bog catchment. The difference in $SUVA_{254}$ between the palsa and bog could be a result of increased importance of DOC derived from recent photosynthetic activity in the more productive bog (Bäckstrand et al., 2010). *Sphagnum* moss has been found to quickly contribute recently fixed atmospheric C to the DOC pool (Fenner et al., 2004), and a fraction of this DOC has been found to be highly available for microbial degradation (Wickland et al., 2007). The difference in $SUVA_{254}$ between the palsa and the bog was correlated with runoff (r^2= 0.50, $p<0.01$, n=45), showing a greater difference during periods of low runoff. This pattern can be explained by a variable mixing of DOC from different sources at the bog outflow, which drains a catchment which consists of 45% palsa in addition to the bog peatland type.

3.6.2 FENS

In 2008 the north fen net DOC export was 7.5 ±2.4 g C m^{-2} yr^{-1} compared to 10.5 ±4.6 g C m^{-2} yr^{-1} for the south fen. We could not statistically determine whether the fens were net sinks or sources of POC, with confidence limits of fluxes between -0.5 and 1.5 g C m^{-2} yr^{-1}. The net atmospheric C gas exchange for the fen peatland type in Stordalen is near zero (based on measurements of NEE and THC emissions between 2002 and 2007) (Bäckstrand et al., 2010), so the addition of the net DOC and POC export would result in net loss of C storage, through the uncertainty in quite large in this estimate. It is clear that DOC export from the fens play a critically more important role in the fens' NECB than that of the palsa or bog.

At higher fen flow-through rates the difference between fen outflow and inflow DOC concentrations is less, reducing the influence of total annual runoff on the net DOC export. In 2008 the difference in net DOC export between the south and north fen was 61% while the difference in flow-through magnitude was 145% (south fen > north fen). The relationship between runoff and DOC concentrations in the fens also affected the timing of DOC export. Net DOC export for the fens between July and October represented 40-65% of the annual total net DOC export, a period with 13-35% of the annual runoff. Both fens also had a smaller proportion of the net DOC export during April to June (35-60%) than the palsa or bog (65-100%).

All indices of the fens' DOC composition ($SUVA_{254}$, FI, a_{250}/a_{365} and C/N ratio) changed significantly between their inflows and outflows. The fens consistently exported DOC that shifted towards the DOC composition of the palsa and bog catchments. The fen inflow to outflow difference in $SUVA_{254}$, a_{250}/a_{365} and C/N ratios became larger with lower fen flow-through rate and higher fen outflow water temperature. There were no significant relationships between fen flow-through magnitude and water temperature, so the flow-through and temperature relationships with $SUVA_{254}$ appear independent of each other.

The changes in DOC composition from fen inflow to outflow could be the result of several biotic and abiotic processes including DOC production, sedimentation, transformation and degradation (Berggren et al., 2009a; Bertilsson and Tranvik, 2000; Kalbitz et al., 2003b; von Wachenfeldt and Tranvik, 2008). A mixing model can estimate the hypothetical DOC composition of DOC produced within the fen, if it is assumed that all DOC from upstream sources pass through the fen unaltered, i.e. that within-fen DOC production is the only process affecting fen DOC composition and export. $SUVA_{254}$ was most suitable for this analysis since it is linearly correlated with DOC aromaticity:

$$SUVA_{Fen} \times DOC_{Fen} = (SUVA_{Out} \times DOC_{Out}) - (SUVA_{In} \times DOC_{In})$$

where SUVA is the annual flow-weighted $SUVA_{254}$, DOC is the annual DOC export and $_{Fen}$, $_{Out}$ and $_{In}$ denotes composition and flux of DOC from within the fen, at the fen outflow and at the fen inflow. The mixing model was solved for $SUVA_{Fen}$ for the north fen in 2007 and 2008, and for the south fen in 2008 (also taking into account the DOC inputs from the palsa/bog part that drains into the south fen), and was estimated at 3.04 ± 0.11 l mg^{-1} C m^{-1} (average ± standard error, n=3). This estimate of aromaticity is slightly higher than that measured at the palsa outflow, at 2.94 l mg^{-1} C m^{-1} (Table 3.3). A previous study has however found that DOC extracted from fen and palsa peat cores in Stordalen have significantly differing $SUVA_{254}$, at 2.24 l mg^{-1} C m^{-1} in the fen and at 4.81 l mg^{-1} C m^{-1} in the active layer of the palsa (Roehm et al., 2009). In addition it has been found that *Carex rostrata*, which is common in the fens, is a significant source of non-aromatic low molecular weight organic acids (Koelbener et al., 2010). This suggests that the assumptions of the pure mixing model are not valid, and that processes other than within-fen production of DOC are needed in order to explain the change in DOC composition from fen inflow to outflow. Microbial heterotrophic transformation and degradation of DOC is likely contributing to the change in DOC composition as it has been shown to result in the release DOC with higher $SUVA_{254}$ than the substrate DOC (Berggren et al., 2009a). The fens in Stordalen receive an ample supply of low aromatic DOC from upstream sources,

at between 16 and 47 g C m^{-2} yr^{-1}, and there is a significant surface area on sedge stalks for microbial communities to inhabit. Thus while the fens are net sources of DOC to the catchment, they are simultaneously likely substantive sinks for DOC from upstream sources through microbial degradation. For lakes it has been found that their DOC sink strength is related to water residence time and water temperature (Algesten et al., 2004; Mattsson et al., 2005). For the fens of Stordalen we found that water residence time (indicated by water flow-through rate) and water temperature affected the shift in DOC composition from inflow to outflow. The fens in Stordalen have been found to be large sources of CH_4 (32 g C m^{-2} yr^{-1}) (Bäckstrand et al., 2010), and it is possible that some of the CH_4 emissions along with respired CO_2 is derived from DOC that has reached the fens from upstream sources. Further studies are required to confirm or reject our speculations on the importance of degradation of DOC from upstream sources within the fen for its atmospheric C exchange.

The difference in flow-through per unit fen area between the north and south fen highlights the importance of the hydrological setting for fens. As shown, fen flow-through magnitude affects both the mass balance and composition of fen DOC export. A fen with a lower rate of flow-through has less potential for DOC transport but the associated increased residence time enhances the potential for within-fen DOC degradation and transformation. Flow-through rate thus regulates the relative importance of processes involved in the DOC dynamics of fens. The location of a fen within its catchment is important to its DOC dynamic, while the location of peatland types such as palsas and bogs should have no effect on their DOC dynamics as they behave as headwater catchments.

3.7 CONCLUSIONS

The results in this study show that interactions between hydrology and permafrost are important in determining DOC export from a northern peatland complex. DOC export from the ombrotrophic palsa and bog, both containing permafrost, was constrained by runoff and its DOC composition was indicative of poor substrates for microbial degradation. However, there was a significant shift in

DOC composition in early snowmelt as the active layer deepened, and a significant portion of the annual DOC export occurred before this shift in DOC composition. The bog had slightly higher DOC export than the palsa and the DOC had lower aromaticity, indicating additional fresher C sources. The fens had the highest rates of DOC export of the peatland complex. The location of the fens results in significant flow-through as they convey runoff from a sizeable upstream catchment. Hence their DOC transport potential was much greater than the portions of the peatland with permafrost. DOC composition shifted towards higher aromaticity from fen inflow to outflow, a greater shift than what could be expected from within-fen DOC production alone, indicating that the fens are sites for DOC transformation and degradation as well as production. Relative to the palsa and bog, the fens are DOC hotspots (McClain et al., 2003) both for production and degradation, with the strength of each masked by their opposing effects on net DOC export. Terrestrial ecosystems are thought of as DOC sources and aquatic ecosystems as leaky DOC conduits (Cole et al., 2007), but the fens are shown here to exhibit some of the characteristics of both terrestrial and aquatic ecosystem. With continued loss of permafrost in the Stordalen peatland complex we would expect to see increased DOC export as the areal extent of fens increase at the expense of the palsa. In addition increasing temperatures would enhance DOC production, and a potential shift to more summer runoff relative to snowmelt runoff would also favor greater DOC export. Altered fen flow-through magnitude and water temperatures could also alter the balance between DOC production, transformation and degradation with implications for fen net DOC export and composition.

CONTEXT OF CHAPTER 4 WITHIN THESIS

The aim of the second study is to assess the importance of DOC export from the palsa/bog part of Stordalen peatland complex for its NECB, i.e. the sum of all significant C fluxes. This chapter uses the DOC export estimates from the previous study, in combination with estimates of the atmospheric CO_2 exchange from an eddy covariance tower and CH_4 emissions from a chamber set-up in order to assess the complete C balance of the palsa part of Stordalen peatland. By comparing the NECB of the studied palsa with non-permafrost peatlands of a similar low nutrient status we can assess what distinguishes the palsa/bog peatland NECB, both with regards to total NECB and its dependence on individual C fluxes.

4. CARBON ACCUMULATION OF A HIGH LATITUDE PERMAFROST PEATLAND

4.1 ABSTRACT

Palsas, permafrost peatlands with an ice core and therefore raised above the surrounding landscape, are a common peatland type in the subarctic with significant C storage and whose NECB has been proposed to be sensitive to climate change. Over two consecutive years we measured the NECB for a non-treed palsa part of Stordalen peatland complex and found it to have a net C uptake of 58 and 33 g C m^{-2} yr^{-1}, which is within the upper half of NECBs reported from non-permafrost bogs. While the atmospheric CO_2 exchange was similar to non-permafrost bogs - albeit with both low growing season uptakes and wintertime losses - export of DOC (average -3.2 g C m^{-2} yr^{-1}) and total hydrocarbon loss (-2.7 g C m^{-2} yr^{-1}) were in the lower range of observations. Thus while the NECB of palsas in Stordalen is similar to that of non-permafrost bogs, it is due to a different partitioning of C fluxes.

4.2 INTRODUCTION

The contemporary C balance of northern peatlands is of interest with respect to climate change because of their very large C storage and associated feedbacks (McGuire et al., 2009; Schuur et al., 2008; Tarnocai, 2009). There has been disproportionally fewer assessments of their NECB compared to other ecosystems (Nilsson et al., 2008; Roulet et al., 2007), and there are no multiyear NECB reported for permafrost peatlands. To assess a NECB, all significant C fluxes must be accounted for. While net exchange of CO_2, expressed as net ecosystem productivity (NEP or -net ecosystem exchange [NEE]), is the largest C flux, not including the smaller C fluxes of waterborne C export (mainly DOC) and CH_4 or total hydrocarbon (THC) exchange, can lead to >100% error in NECB estimates for peatlands (Billett et al., 2004; Dinsmore et al., 2010; Nilsson et al., 2008; Roulet et al., 2007). The purpose of our study is to quantify the NECB from a subarctic ombrotrophic peatland that contains permafrost.

Palsas are permafrost peatlands that have an ice core that raises the peat surface above its surroundings thus creating ombrotrophic – i.e. precipitation fed, conditions (Seppälä, 1994). Palsas along with bogs and fens constitute the peatland mosaic of the discontinuous permafrost region. Peatlands in the circumpolar discontinuous region are estimated to store 280 Pg C (Tarnocai et al., 2009), representing a significant fraction of the total C storage of northern peatlands. Analysis of peat cores show that bogs in the permafrost region often have similar long term C accumulation rates as bogs outside the permafrost region, while the accumulation rate of palsas often is lower (Robinson, 2006; Sannel and Kuhry, 2009; Turunen et al., 2002; Vardy et al., 2000).

Climate change has led to a recent circumpolar loss of permafrost in palsas (Åkerman and Johansson, 2008; Camill, 2005). Loss of permafrost in palsas affects their hydrology, vegetation composition, CH_4 emissions and C accumulation rates (Bäckstrand et al., 2008; Camill et al., 2001; Malmer et al., 2005; Turetsky et al., 2007), and may alter DOC export at a regional scale (Frey and McClelland, 2009; Walvoord and Striegl, 2007). Our objective is to construct a two year C budget of a subarctic peatland that is undergoing permafrost thaw. We assess the importance of NEP, DOC export and THC exchange to the NECB, and compare the results from our subarctic site with that of boreal peatlands outside the permafrost region.

4.3 STUDY SITE

This study focuses on the palsa and bog part of Stordalen peatland complex (Malmer et al., 2005), located in northern Sweden (68°22'N, 19°03'E) (Fig. 4.1). This peatland complex has been a long term study site - e.g. see Malmer et al. (2005) and Johansson et al. (2006b). Both the palsa and bog parts are underlain by permafrost, but the palsa has ice lenses in the underlying silt layer that elevate the peat surface 0.5 to 2 m above the surrounding fens. The palsa vegetation is composed of dwarf shrubs (e.g. *Empetrum hermaphroditum*), mosses (*Sphagnum fuscum* and *Dicranum elongatum*), lichens (*Cetaria* spp. and *Cladonia* spp) and a moderate abundance of sedges (*Eriophorum vaginatum*). The palsa partly drains

inwards into a central bog area, which in turn drains southwards into a fen. The bog vegetation is dominated by *Sphagnum balticum* and *Eriophorum vaginatum*.

Over the last 30 years there has been an increase in average annual average temperature from -0.7°C (1913-1979) to 0.0°C (1980-2009) and a concurrent increase in precipitation from 292 to 336 mm years [*NORDKLIM, data available at http://www.smhi.se/hfa_coord/nordklim*]. The permafrost in the peatland complex is currently thawing, leading to an increased maximum active layer depth (from 55 to 75 cm over the last 30 years) and conversion of the perimeter of the palsa into bog or fen, depending on location (10% of the palsa area has been converted over the last 30 years) (Christensen et al., 2004; Johansson et al., 2006b).

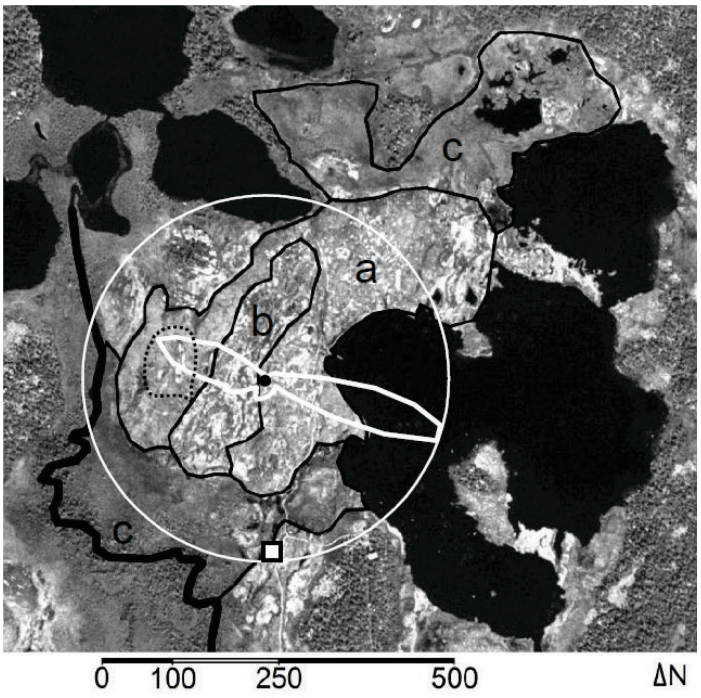

Figure 4.1. Aerial photo of Stordalen peatland (68°22'N, 19°03'E) (available at Abisko Scientific Research Station). Letters indicate dominant peatland type, a: palsa, b: bog, c: fen. The dashed black line delineates the palsa catchment that was used for peatland runoff and DOC export estimates. Black square indicates the location of the THC chambers. Black dot indicates the location of the micrometeorological tower, with the predominant wind-directions represented by a windrose (thick white line), with the scale (thin white line) representing 7.5% of the total time in 2008 and 2009 within a 5° sector.

4.4 METHODS

An eddy covariance (EC) flux tower was set up centrally on the peatland (Fig. 4.1). The EC system included a 3D anemometer (Campbell Scientific Inc. [SCI] C-SAT3) and an open path CO_2/H_2O sensor (Li-COR LI-7500) mounted at 1.7 m above the peat surface. Readings were taken at 5 Hz during the winter (mid September to early April) and at 10 Hz during the remainder of the year. Additional sensors included a photosynthetic photon flux density (PPFD) sensor (Li-COR LI-190SA), a net radiometer measuring incoming and outgoing longwave (L_{in}, L_{out}) and shortwave (K_{in}, K_{out}) radiation (Kipp & Zonen CNR1), an air temperature (T_a) probe (CSI HMP-45C), a tipping bucket precipitation gauge, thermocouples (Omega type T) monitoring soil temperature at 5 (T_{s5}) and 50 (T_{s50}) cm and TDR soil moisture probes (CSI CS605) inserted in the top 10 cm of the peat matrix. Soil temperature and moisture was measured in four profiles, two in the palsa and two in the bog.

The quality control procedure used for NEP and evapotranspiration (ET) is described in detail by Bergeron and Strachan (submitted) and further excluded data when night-time friction velocities (u*) were <0.15 m s^{-1} or positive NEP (CO_2 uptake) was measured during winter. After post processing and data filtering, 68% of data between April 1st and October 31st and 42% of data from the remainder of the year was acceptable. No data was collected from the EC system after Dec 5th 2009. Gap-filling of NEP followed the approach described by Barr et al. (2004) where NEP is partitioned into gross ecosystem production (GEP) and total ecosystem respiration (TER). TER was assumed to equal NEP when GEP was assumed to be 0, i.e. during nighttime (K_{in} < 5 W m^{-2} + minimum daily theoretical radiation received at the top of the atmosphere) and during the cold season (T_{air} < 0 and T_{s5} < 5). Daytime and missing TER data were estimated through an annual empirical logistical function between TER and the mean of T_{s5} and T_{s50} and adjusted with a time-varying factor (regression slope of estimated measured values for 100-point moving windows). GEP was assumed to equal NEP + TER during daytime outside cold season periods. Missing GEP was gap-filled using an annual rectangular hyperbola function, also adjusted with a time-

varying factor based on the relationship between GEP and PPFD. NEP was finally gap-filled as GEP – TER. ET was gap-filled with separate linear relationships against available energy (net radiation minus change in storage) using a moving window of 240 measured data points. NEP and ET were not corrected for energy closure (75% in 2008, 70% in 2009).

Water table position and active layer depth were measured every 3 to 7 days in 9 wells on the palsa and 12 wells on the bog between late April and mid-October of 2008 and 2009. Runoff and peatland DOC export was measured at a weir at the outflow of a well defined catchment on the palsa (Fig. 4.1). Manual measurements of discharge was used to construct a rating curve which spanned the measured range of weir stage ($n=10$, $r^2=0.99$, $p<0.001$). Water samples for DOC analysis were taken at the weir every 1 to 3 days during periods of runoff, with higher sampling frequency using an auto-sampler during peak snowmelt (twice daily) and following large rain events (10 to 15 samples the following three days). A total of 101 and 118 DOC samples were collected in 2008 and 2009 respectively. Water samples were filtered through 0.45 μm glass fibre filters, acidified to pH 2 with HCl and analyzed for DOC concentration on a Shimadzu TOC-V CPH analyzer within 3 weeks of sample collection. DOC export was estimated through the product palsa runoff rate and DOC concentrations, with linearly interpolated DOC concentrations between sampling occasions. In 2008 DOC export was also measured at the outflow of the central bog area, but total DOC export differed by <10% between the two sites (Chapter 3) and thus we assume that the DOC export from the palsa (measured in 2008 and 2009) is representative of the peatland part that is covered by the EC footprint. Rain water and snow samples were also analyzed for DOC and used to estimate atmospheric DOC inputs.

THC exchange was measured by an automated chamber system (three chambers on the palsa and three on the bog) located ~300 m south of the eddy covariance tower (Bäckstrand et al., 2008). A single annual THC emission record for the ombrotrophic part of Stordalen (used for both 2008 and 2009) was constructed by using average daily THC exchanges (measurements done 2002-2007 and data

indexed by day of year) for both the palsa and bog chambers and weighting by their relative aerial coverage (57% palsa and 43% bog) (Bäckstrand et al., 2010; Johansson et al., 2006b). Because the years with THC measurement do not correspond to when NEP and DOC data was measured we performed a sensitivity analysis of the resulting NECB using an THC exchange uncertainty of ±2 SD for the daily THC exchange within each season (Table 4.1).

4.5 RESULTS

The annual (1st Apr - 31st March) average temperatures measured at Abisko research station for the two years of the study were -0.2 and -0.4 °C (2008 and 2009), both warmer than the long term (1913-2009) average of -0.5°C but colder than the preceding nine years. Precipitation in Abisko was below the long term average during both study years, with 2009 being the 11th driest year since measurements started in 1913. Annual precipitation at Stordalen was 321 and 281 mm, while annual ET was 256 and 246 mm and palsa runoff was 122 and 102 mm. Solving the water budget for peatland runoff (taking into account peatland storage change in addition to precipitation and evapotranspiration) gave lower estimates (111 mm total runoff for 2008 and 2009) than runoff measured directly at the palsa outflow (224 mm).

Snowmelt started in the second half of April in both years of the study, lasted about a month each year and resulted in 82 and 90 mm palsa runoff; representing 77% of the total annual runoff for the two years (Fig. 4.2). The summer of 2009 was dry and warm: 31 mm of rain in June to July compared to long term average of 81 mm and August and September average temperature of 9.6°C compared to the long term average at 7.8°C. This led to lower water table and soil moisture in late summer and early autumn of 2009 compared to 2008 (Fig. 4.2). No runoff was recorded in 2009 after the 18th of June, while 28 mm of runoff was recorded during September and October of 2008.

From the seasonal patterns in daily C fluxes it was possible to discern four distinct NECB seasons; thaw, growing season, autumn and winter (Fig. 4.2 and Table 4.1). We found that the start of thaw was best defined by when the 3 day running

average T_a rose above 0°C; the start of the growing season when the active layer depth reached 10 cm; the start of autumn when the 5 day running average PPFD declined <250 μmol m^{-2} s^{-1} and the start of winter when the upper 10 cm of peat froze up (indicated by a decline in liquid phase soil moisture). Positive daily NECB only occurred during the growing season, while autumn and thaw had similar rates of C loss which were significantly greater than during the winter season.

Estimates of annual NECB were 56 and 33 g C m^{-2} yr^{-1} (Table 4.1). NEP dominated the annual NECB at 62 and 38 g C m^{-2} yr^{-1}, while THC and DOC losses jointly averaged -5.8 g C m^{-2} yr^{-1}. A conservative estimate of the confidence bounds of the THC exchange, due to not having been measured concurrently in 2008 or 2009, was ±1.9 g C m^{-2} yr^{-1} if using ±2 SD of the daily exchange within each season.

4.6 Discussion and conclusions

Stordalen annual NEP uptake at 62 and 38 g C m^{-2} yr^{-1} is similar to the range of 20 to 60 g C m^{-2} yr^{-1} reported for bogs in the non-permafrost region (Limpens et al., 2008). However, the annual NEP of Stordalen results from the difference between smaller growing season uptake and non-growing season release (72 / -22 g C m^{-2} yr^{-1} respectively, two year averages) than multiyear averages of uptake and release at Mer Bleue (97 / -58 g C m^{-2} yr^{-1}) and Degerö Stormyr (92 / -39.5 g C m^{-2} yr^{-1}) (Roulet et al., 2007; Sagerfors et al., 2008). The daily growing season NEP uptake rates in Stordalen were similar to those observed from non-permafrost peatlands (Humphreys et al., 2006), but the duration of daily NEP uptake at Stordalen was short (average 119 days in 2008-2009 compared to average 170 at Mer Bleue peatland and 138 at Degerö Stormyr). Stordalen also has an identifiable autumn NEP season, during which the daily C loss rates are significantly greater than during the following winter season (-0.19 and -0.05 g C m^{-2} d^{-1} respectively). However, the impact of the autumn season on the annual C balance is small due to its shortness (51-58 days in this study) truncated by its start (daily average PPFD <250 μmol m^{-2} s^{-1}) and end (freeze up of the top 10 cm of the peat matrix).

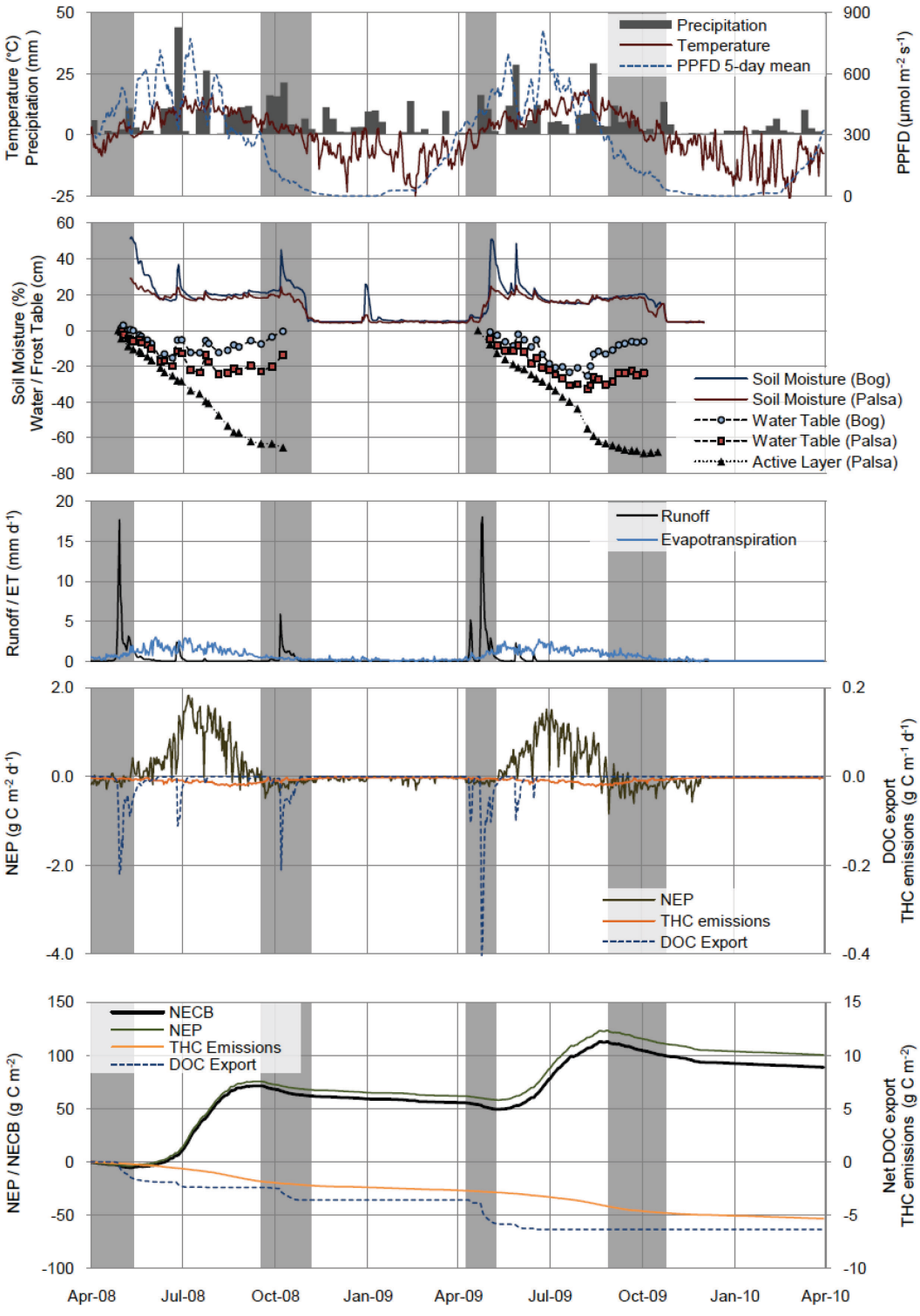

Figure 4.2. Two year patterns of environmental variables and carbon fluxes for the ombrotrophic parts (palsa and bog) of Stordalen peatland complex. Shaded periods indicate the duration of thaw and autumn seasons, while the growing season and winter season have transparent background.

Table 4.1. Annual and seasonal carbon fluxes for the ombrotrophic parts of Stordalen peatland complex.

	Annual	**Thaw**		**Growing season**		**Autumn**		**Winter**	
2008		31 Mar-12 May (43 Days)		13 May-18 Sep (129 Days)		19 Sep-8 Nov (51 Days)		9 Nov-8 Apr (151 Days)	
2009		9 Apr - 7 May (29 Days)		10 May-28 Aug (113 Days)		29 Aug-25 Oct (58 Days)		26 Oct-30 Mar (156 Days)	
	Total Flux (g C m^{-2})	Daily Flux ± SD (g C m^{-2} d^{-1})	Total Flux (g C m^{-2})	Daily Flux ± SD (g C m^{-2} d^{-1})	Total Flux (g C m^{-2})	Daily Flux ± SD (g C m^{-2} d^{-1})	Total Flux (g C m^{-2})	Daily Flux ± SD (g C m^{-2} d^{-1})	Total Flux (g C m^{-2})
NECB									
2008	55.77	-0.11 ±0.13	-4.88	0.59 ±0.57	76.03	-0.19 ±0.11	-9.54	-0.04 ±0.05	-6.06
2009	33.01	-0.20 ±0.12	-5.93	0.56 ±0.47	62.83	-0.23 ±0.18	-13.17	-0.07 ±0.08	-10.50
NEP									
2008	61.98	-0.07 ±0.12	-3.12	0.61 ±0.57	78.51	-0.16 ±0.10	-8.00	-0.04 ±0.05	-5.59
2009	38.42	-0.12 ±0.04	-3.60	0.57 ±0.46	64.73	-0.22 ±0.18	-12.54	-0.06 ±0.08	-9.99
DOC									
2008	-3.56	-0.04 ±0.06	-1.55	-0.01 ±0.02	-0.86	-0.02 ±0.04	-1.16	0.00 ±0.00	0.00
2009	-2.76	-0.08 ±0.10	-2.19	-0.01 ±0.02	-0.57	0.00 ±0.00	0.00	0.00 ±0.00	0.00
THC 2002-2007	-2.65	0.00 ±0.00	-0.18	-0.01 ±0.00	-1.48	-0.01 ±0.00	-0.50	0.00 ±0.00	-0.49

Our results indicate that the TER at Stordalen was lower than observed in other peatlands. This could be due, in part, to lower annual T_a than at the other sites and a shorter frost free season, but the functional relationship between T_a and TER at Stordalen was also found to be dampened compared to those of other peatlands. Measured mean half-monthly nighttime NEP estimates fitted to Lloyd and Taylor's (1994) exponential equation (r^2=0.93, $p<0.01$) showed that the Stordalen TER at 10°C was lower than previously measured in four non-permafrost peatlands in northern Europe (-1.05 vs. a range of -1.32 to -1.89 g C m^{-2} d^{-1}) (Lindroth et al., 2007). Low respiration rates could be related to the presence of permafrost in Stordalen, because respiration is restricted to the seasonal active layer – i.e. less mass of peat subject to decomposition.

Increased seasonal temperatures can alter annual NEP dynamics in several ways. While the length of the period of the year with temperatures above 0°C increases, light availability is set by latitude. Thus an earlier snowmelt is likely to lengthen the growing season while warmer temperatures during late summer are likely to lengthen the autumn NEP season since the shift from C sink to source is determined by light conditions. Increased air temperatures also lead to increased soil temperatures and decreased moisture availability which has been shown to decrease growing season NEP (Dorrepaal et al., 2009; Schuur et al., 2009; Strack et al., 2009). The Stordalen mean daily July NEP in 2009 (0.81 ± 0.47 (1 SD) g C m^{-2} d^{-1}) was lower than during the wetter July in 2008 (1.30 ± 0.37 g C m^{-2} d^{-1}), but the resulting NEP of the 2009 growing season was only 14 g C m^{-2} or 18% lower than in 2008. This is a moderate response to an unusually dry season compared to results from a continental temperate bog (Roulet et al., 2007), showing that palsa summer NEP might be less sensitive to moisture conditions than other peatland types. In Stordalen, and other peatlands experiencing permafrost thaw, it is however likely that the greatest influence on annual NEP will be the continued conversion of palsa into bog or fen, peatland types with significantly different C budgets (Bäckstrand et al., 2010; Camill et al., 2001; Johansson et al., 2006b).

Average waterborne DOC export was estimated at -3.2 g C m^{-2} yr^{-1}, which is lower than the range 5-15 g C m^{-2} yr^{-1} that has been reported for other northern peatlands (Fraser et al., 2001; Kohler et al., 2008; Nilsson et al., 2008; Roulet et al., 2007). In Stordalen DOC export from the ombrotrophic part is primarily restricted by low annual runoff (122 and 102 mm) although the flow-weighted average DOC concentration at 28 mg C l^{-1} is also in the low range of what has been reported for boreal bogs (25 to 40 mg C l^{-1}) (Fraser et al., 2001; Moore, 2003; Nilsson et al., 2008). Both years of the study were drier than average, making it likely that both runoff and waterborne DOC export in this study were less than average. An additional 50 mm runoff during the growing and autumn season would increase the DOC export by ~2 g C m^{-2} yr^{-1}, and thus still not alter the partitioning of the NECB significantly. Influx of DOC from precipitation was estimated at 0.45 g C m^{-2} yr^{-1}. Waterborne export of DIC was not measured directly in Stordalen, but assuming an average DIC concentration of 10 mg C l^{-1} (Nilsson et al., 2008; Wallin et al., 2010) would yield a DIC export from Stordalen of an additional 1.1 g C m^{-2} yr^{-1}.

The THC emissions at -2.5 g C m^{-2} $yr^{-1}$are at the lower half of the range reported from boreal bogs (1-10 g C m^{-2} yr^{-1}) (Limpens et al., 2008), primarily due to low THC emissions (0.4 g C m^{-2} yr^{-1}) from the palsa parts of the peatland while wetter conditions in the bog promotes higher THC emissions (5.6 g C m^{-2} yr^{-1}) (Bäckstrand et al., 2010). The change from palsa into bog has been identified as an important shift in the greenhouse gas budget when taking radiative forcing into account (Johansson et al., 2006b).

The NECB of Stordalen (56 and 33 g C m^{-2} yr^{-1}) is in the upper half of the reported NECB range from bogs (-20 to 70 g C m^{-2} yr^{-1}) (Dinsmore et al., 2010; Nilsson et al., 2008; Roulet et al., 2007). The substantive C sink of Stordalen can be explained through its conservative C losses. A substantive annual NEP sink is primarily due to low C losses during the winter season and a dampened response of TER to T_a during non-winter seasons. In addition, restricted DOC and THC losses (average 5.8 g C m^{-2} yr^{-1}) represented only 12% of the average annual NEP

in Stordalen. This can be compared to multiyear average losses between 19 and 26 g C m^{-2} yr^{-1} representing 24-46% of the annual NEP at Mer Bleue (Canada), Degerö Stormyr (Sweden) and Auchencorth Moss (Scotland) (Dinsmore et al., 2010; Nilsson et al., 2008; Roulet et al., 2007). Thus while the NECB of Stordalen is similar to that of non-permafrost bogs, it is due to a different partitioning of C fluxes.

CONTEXT OF CHAPTER 5 WITHIN THESIS

The following third study transitions from the peatland scale to the catchment scale. Stordalen peatland complex, the focus of the two previous studies is located in the lower part of the catchment in this study, but is only one of several peatland complexes that it contains. By studying the DOC export, with regards to both quantity and composition, from 10 nested catchments with a differing peatland cover, over three consecutive years we aimed to evaluate the influence of the peatlands for catchment DOC export. This study also includes the catchment DIC export in order to get an estimate of the total waterborne C export. Because the three years of the study differed significantly in the annual precipitation magnitude, they were suitable for a first order analysis of inter-annual variation of waterborne C export. While this study did not allow for a more detailed study of the different influence of palsas and fens on catchment DOC export, two of the catchments in this study were studied in greater detail and are the focus of the fourth study (Chapter 6) where palsa and fen influence at the catchment scale is investigated.

5. TOTAL WATERBORNE CARBON EXPORT AND DOC COMPOSITION FROM TEN NESTED SUBARCTIC PEATLAND CATCHMENTS

5.1 ABSTRACT

Waterborne C transport is a potentially important flux for the C balance of a catchment and intimately linked to the terrestrial ecosystems of the catchment. We have monitored hydrology and stream chemistry of ten nested catchments (0.6-15.1 km^2) with differing peatland cover (0-22%) in subarctic Sweden over three years. Total waterborne C export, including DOC, POC and DIC ranged 2.77 to 7.31 g C m^{-2} yr^{-1}. Catchments with greater peatland cover had higher flow-weighted average DOC concentrations but not higher DOC export due to variable groundwater influence between catchments. Waterborne C export was greater in years with higher total runoff, an increase that was equivalent to an average increase of ~0.2 g C m^{-2} yr^{-1} per 10 mm of precipitation. Wetter years led to a greater relative increase in DIC export than DOC export. These results stress the importance of hydrological transport for waterborne C export in addition to catchment ecosystem composition. Indices of DOC composition ($SUVA_{254}$ and a_{250}/a_{365}) indicated that DOC aromaticity and average molecular weight were higher in outflows of catchments with a greater peatland cover. Catchment peatland cover, along with other catchment variables such as groundwater influence and lake cover were found to affect seasonal patterns of DOC composition and the relationship between DOC composition and runoff rates. Our results provide examples on how waterborne C export and DOC composition can be affected by altered runoff patterns and continued permafrost loss in the peatlands as a result of continued climate change.

5.2 INTRODUCTION

Waterborne transport of C from terrestrial ecosystems to downstream aquatic environments is of interest for several reasons. The combined transport of DOC, POC and DIC represents a C flux that is seldom explicitly included in studies of NECB (Billett et al., 2004; Striegl et al., 2007). Terrestrially exported DOC also

serves as a substrate for microbial metabolism in lakes and rivers (Cole et al., 2007), stressing the importance of linking terrestrial and aquatic ecosystems for the total catchment C dynamics. Aquatic metabolism of DOC is among other aspects linked to DOC composition (Kalbitz et al., 2003a), and DOC composition has been shown to vary both with hydrological conditions and the ecosystem from which the DOC originates (Holmes et al., 2008; Prokushkin et al., 2007; Raymond et al., 2007; Spencer et al., 2008). In this paper we report on three years of waterborne C transport from ten nested catchments in subarctic Sweden with varying peatland coverage, including peatlands that are in a state of permafrost degradation (Åkerman and Johansson, 2008).

Northern peatlands are generally large sources of DOC compared to other ecosystems (Ågren et al., 2007; Dawson et al., 2002; Kohler et al., 2008; Laudon et al., 2004; Mattsson et al., 2005). However, most of the peatland DOC research has been done on non-permafrost peatlands. Subarctic peatlands constitute a major C reservoir, with an estimated 133 Pg C stored in peatlands of the discontinuous, sporadic and isolated zone of permafrost (Tarnocai et al., 2009). Loss of permafrost in peatlands alters the hydrological setting and plant species composition (Camill, 2005; Malmer et al., 2005; Payette et al., 2004), which in turn could affect peatland DOC export. Increased hydrological access to thawed peat has been hypothesized to increase DOC export (Frey and Smith, 2005), while decreased DOC export has been suggested as a response to deepened flow paths that reach into the mineral soil where DOC absorption occurs (Walvoord and Striegl, 2007).

Export of DIC can represent a variable proportion of the waterborne C export, depending on bedrock and landscape composition (Dawson et al., 2002; Nilsson et al., 2008; Striegl et al., 2007). Increased peatland cover has been linked with increased DIC export (Wallin et al., 2010), but DIC export is also greater from catchments with a carbonate bedrock due to weathering processes (Meybeck, 1993):

$$\text{Carbonate mineral} + CO_2 + H_2O \rightarrow 2\ HCO_3^- + Ca^{2+}\ (\text{or } Mg^{2+})$$

The CO_2 for the weathering process comes either from soil respiration or the atmosphere and thus connects weathering processes and DIC export directly to the atmospheric CO_2 exchange with an ecosystem. In streams with a pH range 6-8.4, DIC is primarily in the form of bicarbonate (HCO_3^-), while lower pH favours free CO_2 which is conducive to outgassing under super-saturated conditions (Dinsmore and Billett, 2008; Öquist et al., 2009). Deepened flow paths into the mineral soils due to permafrost thaw has been linked to increased DIC export from northern catchments (Walvoord and Striegl, 2007).

Runoff represents the transport potential for waterborne C export. As such, regional differences as well as inter-annual variations in precipitation and runoff constitute a significant controlling variable on waterborne C export (Eimers et al., 2008; Kohler et al., 2008; Wallin et al., 2010; Worrall and Burt, 2007). Different landscape units within a catchment can have differing runoff patterns, due to differences in water supply, storage and evapotranspiration that are linked to differences in vegetation, pedology, and lithology. This has been shown to lead to differing thresholds and sensitivities of the annual waterborne C export in relation to inter-annual variation in precipitation between peatlands and non-peatland ecosystems (Kohler et al., 2008). Hydrological setting (i.e. ombrotrophic or minerotrophic) and differences in annual precipitation patterns have been found to cause peatland DOC export to vary between 1.5 and 50 g C m^{-2} yr^{-1} (Fraser et al., 2001). The importance of runoff for the resulting waterborne C export along with the possible variability in runoff patterns between adjacent catchments stresses the importance of measuring runoff independently at each catchment outflow, even in a nested catchment study.

Streams and lakes are not simply conduits delivering terrestrial C to the ocean. Globally about half of terrestrially derived DOC is lost in lakes and streams before reaching the ocean, through sedimentation or degradation and subsequent outgassing (Cole et al., 2007). Intra-catchment variation of estimated aquatic DOC loss is substantial; ranging between 30-80% in boreal catchments (Algesten et al., 2004). While catchment size, water residence time and temperature regime

are responsible for much of this variation, it is likely that differences in composition of the DOC pool supplied to aquatic ecosystems from terrestrial sources is also important (Berggren et al., 2009b). Two indices that are used to assess DOC composition are specific UV absorbance at 254 nm ($SUVA_{254}$), and the ratio between spectrophotometric absorbance at 250 μm and 365 μm (a_{250}/a_{365}). While $SUVA_{254}$ has been associated with the average aromaticity of the DOC (Weishaar et al., 2003), a_{250}/a_{365} has been linked to the DOC average molecular weight (Lou and Xie, 2006; Peuravuori and Pihlaja, 1997). Both DOC aromaticity and molecular size have in laboratory experiments been shown influence bioavailability - i.e. the fraction of the DOC pool that is available for rapid microbial degradation (Bengtsson and Torneman, 2004; Kalbitz et al., 2003a; McDowell et al., 2006; Wickland et al., 2007). Peatland derived DOC composition has been found to differ from that of other sources, with effects on DOC bioavailability (Ågren et al., 2008b; Roehm et al., 2009; Wickland et al., 2007). However, DOC composition has also been found to be altered through microbial degradation (Kalbitz et al., 2003b), photodegradation (Bertilsson and Tranvik, 2000) and selective absorption while passing through mineral soils (Kaiser and Zech, 1998). Thus, although caution should be observed when drawing conclusions, the use of DOC composition indices can provide additional information on DOC sources, bioavailability and processes that has affected the DOC between its source and the catchment outflow.

The aim of this study is to assess the importance of peatlands and catchment hydrology for waterborne C export and DOC composition of ten nested subarctic catchments. By evaluating both magnitude and composition of waterborne C fluxes, our results are pertinent to C balances at both individual ecosystem and catchment scales. Studying the total C export over three years allows us to evaluate both inter-annual and intra-annual variability. Special consideration is paid to the possible influence on waterborne C fluxes from permafrost loss in the peatlands of the catchment.

5.3 SITE DESCRIPTION

This study was conducted in the Stordalen catchment, a 15 km^2 catchment located 10 km east of Abisko in northern Sweden (68.20N, 19.03E). The geology of the catchment is part of the Rautas complex which contains thrusted quartzite, shales and carbonate bedrock including dolomite (Andersson et al., 1996). The catchment is partly mountainous (~500 m of relief) and has a clearly defined break in the topography when entering the lowland part of the catchment (Fig. 5.1). Just uphill of the break in topography there are significant forested scree slopes. Most of the catchment is an open canopy mountain birch forest (*Betula pubescens* ssp. *czerepanovii*) with a heath ground layer of *Empetrum nigrum* ssp. *hermaphroditum, Vaccinium vitis-idaea*, *V. myrtillus* and *Arctostaphylos uva-ursi*, but also has arctic-alpine heath above the tree line and several lakes and peatlands in the lower flatter portions. The peatlands in the catchment consist of palsas and fens. Palsas are peatlands with a permafrost core that raise it above the surrounding fens and cause ombrotrophic conditions. The palsas are the only parts of the catchment that contain permafrost (Johansson et al., 2006a) and ongoing permafrost loss is converting palsa into fen, something which significantly alters the peatland complex atmospheric C exchange (Bäckstrand et al., 2008; Johansson et al., 2006b; Malmer et al., 2005), and DOC dynamics (Chapter 3).

The average annual temperature measured at the nearby Abisko Scientific research station has increased over the last three decades from -0.7 ±1.0 °C (mean ± std) (1913-1979) to 0.0 ± 0.9 °C (1980-2009) (NORDKLIM, data available at http://www.smhi.se/hfa_coord/nordklim). Mean January and July temperatures are -10.7 °C and 11.7 °C respectively (1913-2009). The temperature stays above 0 °C from mid-April until late October. Precipitation has increased from 292 ± 50 mm (1913-1979) to 335 ± 67 mm (1980-2009). June to August receives 40% of the annual total precipitation, and accounts for >50% of the recent increase in annual precipitation. The period of permanent snow cover has decreased by one month since 1986 (Malmer et al., 2005), while snow depth has increased by 10% per decade since the 1930s (Kohler et al., 2006).

In this study the hydrological year in Stordalen catchment was chosen to start on Nov 1st, which is approximately when snow accumulation starts and stream discharge enters a winter low-flow period. We further divided the hydrological year into a spring and summer season. Spring hydrological season was set to end by June 20th, which corresponded to the end of high runoff rates due to snowmelt in all years of the study. During the following summer season all increase in discharge was caused by rain fall rather than snowmelt. Of the years in the study, 2007 had the highest total annual, spring and summer precipitation while 2009 had the lowest annual and summer precipitation (Table 5.1). The annual and spring precipitation in 2007 was more than a standard deviation greater than the long term (1913-2009) average, while annual and summer precipitation of 2009 was more than a standard deviation lower. Temperatures for all years were above both the long term (1913-2009) and short term (1979-2009) averages, especially due to warm 2007 and 2008 winters.

Table 5.1. Annual and seasonal precipitation and air temperature in Stordalen catchment. The hydrological year of the study area (1st Nov - 31st Oct) divided into a spring (1st Nov – 20th June) and a summer (21st June – 31st Oct) season. Bold indicates that the precipitation or temperature is a standard deviation greater or lesser than the long term (1913-2009) average. The seasonal contribution to annual precipitation is given in brackets.

Year	Precipitation (mm)			Temperature (°C) [a]		
	Annual	Spring	Summer	Annual	Spring	Summer
1913-2009 Means	352[b]	172[b]	180[b]	-0.5	-4.8	6.8
2007	**414**[c]	**216**[c] (52%)	198[c] (48%)	**0.9**	**-3.0**	**7.9**
2008	321[c]	156[c] (49%)	164[c] (51%)	**0.7**	**-2.8**	6.8
2009	**290**[c]	178[c] (61%)	**112**[c] (39%)	0.3	-3.8	7.6

[a]Temperatures measured at Abisko research station.

[b]Long term average precipitation measured at Abisko research station, but increased by 15.5% to account for the difference in precipitation between Stordalen and Abisko as indicated by 3 years of synchronous frost-free season measurements.

[c]Stordalen precipitation estimated from frost-free season measurements at Stordalen peatland and frost-season measurements at Abisko research station, adjusted by 15.5%.

5.4 METHODS

5.4.1 SAMPLING SITES

Sampling points were chosen for catchments to represent different landscape compositions (Fig. 5.1 and Table 5.3). Seven sampling points (A1-A7) were located along the main stream of the catchment, two were located on the largest tributary (B1, B2) and one on a lesser tributary which drains a catchment with the highest peatland proportion in the study (C1).

A high resolution digital elevation model (DEM) derived from light detection and ranging (LIDAR) data was produced for the whole area. The LIDAR precision was approximately ± 5 cm. The resolution chosen for the estimations of hydrological divides and catchment surface areas was 10 m. Sink removal and flow accumulation calculations were performed using a form-based model (Pilesjo et al., 2006) prior to locating water courses and catchment delineations. Water courses and catchment delineations were estimated with hydro tools in the ESRI ArcGIS 9.3 package (ArcINFO version), and confirmed through ground observations. Surface areas of lakes and peatlands, with peatland areas further divided into palsa and fen, were determined from aerial photographs. With a DEM resolution of 10 m, the theoretical maximum error of the smallest catchment area is 4.3%, but the expected error is zero for all catchments since the errors are random.

5.4.2 PRECIPITATION AND HYDROLOGY

Precipitation was measured during the frost free season with a tipping bucket gauge located at Stordalen peatland in the lower part of Stordalen catchment. Frost season precipitation at Stordalen peatland was estimated using daily precipitation measurements from Abisko research station (located 10 km west of Stordalen), but taking into account a systematic difference between the two locations. Synchronous precipitation measurements during the frost-free season found that precipitation at Stordalen peatland was 15.5% greater than at Abisko research station (range 8-18% annually, measured over 3 years). In addition, bulk rain gauges were set up at five different elevations within the Stordalen

catchment, between 351 and 756 m. The cumulative rainfall was sampled every 2 weeks during May to September in 2009. The total precipitation from the bulk rain gauges increased by 6.5% for every 100 m of altitude (linear correlation, r^2=0.93 $p<0.05$). Precipitation for each catchment was estimated based on the relationship between precipitation and elevation, using the average elevation of each catchment as derived from the DEM and the continuous precipitation measurements recorded at Stordalen peatland. This led the estimated precipitation to be 15% greater in the highest (B2) than in the lowest (C1) catchment. Precipitation estimates were used to calculate the ratio between runoff and precipitation (R/P ratio).

Hourly discharge was estimated from continuous stage records at all sites using rating curves based on stream stage and discharge measurements. Stream stage was recorded hourly using Odyssey capacitance probes (resolution <1 mm, accuracy ±5mm), and was verified against manual measurements of stream stage on each water sampling occasion. Discharge was estimated by the velocity-area method where stream velocity across a cross-section was measured with an Aqua Data Sensa Electromagnetic Current Meter (resolution 0.01 m s^{-1}). Rating curves were constructed using exponential equations where n=15-25 and r^2>0.95 for all sites except B1 where r^2=0.85. Prediction bounds of the rating curves (95%) were found to represent 7-15% of the average 2008 spring runoff rate, except for B1 where it represented 81%. Despite a lower precision of the B1 rating curve, the site was included in the study since its discharge measurements were in accordance with B2, which is located just upstream. Discharge was also measured by velocity-area method every 1 to 3 days during early snowmelt, as rating curves could not be applied due to ice conditions in the streams.

5.4.3 Sample collection and analysis

Water samples were collected in all sites in 2007 and 2008, while A1, A3, A5 and B2 were also sampled in 2009. Water sampling was initiated before snowmelt each year and ended in mid-September in 2007 and late October in 2008 and 2009. Sampling frequency depended on hydrological conditions. Grab samples

were taken every 1 to 2 days during snowmelt and following significant rainfall, and every 3 to 6 days during low flow conditions. Two autosamplers (Hach Sigma 900) were installed at site A5 and B2 in 2008 and 2009, taking two samples per day during snowmelt and 10 to 25 samples during the first three days following storm events. Samples were collected from autosamplers within 48 h of sampling. Total number of samples per site ranged between 35 to 50 grab samples over a season, and 160 to 204 samples for sites with autosamplers.

Water samples were filtered through 0.45 µm glass fibre filters and kept in 25 ml airtight bubble-free vials in a dark refrigerator at 5°C. Samples for DOC analysis were acidified to pH 2 with 0.5 M HCl on the day of collection, and analyzed for DOC concentration ([DOC], see Table 5.2 for notation) on a Shimadzu TOC-V CPH analyzer within 3 weeks of collection. DIC concentration ([DIC]) was measured on samples from every second water sampling occasion from six sites (A1, A2, A4, A5, A7 and B2) in 2007 through headspace analysis on a Perkin Elmer Clarus 500 gas chromatograph. POC concentrations were measured in 2008 on 10 occasions for each site. POC was analysed through loss on ignition at 375 °C for 16 hours, after filtering 1 l of sample water through 0.45 µm glass fibre filter (Ball, 1964).

Electrical conductivity (Ec) (adjusted to 20°C) and pH were measured directly during each water sampling occasion with a hand held Oakton pH/Con 10, except after Aug 12th in 2007 due to instrument malfunction. In addition, Ec was measured hourly by AquiStar CT2X loggers in sampling site A5 and B2 throughout 2008 and 2009. It has been shown that in streams with pH close to neutral, conservative mixing of Ec can be assumed (Schleppi et al., 2006), which allows Ec to be treated in the same way as dissolved solutes when estimating annually and seasonally flow-weighted average Ec (Ec^{An},Ec^{Sp},Ec^{Su}). Water samples from 2008 and 2009 were analyzed for ion concentrations (sodium, ammonium, potassium, magnesium, calcium, chloride, bromide, nitrate, phosphate and sulphate) on a Dionex ICS-1600. Calcium was in all samples the dominant ion and its concentration correlated significantly with Ec ($p<0.001$,

r^2=0.83, n=270). Calcium can be assumed to be primarily derived from bedrock weathering, and we therefore interpret the flow-weighted average Ec of combined data from 2007 and 2008 ($Ec^{An(07/08)}$) as a relative measure of groundwater influence between catchments of this study. In 2008 and 2009 no direct measurements of DIC were made and the 2007 relationship between [DIC] and observed Ec was used to produce estimated DIC concentrations ($[DIC]_{Est}$):

$[DIC]_{Est}$ (mg l^{-1}) = 0.14*Ec (µS cm^{-1}) -2.38, (r^2=0.79, p<0.001, n=135).

All samples were analyzed for absorbance at 250, 254 and 365 nm (a_{250}, a_{254} and a_{365}) with a Shimadzu UV-160A through a 1 cm quarts cuvette on the same day as collection, and used to calculate $SUVA_{254}$ and a_{250}/a_{365}. The reported range for $SUVA_{254}$ of boreal and subarctic stream samples and soil leachates is between 0.5 and 7 l mg^{-1} m^{-1} (Roehm et al., 2009; Wickland et al., 2007) representing a DOC aromaticity of between 5 and 50% (Weishaar et al., 2003). Similarly the reported range of a_{250}/a_{365} is between 3 and 7.5 which represents a range of weight-averaged molecular DOC weight between ~10 and ~1 kDa (Lou and Xie, 2006; Peuravuori and Pihlaja, 1997). We also report a_{254} as a measure of the absolute concentration of aromatic DOC.

5.4.4 Flux calculations, uncertainties and statistics

Hourly export of DOC was estimated by multiplying discharge and linearly interpolated [DOC] between sampling occasions. Hourly DOC export yielded estimates of annual, spring and summer export, as well as estimates of the annual, spring and summer flow-weighted average DOC concentrations ($[DOC]^{An}$, $[DOC]^{Sp}$, $[DOC]^{Su}$). Flow-weighted annual and seasonal averages of Ec, POC, $SUVA_{254}$, a_{254} and a_{250}/a_{365} were estimated analogously (see Table 3 for notation). Flow-weighted estimates using joint data from 2007 and 2008 (years when all catchments were sampled) were used to compare the catchments (e.g. $[DOC]^{An(07/08)}$).

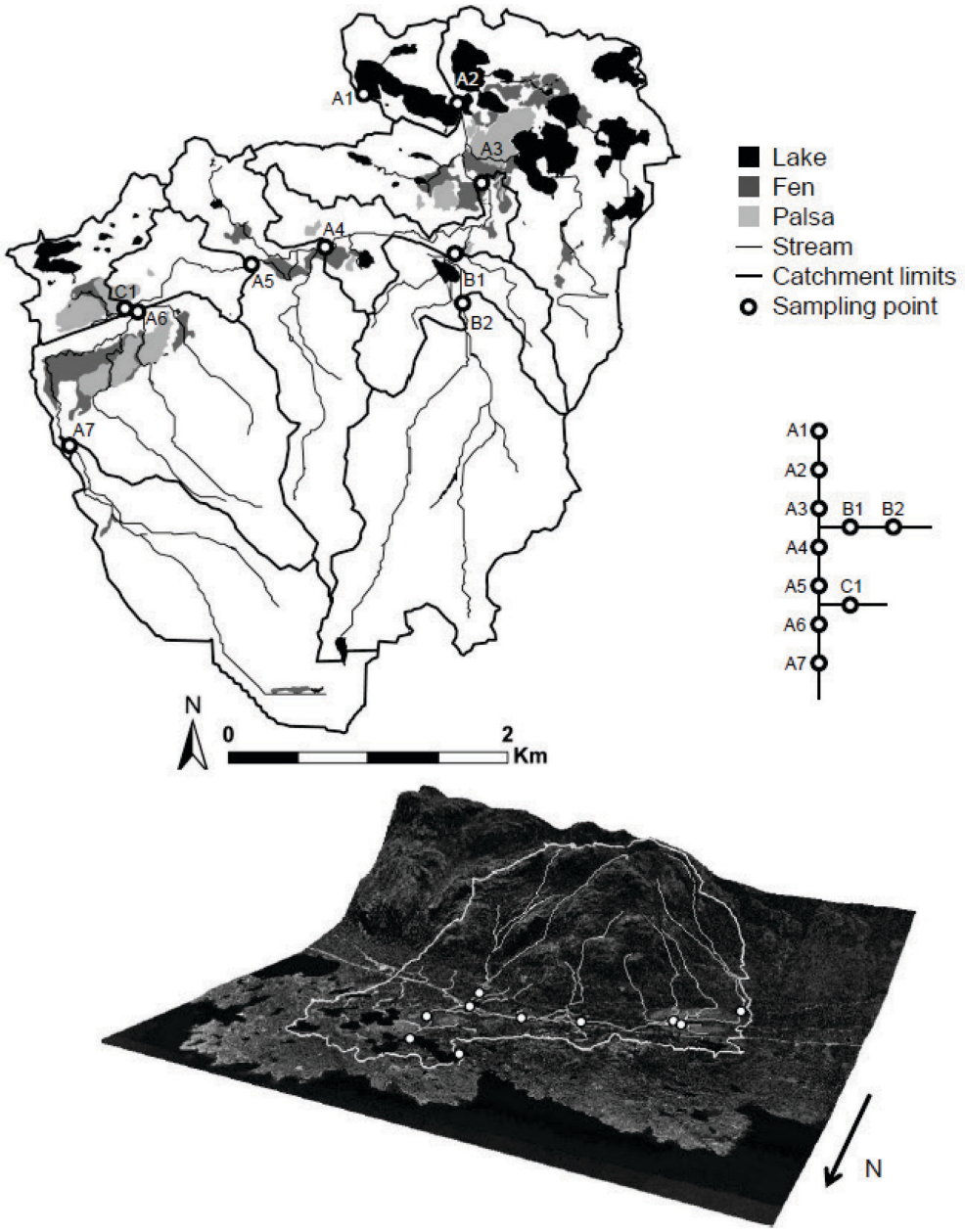

Figure 5.1. Stordalen catchment images. Upper image shows all nested catchments and their sampling points, along with main streams and all lake, fen and palsa areas. The lower aerial photograph is draped on a digital elevation map (elevation enhanced three times) with the A1 catchment limits (thick white line), along with all sampling points (circles) and main streams (thin white lines). The two color infrared aerial photograph (CIR, wavelengths 500-900 nm) was taken on the 29th of July 2000 from a height of 4600 m (image available at Abisko Scientific Research station).

Uncertainties of DOC and DIC export estimates were estimated using Monte Carlo simulations with 10 00 realizations for each estimate. Export uncertainties for DOC are a composite of the uncertainties of $[DOC]^{An}$ and the total annual runoff. Uncertainty of $[DOC]^{An}$ is assumed to be primarily due to the interpolation method, and thus dependent on sampling frequency. We used a 7.5% uncertainty (SD) of $[DOC]^{An}$ of manually sampled sites and 5% for sites with autosamplers (Nilsson et al., 2008). The prediction bounds of the rating curves, as described above, were used as an estimate of the uncertainty of the annual runoff. Export uncertainty of DIC also included a 5% uncertainty derived from relationship between $[DIC]^{An}$ and $[DIC]_{Est}{}^{An}$ of measured sites in 2007.

5.5 RESULTS

5.5.1 HYDROLOGY

Total annual runoff of measured catchments was close to double in 2007 to what it was in 2009, with 2008 as an intermediate year (Table 5.3). Annual R/P ratios were also higher in 2007 and 2008 than in 2009. High runoff in 2007 was primarily due to the spring season when all sites had a total runoff that was >50 mm greater than in either 2008 or 2009. An extended dry period during the summer of 2009 led to a total summer runoff from all catchments that was >80 mm less than in 2007 or 2008. Spring runoff dominated the annual runoff, representing on average 58% of total runoff (range 46 to 91% for all sites and years). Spring R/P ratios were also higher and had less variability both between sites and years than summer R/P ratios (spring range 0.70-1.08 v.s. summer range 0.13-0.98) (see Fig. 5.3).

Total annual runoff and annual R/P ratios varied considerably between catchments (Table 5.3), e.g. catchment B2 and C1 had R/P ratios at 0.95 and 0.54 respectively (using 2007 and 2008 data). The variability in total annual runoff and R/P ratios was best explained through their correlation with $Ec^{An(07/08)}$ - i.e. the groundwater influence. Increased catchment $Ec^{An(07/08)}$ was correlated with increased runoff (r^2=0.86, $p<0.01$) and R/P ratio (r^2=0.94 $p<0.01$), indicating that

variable groundwater contribution to stream flow between catchments strongly affected the runoff magnitude of individual catchments.

Periods of the year with high runoff rates, e.g. during snowmelt and during larger storm events, were associated with lower Ec (Fig. 5.2), consistent with a temporally decreased relative groundwater contribution to stream flow. In contrast, higher annual flow-weighted Ec (Ec^{An}) was found for 2007, which had higher runoff than both 2008 and 2009 (Table 5.3). This indicated that the relative groundwater contribution increases during wet years in all sites.

Table 5.2. List of abbreviations used for stream chemistry.

Description	Abbreviation
Measured DOC concentration at each sampling occasion	$[DOC]$
Flow-weighted annual, spring and summer DOC concentration	$[DOC]^{An}$, $[DOC]^{Sp}$, $[DOC]^{Su}$
Flow-weighted annual, spring and summer DOC concentration, using joint data from 2007 and 2008	$[DOC]^{An(07/08)}$, $[DOC]^{Sp(07/08)}$, $[DOC]^{Su(07/08)}$
Measured DIC concentration at each sampling occasion	$[DIC]$
Estimated DIC concentration at each sampling occasion using the Ec/[DIC] relationship (See results section)	$[DIC]_{Est}$
Flow-weighted annual, spring and summer DIC concentration	$[DIC]^{An}$, $[DIC]^{Sp}$, $[DIC]^{Su}$
Flow-weighted annual, spring and summer DIC concentration, based on $[DIC]_{Est}$	$[DIC]_{Est}^{An}$, $[DIC]_{Est}^{Sp}$, $[DIC]_{Est}^{Su}$
Measured a_{254} at each sampling occasion	$[a_{254}]$
Flow-weighted annual, spring and summer a_{254}	$[a_{254}]^{An}$, $[a_{254}]^{Sp}$, $[a_{254}]^{Su}$
Flow-weighted annual, spring and summer a_{254}, using joint data from 2007 and 2008	$[a_{254}]^{An(07/08)}$, $[a_{254}]^{Sp(07/08)}$, $[a_{254}]^{Su(07/08)}$
Measured $SUVA_{254}$ at each sampling occasion	$[SUVA_{254}]$
Flow-weighted annual, spring and summer $SUVA_{254}$	$[SUVA_{254}]^{An}$,$[SUVA_{254}]^{Sp}$,$[SUVA_{254}]^{Su}$
Flow-weighted annual, spring and summer $SUVA_{254}$, using joint data from 2007 and 2008	$[SUVA_{254}]^{An(07/08)}$,$[SUVA_{254}]^{Sp(07/08)}$, $[SUVA_{254}]^{Su(07/08)}$
Measured a_{250}/a_{365} at each sampling occasion	$[a_{250}/a_{365}]$
Flow-weighted annual, spring and summer a_{250}/a_{365}	$[a_{250}/a_{365}]^{An}$,$[a_{250}/a_{365}]^{Sp}$, $[a_{250}/a_{365}]^{Su}$
Flow-weighted annual, spring and summer a_{250}/a_{365}, using joint data from 2007 and 2008	$[a_{250}/a_{365}]^{An(07/08)}$,$[a_{250}/a_{365}]^{Sp(07/08)}$, $[a_{250}/a_{365}]^{Su(07/08)}$
Measured Ec at each sampling occasion or by logger	Ec
Flow-weighted annual, spring and summer Ec	Ec^{An}, Ec^{Sp}, Ec^{Su}
Flow-weighted annual, spring and summer Ec, using data joint from 2007 and 2008	$Ec^{An(07/08)}$, $Ec^{Sp(07/08)}$, $Ec^{Su(07/08)}$

Table 5.3. Catchment description (area, landscape composition) and annual stream chemistry (total runoff, R/P ratio, flow-weighted DOC concentration, a_{254}, $SUVA_{254}$, a_{250}/a_{365}, Ec and pH) and waterborne C export (DOC, POC and DIC).

Catchment		A1	A2	A3	A4	A5	A6	A7	B1	B2	C1
Area (ha)		1507	1474	1230	790	617	509	287	368	284	61
Wetlands (%)		6.4	6.5	4.7	6.4	7.2	6.1	0.6	0.1	0.0	21.8
- Fen (%)		3.6	3.6	2.6	3.3	3.3	3.6	0.6	0.1	0.0	3.6
- Palsa (%)		2.8	2.9	2.1	3.0	3.9	2.5	0.0	0.0	0.0	18.2
Lakes (%)		5.2	4.3	1.1	1.3	1.6	0.5	0.4	0.6	0.0	11.4
Runoff	**2007**	338	325	365	321	299	274	322	430	470	225
mm	**2008**	272	264	298	260	237	212	223	330	350	179
	2009	177	-	169	-	159	-	-	-	248	-
R/P	**2007**	0.75	0.72	0.79	0.70	0.65	0.58	0.66	0.91	0.97	0.53
	2008	0.78	0.76	0.84	0.73	0.66	0.58	0.59	0.90	0.93	0.54
	2009	0.56	-	0.53	-	0.49	-	-	-	0.73	-
DOC	**2007**	9.2	9.7	10.4	11.6	13.4	13.6	11.2	9.5	9.0	19.3
mg l^{-1}	**2008**	10.1	11.1	12.0	11.1	11.6	11.7	9.7	9.6	8.0	15.2
	2009	11.4	-	12.5	-	14.6	-	-	-	10.7	-
a_{254}	**2007**	0.25	0.28	0.28	0.30	0.34	0.35	0.26	0.23	0.19	0.57
cm^{-1}	**2008**	0.25	0.29	0.29	0.31	0.36	0.35	0.27	0.21	0.18	0.44
	2009	0.30	-	0.35	-	0.42	-	-	-	0.26	-
$SUVA_{254}$	**2007**	2.70	2.92	2.65	2.55	2.58	2.59	2.29	2.41	2.10	2.94
l mg^{-1} m^{-1}	**2008**	2.50	2.60	2.42	2.84	3.08	3.01	2.78	2.18	2.30	2.91
	2009	2.61	-	2.78	-	2.86	-	-	-	2.46	-
a_{250}/a_{365}	**2008**	5.03	4.73	4.81	4.91	4.65	4.69	5.12	5.09	5.13	4.45
	2009	5.18	-	5.04	4.81	-	-	-	-	5.26	-
Ec	**2007**	52.1	53.5	54.6	54.5	53.6	47.3	44.6	60.3	61.6	-
µS cm^{-1}	**2008**	48.4	45.9	47.3	43.7	41.8	37.0	37.2	54.2	55.9	-
	2009	44.2	-	40.4	-	37.2	-	-	-	45.7	-
pH	**2007**	6.77	6.69	6.77	6.58	6.49	6.18	6.56	6.97	7.01	6.39
	2008	6.83	6.79	6.68	6.66	6.62	6.39	6.93	6.97	7.07	6.50
	2009	6.65	-	6.52	-	6.50	-	-	-	6.93	-
DOC exp[a]	**2007**	3.1±0.7	3.2±0.7	3.8±0.7	3.7±0.9	4.0±0.8	3.7±0.8	3.6±0.9	4.1±0.8	4.2±1.0	3.0±1.1
g C m^{-2} yr^{-1}	**2008**	2.7±0.6	2.9±0.7	3.6±0.7	2.9±0.7	2.8±0.5	2.5±0.5	2.2±0.5	3.2±1.4	2.8±0.6	2.7±0.7
	2009	2.0±0.5	-	2.1±0.4	-	2.3±0.4	-	-	-	2.7±0.5	-
POC exp	**2008**	0.10	0.09	0.08	0.04	0.05	0.04	0.03	0.05	0.11	0.08
DIC exp[a]	**2007**	1.7±0.4	1.7±0.4	1.9±0.4	1.7±0.4	1.6±0.4	1.2±0.3	1.3±0.3	2.6±1.1	3.0±0.7	1.0±0.3
g C m^{-2} yr^{-1}	**2008**	1.2±0.3	1.1±0.3	1.3±0.3	1.0±0.3	0.8±0.2	0.6±0.1	0.6±0.2	1.7±0.8	1.9±0.4	0.6±0.2
	2009	0.7±0.2		0.6±0.1		0.5±0.1				1.0±0.2	

[a] Export estimates ± 2 standard deviations of the estimate, derived from a Monte Carlo simulation (see method for assumptions).

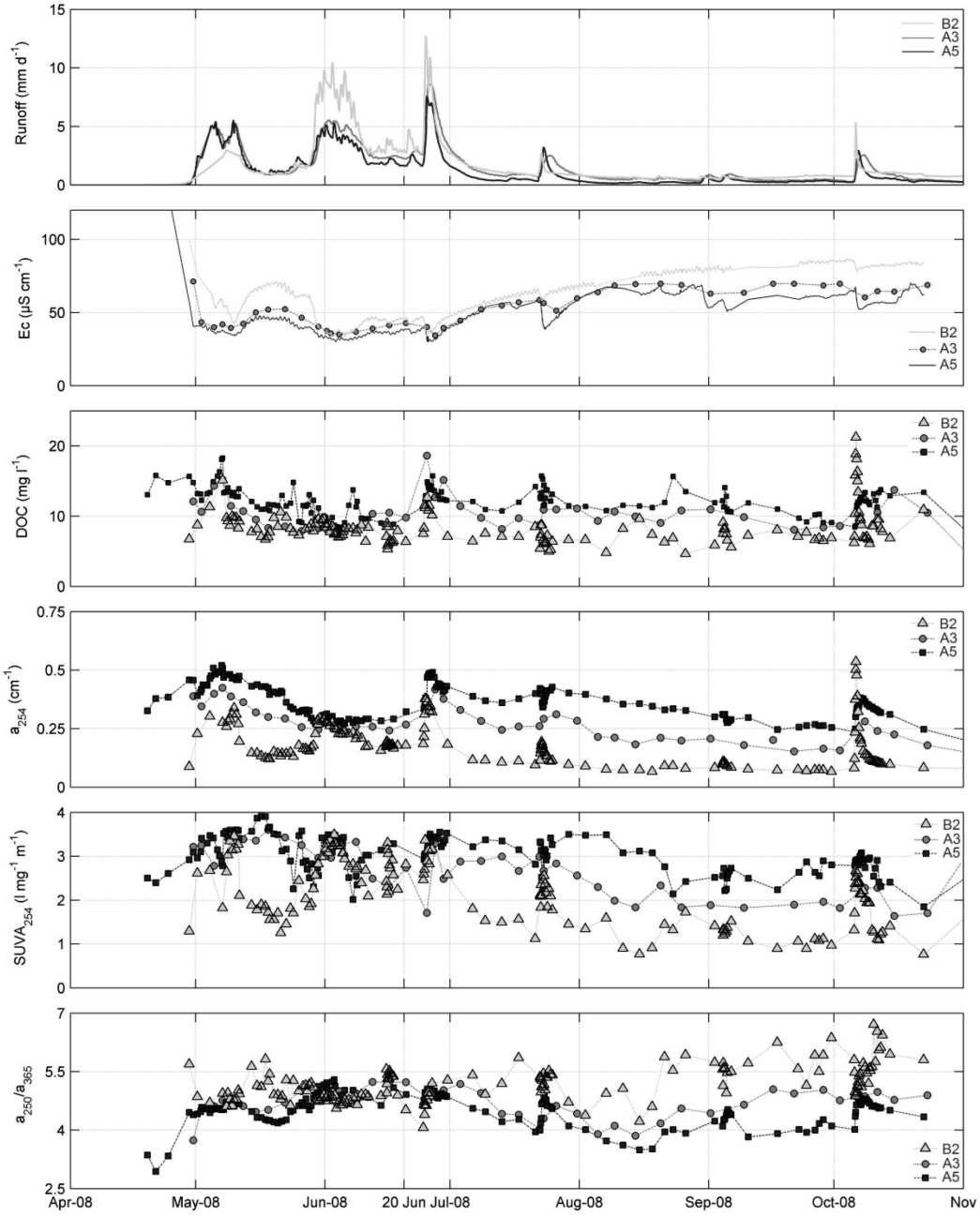

Figure 5.2. Stream data from 2008, including runoff rate, Ec, DOC concentration, a_{254}, $SUVA_{254}$ and a_{250}/a_{365}. Data from catchments B2, A3 and A7 shown, representing 0.0, 4.7 and 7.2 % catchment peatland cover respectively. The 20th of June is end of spring season and start of the summer season as defined in this study.

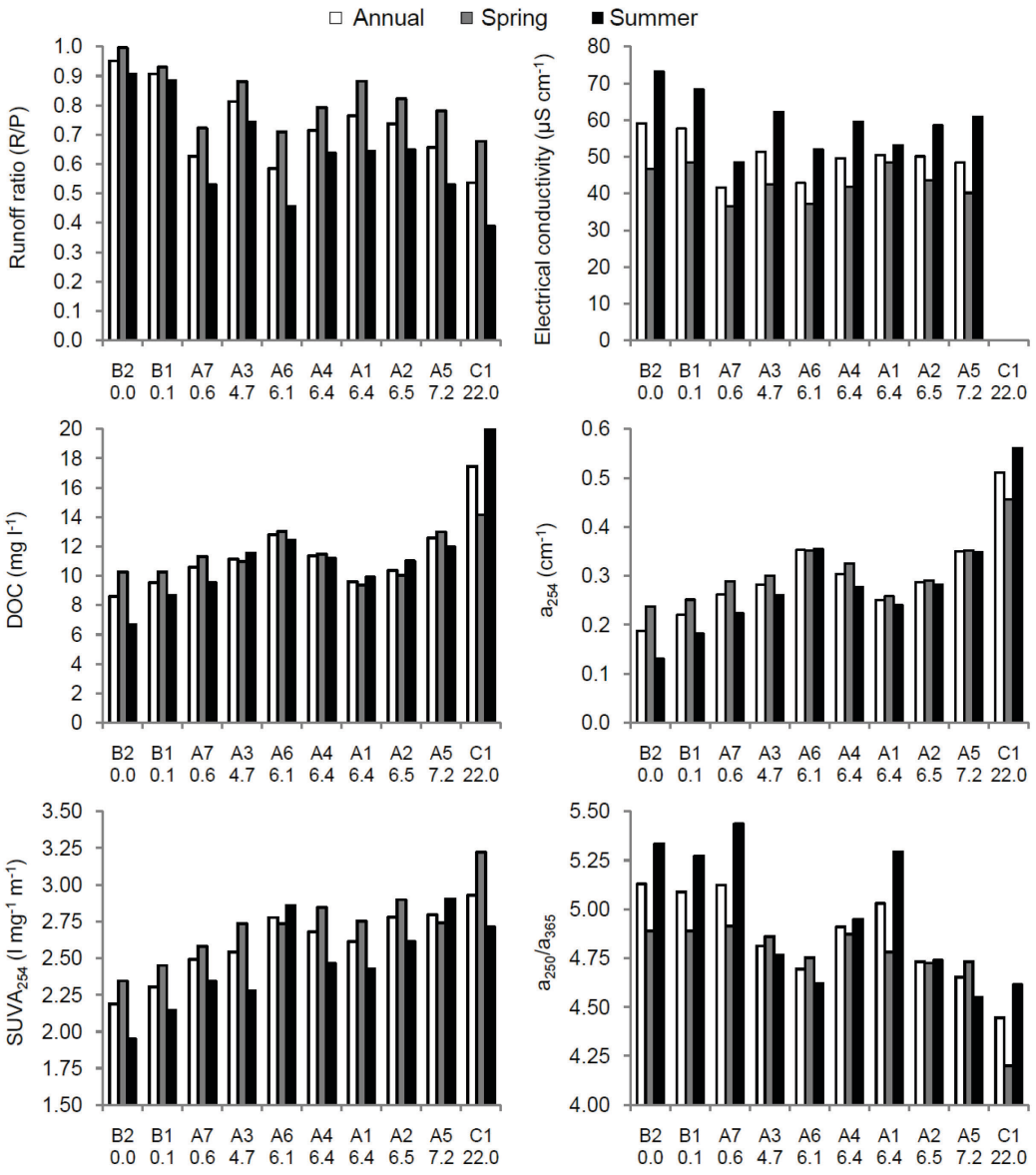

Figure 5.3. Annual and seasonal estimates of R/P ratio, flow-weighted electrical conductivity, DOC concentration, a_{254}, $SUVA_{254}$ and a_{250}/a_{365} ratio from ten nested catchments. Catchment peatland coverage indicated in % below catchment notation. Joint data from 2007 and 2008 used.

5.5.2 DOC AND A_{254}

Figure 5.2 shows [DOC] and a_{254} data from three catchments in 2008. These catchments (B2, A3, A5) have differing peatland cover (0.0, 4.3 and 7.2% respectively) and also represent different sampling schemes (autosamplers were used in addition to manual sampling in B2 and A5). Increased peatland cover was associated with higher annual and seasonal DOC concentrations and a_{254} values, with the most pronounced influence during summers (Fig. 5.2 and 5.3).

Relationships between instantaneous runoff rate and [DOC] (using data from 2007 and 2008 jointly) was also influenced by catchment peatland coverage. Catchments with <5% peatland cover (A3, A7, B1, B2) exhibited increased [DOC] during periods of high runoff rates, while C1 (22% peatland cover) had lower [DOC] during periods of high runoff rates (Fig. 5.4). The correlation coefficients between a_{254} and runoff rates were generally stronger than those between [DOC] and runoff rate, particularly for catchments with <5% peatland (Fig. 5.4).

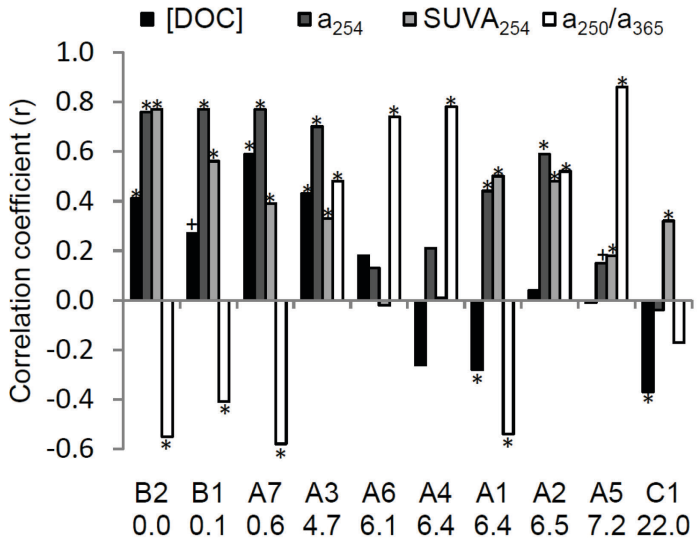

Figure 5.4. Correlation coefficients (Pearson's r) between runoff rate and DOC concentration, a_{254}, $SUVA_{254}$ and a_{250}/a_{365} for ten nested catchments. Significance of correlation: * $p<0.01$, + $p<0.05$. Correlation analysis is using data from 2007 and 2008 jointly, n=77-217.

5.5.3 WATERBORNE C EXPORT

Total C export (including DOC, POC and DIC) ranged between 2.77 and 7.31 g C m^{-2} yr^{-1}. The DOC export dominated the total C export from all catchments and varied between 2.01 and 4.24 g C m^{-2} yr^{-1}. Export of POC export in 2008 ranged from 0.03 to 0.11 g C m^{-2} yr^{-1} (Table 5.3), and thus represented only 1.0 - 2.5% of the total C export. Neither annual DOC or POC exports were significantly correlated with catchment peatland cover. Instead the greatest DOC export came from catchment B2 that had the lowest peatland cover and $[DOC]^{An}$ but the highest annual runoff.

Export estimates of DIC, based on $[DIC]_{Est}$ (derived from the relationship between [DIC] and Ec in 2007), ranged between 0.45 and 2.96 g C m^{-2} yr^{-1} (Table 5.3). Estimates of DIC export based on direct measurements of DIC in 2007 (catchments A1, A2, A4, A5, A7 and B2) differed by -0.06 to 0.04 g C m^{-2} yr^{-1} compared to the estimates based on $[DIC]_{Est}$, always representing a <7% relative error. This minor difference led us to accept the estimates of DIC export based on $[DIC]_{Est}$. Peatland cover did not significantly correlate with DIC export.

The response of DOC and DIC export to inter-annual variability in runoff magnitude differed markedly (Fig. 5.5). While $[DOC]^{An}$ were higher during the drier 2009 than in the wetter 2007, $[DIC]_{Est}^{An}$ decreased from 2007 to 2009. This resulted in DIC export representing a greater fraction of the total C export in 2007 (28-41%) than in the dry 2009 (16-27%). Correlation between waterborne C export and annual precipitation for the four catchments that were sampled during all years (A1, A3, A5 and B2) showed that waterborne C export increased by 0.19 ±0.04 (1 SD) g C m^{-2} per 10 mm of precipitation (no correlation was significant for any site since only three years were available, but relationships for all sites were in agreement).

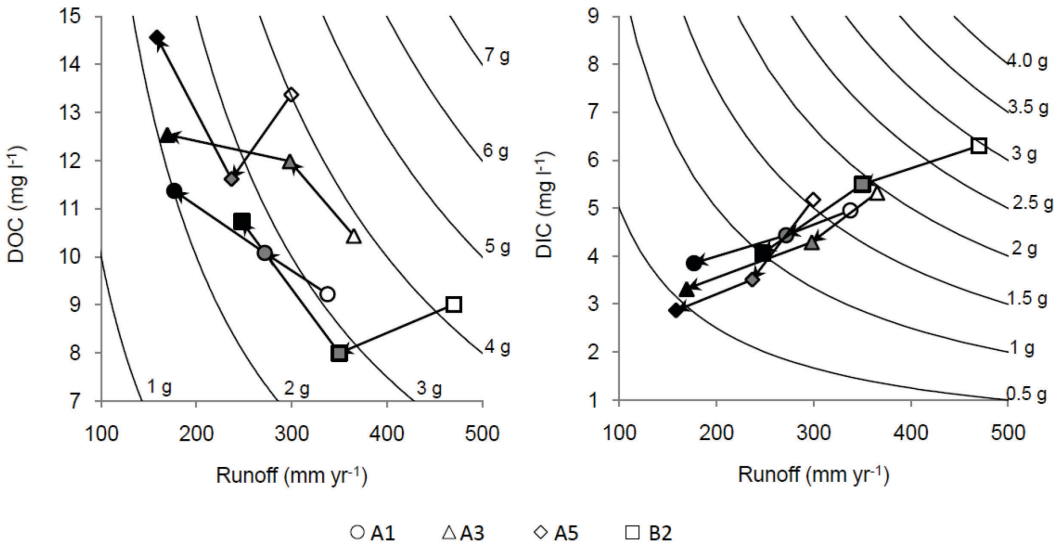

Figure 5.5. Annual flow-weighted DOC and DIC concentrations plotted against annual runoff. Grid indicates the resulting DOC and DIC export in g C m^{-2} yr^{-1}. Four sites are included, A1 (6.4% wetland), A3 (4.7%), A5 (7.2%) and B2 (0.0%). Symbol filling indicate the year, 2007 (white), 2008 (gray) and 2009 (black).

5.5.4 DOC COMPOSITION ($SUVA_{254}$ AND a_{250}/a_{365})

A greater catchment peatland cover was associated with higher DOC aromaticity and average molecular weight, as indicated by $SUVA_{254}^{An(07/08)}$ and $a_{250}/a_{365}^{An(07/08)}$ (Fig. 5.3). However, while correlations were significant between total catchment peatland cover and DOC composition during spring ($SUVA_{254}^{Sp}$ and a_{250}/a_{365}^{Sp}, r^2=0.85, $p<0.01$ and r^2=0.92, $p<0.01$), DOC composition during summers was only significantly correlated with catchment fen cover ($SUVA_{254}^{Su}$ and a_{250}/a_{365}^{Su}, r^2=0.61 $p<0.01$ and r^2=0.56 $p<0.05$) and not palsa cover or total peatland cover.

General seasonal trends in DOC composition were detected, but they were not necessarily linked to catchment peatland cover. All catchments, except A5 and A6, had higher $SUVA_{254}^{Sp}$ than $SUVA_{254}^{Su}$ (Fig. 5.3), indicating a general pattern of higher DOC aromaticity during spring than during summer. Five catchments (A1, A7, B1, B2 and C1) exhibited a marked decrease in inferred average molecular weight from spring to summer, indicated by higher a_{250}/a_{365}^{Su} than

a_{250}/a_{365}^{Sp} estimates. Three of these catchments (A7, B1 and B2) had <1% catchment peatland cover, while the A1 catchment outflow is the outlet of the largest lake in the catchment. Catchment C1 also had a sizeable lake coverage, but it should be noted that the summer increase in a_{250}/a_{365} was from a low spring estimate.

Relationships between instantaneous runoff rate and DOC composition indices were variable (Fig. 5.4). Catchments A7, B1 and B2, all with <1% peatland cover, had significant positive correlations between instantaneous runoff rate and $SUVA_{254}$ and significant negative correlations with a_{250}/a_{365} (increased DOC aromaticity and average molecular weight at high runoff rates) Most catchments with >5% peatland cover instead had significant positive correlations between runoff rate and a_{250}/a_{365} (decreased average molecular weight at high runoff rates), with the exceptions of catchment A1 and C1 which have the greatest lake coverage.

5.5.5. PRINCIPAL COMPONENT ANALYSIS

A principal component analysis (PCA) was performed using $[DOC]^{An(07/08)}$, $SUVA_{254}^{An(07/08)}$, $a_{250}/a_{365}^{An(07/08)}$, $a_{254}^{An(07/08)}$, $pH^{An(07/08)}$, $Ec^{An(07/08)}$, 2007 to 2008 total runoff, R/P ratio, DOC export and total C export as variables (Fig. 5.6) (Analysis performed in MatLab R2009b – Statistics Toolbox). Each variable was standardized before analysis through division by its standard deviation. The PCA was performed to see how many principal components that were needed to adequately explain the exhibited variability between catchments and which variables that contributed to each component, while acknowledging that several of the variables are not independent. The two first components explained 79.2 and 13.2% respectively of the observed variability. Principal component coefficients for each variable are represented in Fig. 5.6 by vectors, where the direction and length of each vector indicates how each variable contributes to the two principal components in the plot. The plotting of principal component coefficients led us to interpret the first principal component primarily as an indicator of increased catchment groundwater influence, while the second principal component can be thought of primarily as the influence of increased catchment peatland cover.

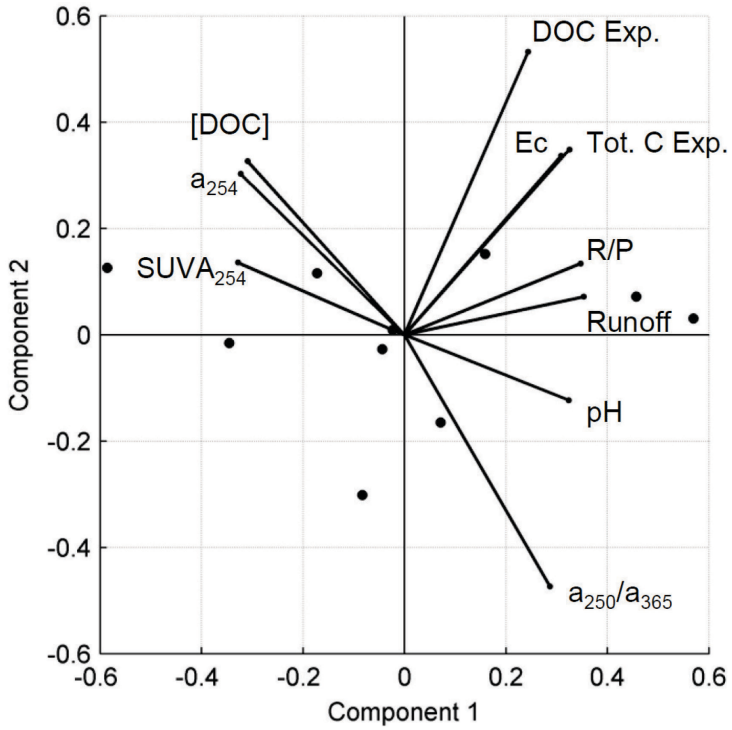

Figure 5.6. Principal component analysis on catchment data from 2007 and 2008. The plot shows principal component scores for each catchment and principal component coefficients for each variable. Principal component 1 explains 79.2% of the total variability, while component 2 explains 13.2%. Data was standardized by diving each variable by its standard deviation prior to analysis.

5.6 Discussion and conclusions

Catchment peatland cover and relative groundwater importance are the two main variables that appear to influence measured stream characteristics of the nested Stordalen catchments. While a variable groundwater influence between catchments is due to local conditions, the influence of peatland cover represents a general pattern. However, variable groundwater influence helps highlight important processes involved in waterborne C export. The following discussion explores how peatland cover and groundwater influence affect waterborne C transport, including concentrations, exports and DOC composition. We also discuss the possible influence of other catchment variables, such as lake coverage and the partitioning of peatland cover into fen and palsa. Our understanding of the processes that control waterborne C export is then used to assess sensitivities to continued climate change.

5.6.1 GROUNDWATER INFLUENCE AND RUNOFF PATTERNS

Runoff represents the transport potential for waterborne C export, and we found that total annual runoff varied considerably between the studied catchments. Our data suggest that the difference in runoff patterns is primarily linked to differences in catchment groundwater discharge, since $Ec^{An(07/08)}$, an indication of relative groundwater contribution, was found to be strongly correlated with both catchment runoff and R/P ratios. An example of this is the difference between non-nested catchments B2 and A7 that both lack significant peatland coverage, are of similar size, have similar energy gradients and have their outflows located just below the break in slope of the catchment (Fig. 5.1 and Table 5.2) – but with catchment B2 having significantly higher Ec^{An}, runoff, R/P ratios and waterborn C transport (Fig. 5.3 and Table 5.3). This pattern could be due to a combination of regional groundwater (Toth, 1963a) (i.e. originating from outside the topographic catchment) reaching catchment B2 but not catchment A5, and differences in groundwater storage and associated recharge/discharge dynamics within each catchments. Catchment B2 has a more concave catchment topography than A5 (Fig. 5.2), which might cause increased thickness of the scree slopes and thus increase the potential groundwater storage and groundwater discharge during years with low precipitation.

Relative groundwater contribution to catchment runoff was found to increase during years with greater precipitation and runoff, as indicated by highest Ec^{An} during 2007, followed by 2008 and 2009 (Table 5.3). This shows that groundwater runoff in this setting is more responsive to annual precipitation than other contributing runoff sources. At the same it is indicated that groundwater storage is large enough to influence runoff patterns of the following year, but not for several years – considering how high R/P ratios were sustained from 2007 (highest precipitation) into 2008 (intermediate precipitation) but then dropped significantly in 2009 (lowest precipitation) (Table 5.3).

Catchment peatland cover had limited influence on catchment runoff and R/P ratios in this study. While all catchments exhibited higher R/P ratios in spring

than in summer, as is common in snowmelt-dominated northern catchments (Yamazaki et al., 2006), the difference between spring and summer R/P ratios increased with increased peatland cover in this study. Studies of the hydrology of palsas have shown that increased storage capacity in peatlands during summers leads to low runoff rates (Wright et al., 2008), or even cessation (Chapter 3), which could explain the decreased R/P ratios from catchments with increased peatland coverage during summers.

5.6.2 WATERBORNE C EXPORT

Waterborne C transport from catchments with widely ranging catchment sizes and ecosystem composition have been found to range between 1.78 and 19.1 g C m^{-2} yr^{-1}(Dawson et al., 2002; Elder et al., 2000; Striegl et al., 2007; Wallin et al., 2010) a range which spans the estimates from the Stordalen catchments in this study (2.77 to 7.31 g C m^{-2} yr^{-1}). The magnitude of the total waterborne C export makes it a significant C flux for the catchment C balance. In comparison it has been found that the net ecosystem exchange (NEE) of the forest, peatlands and heath in the Stordalen catchment are C sinks at -50, -20 and -5 g C m^{-2} yr^{-1} respectively, while the lakes lose C at between 6 and 30 g C m^{-2} yr^{-1} (Christensen et al., 2007; Karlsson et al., 2010). Given the fractional make up of each ecosystem within Stordalen, the waterborne C export represents ~10-30% of catchment NEE.

We compared the DOC export in this study, at between 2.01 and 4.24 g m^{-2} yr^{-1} for all years and sites and representing between 58 and 82% of the total C export, to reported DOC exports from boreal catchments of similar catchment sizes (Creed et al., 2008; Dillon and Molot, 1997; Elder et al., 2000; Kortelainen et al., 2006; Laudon et al., 2004). The range of reported DOC export rates is 0.5 to 15 g C m^{-2} yr^{-1}, and is significantly correlated with catchment peatland cover (Fig. 5.7). In Stordalen we found that $[DOC]^{An(07/08)}$ was strongly linked to catchment peatland cover, but that annual DOC export was not. In Stordalen a variable groundwater influence between catchments led to difference in runoff magnitude between catchments, thus disconnecting DOC concentrations and DOC export.

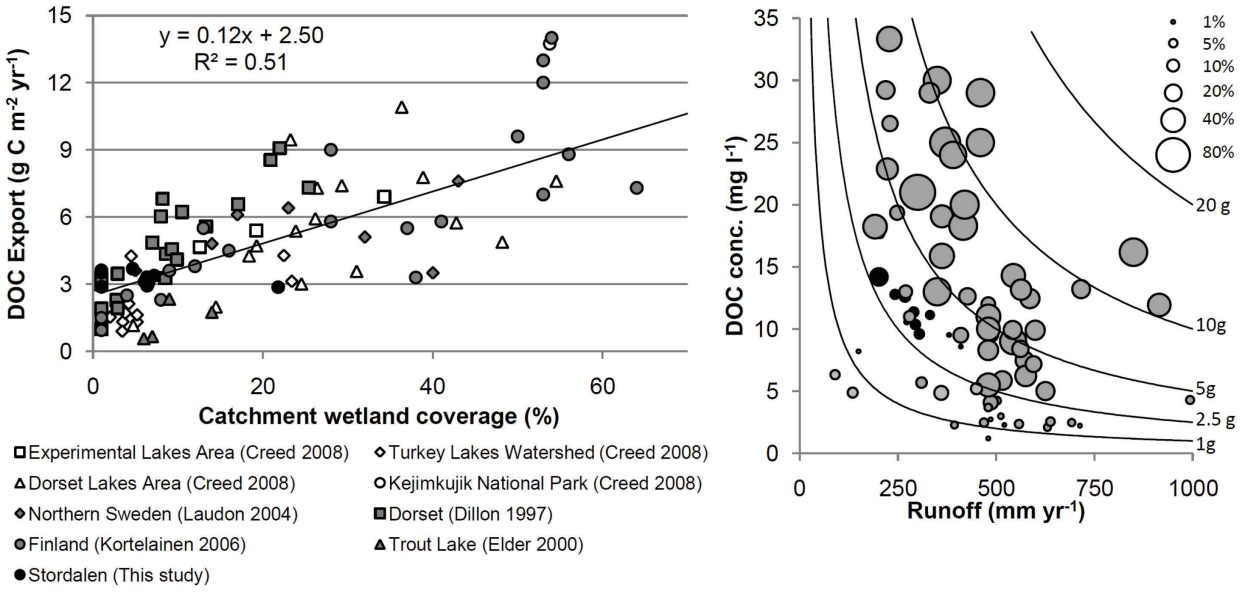

Figure 5.7. Inter-study comparison of the relationship between catchment wetland coverage and DOC export. Figure on left plots catchment peatland cover vs. DOC export, black circles are data from this study. Figure on right shows how runoff and annual flow-weighted DOC concentration result in DOC export, with the size of the bubbles representing the catchment peatland cover. Black circles are data from this study, gray circles are the data also used in figure on left, except data from Dillon and Molot (1997) where annual runoff was not specified. All catchments included in the comparison range in size from 0.05 to 62 km^2.

The DOC export rates in Stordalen were similar to boreal catchments with a similar catchment peatland cover despite relatively low annual runoff rates (Fig. 5.7). This was due to higher $[DOC]^{An}$ than reported for boreal catchments, especially for the Stordalen catchments with <5% catchments peatland cover. A possible explanation for this is the greater importance of snowmelt in high-latitude subarctic catchments for DOC export than in boreal catchments, with snowmelt associated with high DOC concentrations from non-peatland catchments. The proportion of the annual DOC export occurring during spring increased with decreased peatland cover in this study, a pattern that has been observed in both arctic and boreal catchments previously (Ågren et al., 2008b; Finlay et al., 2006; Laudon et al., 2004). The spring season was responsible for between 53 to 64% of the annual DOC export, which is similar to the 60% DOC

exported from the largest arctic rivers over 2 months of snowmelt (Raymond et al., 2007).

Export of DIC was important for the total C export in Stordalen, ranging between 0.51 and 3.54 g C m^{-2} y^{-1} and thus representing 18 to 41% of the total C export. Export of DIC can represent a very variable fraction of the total C export, reported between 2 and 70%, depending on catchment size, ecosystem composition and type of bedrock (Dawson et al., 2002; Öquist et al., 2009; Striegl et al., 2007; Wallin et al., 2010). While both DIC and DOC export increased during years with higher runoff, DIC increased proportionally more. In 2007 DIC export represented on average 38% of the total C export among catchments, but in the drier 2009 it only represented 24%. Carbonate weathering is likely to be the origin of most of the DIC export in Stordalen as [DIC] measurements were well correlated with both Ec and Ca^{2+} concentrations. The importance of DIC for total C export has been suggested to increase with permafrost degradation and deepened flow paths (Walvoord and Striegl, 2007), but we show that a shift towards greater DIC importance can also be achieved through changes in runoff patterns.

5.6.3 DOC COMPOSITION

Increased peatland cover was associated with increased aromaticity and DOC average molecular weight, as indicated by patterns of $SUVA_{254}$ and a_{250}/a_{365}. The annual (2007 and 2008 joint) average aromaticity (using the relationship reported by Weishaar et al. (2003)) from catchments C1 and B2 was 22.7 and 17.8% respectively and thus represented the greatest annual difference between catchments. This influence of peatlands on catchment DOC composition has previously been observed in a study of boreal catchments of similar size to this study (Ågren et al., 2008b). Bioassays on soil leachates have shown that DOC with higher aromaticity and molecular weight, e.g. peat-derived DOC, is generally less bioavailable than DOC from other sources – i.e. a smaller fraction of an initial DOC pool is microbially respired over a period of time (Berggren et al., 2009b; Kalbitz et al., 2003a; McDowell et al., 2006; Roehm et al., 2009).

However, DOC sampled at catchment outflows does not only represent a mixing of DOC from different sources but also any transformation that the DOC has undergone from source to catchment outflow. Microbial degradation, photodegradation and selective adsorption can transform DOC and the combination of processes has largely unknown impacts on DOC composition and bioavailability. For example it has been found that lake DOC was less bioavailable than peat leachate, despite a lower aromaticity (Roehm et al., 2009). Further, it has been found that DOC exported during summers from large arctic rivers is less bioavailable than during spring, despite a lower $SUVA_{254}$ during spring (Holmes et al., 2008). Thus conclusions should be treated with caution when inferring DOC bioavailability at a catchment scale from DOC composition indices.

Decreased significance of the correlation between catchment peatland cover and $SUVA_{254}$ and a_{250}/a_{365} from spring to summer could be due to processes that alter DOC composition from its terrestrial source to the catchment outflow. During spring we assume a smaller influence on DOC composition from microbial degradation, photodegradation and selective absorption due to short residence time, low water temperatures and shallow flow paths. Thus during spring DOC composition at the catchment outflow will be at its closest to representing conservative mixing of DOC from different terrestrial sources. During summers it was found that only catchment fen cover was correlated with DOC composition, a result that is in agreement with results from a study of a fen in the catchment which showed that it was a site for significant DOC transformation during summers (Chapter 3).

DOC from groundwater sources are also indicated to influence catchment DOC composition in this study, especially during summers. DOC from groundwater sources has passed through mineral soils where selective absorption of hydrophobic aromatic DOC acts to decrease $SUVA_{254}$ (Kaiser and Zech, 1998). In this study an increased groundwater contribution, as indicated by $Ec^{An(07/08)}$, was significantly correlated with lower $SUVA_{254}{}^{An(07/08)}$ and $SUVA_{254}{}^{Su(07/08)}$. All

catchments except A5 and A6 had lower $SUVA_{254}$ during summer than spring, consistent with increased groundwater contribution during summer. A pattern of high $SUVA_{254}$ during spring followed by decreasing values over summer and fall has been observed in several of the large arctic rivers (Spencer et al., 2008), where it also coincides with increased ^{14}C age of the DOC (Neff et al., 2006) which is indicative of deeper flowpaths.

Photodegradation in lakes is another factor that is indicated to influence DOC composition and DOC export during summers. The largest lake in the study is located between sampling points of catchment A1 and A2. Since catchment A2 represents 98% of the A1 catchment area, we assume that differences in DOC composition between the catchments are primarily due to within-lake processes. Our data found the lake to be an average DOC sink of ~1400 kg C yr^{-1} which is equivalent to a lake DOC loss rate at 9 g C y^{-1} m^{-2} (lake area), which is close to the lake NEE estimate from Christensen et al. (2007) at 6 g C y^{-1} m^{-2}. At the same time DOC aromaticity and DOC average molecular weight decreased from lake inflow to outflow, as has also been observed in other boreal lakes (Curtis and Schindler, 1997). This pattern is consistent with photodegradation, which affects UV absorbing aromatic structures preferentially, and transforms aromatic DOC into DIC and low molecular weight DOC (Bertilsson and Tranvik, 2000).

5.6.4 Influence of climate change on waterborne C export and DOC composition.

Climate change can be expected to alter total waterborne C export and its composition in subarctic peatland catchments both directly through changes in precipitation and increased temperatures but also indirectly, e.g. through permafrost degradation.

In this study the waterborne C export increased with increased annual precipitation. The difference in total C export between 2007 and 2009 was equivalent to an average change in total C export of 0.19 g C m^{-2} yr^{-1} per 10 mm precipitation. The average annual precipitation has increased by 43 mm between the period 1913-1979 and 1980-2009, which would mean that waterborne C

export could have increased by up to 30% over the last few decades – with probably the greatest increase in DIC export and DOC derived from groundwater sources. While DOC from groundwater sources is associated with low aromaticity, it can't be assumed to increase bioavailability.

The relationship between precipitation and total C export can further be modified as increased temperatures affect evapotranspiration and thus R/P ratios and runoff. Modeling of a subarctic catchment water balance have shown that the effects of increased precipitation and temperature can cancel out and leave total runoff unaltered, although with perturbations to the annual runoff pattern (Woo et al., 2008). Increased temperatures can also potentially alter DOC export and DOC composition through its influence on microbial degradation rates of DOC (Marschner and Kalbitz, 2003). Including the effects of temperature changes on waterborne C export thus add complexity which this study was not suitable to explore.

Permafrost loss in peatlands has been linked to increased POC export, derived from thawed old peat (Guo and Macdonald, 2006; Guo et al., 2007). We did not find evidence of high POC export in this study, despite ongoing permafrost loss in the peatlands. It seems that conditions other than those found in the study catchment are necessary to cause an increase in POC export as permafrost melts, e.g. peat deposits next to higher-energy water-courses.

There is a large uncertainty of the impacts of peatland permafrost degradation on DOC export (Frey and McClelland, 2009). Because fens in Stordalen catchment have been shown to be greater net DOC sources than palsas, an increase of catchment DOC export could be expected as permafrost loss leads to the conversion of palsas into fens (Chapter 3). However, the net DOC export from the fens was also shown to be dependent on the magnitude of flow-through, and especially it was implied that transformation of DOC from upstream sources was inversely linked to fen flow-through magnitude. As the fen areas increase, their area-specific flow-through magnitude will decrease which could decrease their net DOC export while increasing their influence on DOC composition.

CONTEXT OF CHAPTER 6 WITHIN THESIS

This last study focuses on two of the catchments included in the previous study (Chapter 5), catchments that differ with regards to their peatland cover. By comparing the patterns of DOC export and composition between the catchments, and also including the patterns exhibited by the pure palsa catchment presented in the first study (Chapter 3) we aim to show how palsa and fens independently affect the timing, magnitude and composition of the DOC export at the catchment scale. Because permafrost thaw in the region causes a conversion of palsas into fens, this comparison is of interest when discussing the influence of peatland permafrost thaw on catchment DOC export and composition. The methods used include the implementation of a mixing model along with comparisons of hydrographs and DOC composition patterns during snowmelt and storm events – periods of the year that are of greater significance for the annual DOC export and that have the potential to reveal information about sources and flowpaths of DOC.

6. USING HYDROGRAPH SEPARATION AND DOC COMPOSITION TO EVALUATE THE INFLUENCE OF DIFFERENT PEATLAND TYPES ON CATCHMENT DOC TRANSPORT.

6.1 ABSTRACT

Peatlands are important ecosystems for transport and composition of DOC at the catchment scale. In this study we have assessed the function and importance of different peatland types (palsas and fens) for catchment DOC transport and composition in a subarctic setting. Three separate catchments were monitored; one non-peatland catchment, one catchment with 8% combined fen and palsa coverage and one small palsa catchment (i.e. 100% peatland coverage). The catchments were monitored over a two year period, and a mixing model based on electrical conductivity and absorbance (254 nm) was implemented in the non-peatland and 8% peatland catchments, with groundwater, precipitation and forest O-horizon water used as end-members. Hydrograph separation for the entire year successfully reproduced DOC and other solute concentrations (Ca^{2+}, Mg^{2+}, Na^{+}, SO_4^{2-}) for the non-peatland catchment but the same mixing model was less accurate during certain periods of the year for the 8% peatland catchment. The patterns of DOC export and DOC composition from the palsa catchment explained the lack of accuracy of the mixing model during early snowmelt for the 8% peatland catchment, but not during summers. Instead catchment patterns of DOC export and DOC composition during summers in peatland catchments is due to the influence of the fens. Several independent lines of evidence indicate the fens acting as significant catchment sources of DOC, but their locations in the catchment means they receive a large supply of DOC from upstream sources - DOC that is significantly degraded (e.g. through microbial sulfate reduction) or transformed (causing increased aromaticity and average DOC molecular weight) within the fens. With continued permafrost thaw in the region that transforms

palsa peatlands into fens, the importance of fens as sources but also regulators for catchment transport of DOC is expected to increase.

6.2 INTRODUCTION

Concentrations and composition of DOC in runoff from terrestrial ecosystems has been found to be important for the metabolism in northern aquatic ecosystems (Berggren et al., 2010; Buffam et al., 2001; Karlsson et al., 2010; Sobek et al., 2005). Interactions between terrestrial DOC losses and aquatic C turnover determine, in part, the catchment DOC export and composition, with implications for downstream productivity, nutrient cycling and light attenuation. Catchment DOC export and the atmospheric C exchange with aquatic ecosystems are thought to represent significant C fluxes for the total catchment C balance (Cole et al., 2007; Tranvik et al., 2009). Increased catchment peatland cover has been associated with increased DOC concentrations (Laudon et al., 2004; Mattsson et al., 2005) and DOC aromaticity (Ågren et al., 2008b) in streams and lakes. However, studies of the relationships between catchment peatland cover and stream DOC observations at catchment outflows most often do not attempted to isolate the influence of different peatland types (e.g. bog and fen peatland types).

Peatland complexes of the subarctic are often a mosaic of different peatland types which differ with regards to permafrost conditions as well as hydrological setting, exemplified in north-western Eurasia by peatland complexes consisting of palsas, bogs and fens (Masing et al., 2010). Palsas contain permafrost and are ombrotrophic systems in contrast to minerotrophic fens that often do not contain permafrost, leading to differences in vegetation composition and ecosystem functioning and we hypothesize that this variation causes different peatland types to influence catchment export and composition of DOC differently. Warming in the circumpolar subarctic has led to permafrost thaw in palsas, causing changes in vegetation composition and hydrological regime (Camill, 2005; Malmer et al., 2005; Payette et al., 2004), and continued permafrost loss is expected for this century (Lawrence et al., 2008). Loss of permafrost from northern peatlands has been suggested to affect catchment DOC export, but currently there is no

consensus on the direction or magnitude that can be expected (Frey and McClelland, 2009). Potentially important processes include increased microbial and hydrological access to previously frozen peat (Frey and Smith, 2005), altered vegetation composition, ecosystem productivity and hydrological regime following permafrost thaw (Guo et al., 2007) and increased interaction of peatland runoff with mineral soils (Walvoord and Striegl, 2007).

Different geochemical mixing models are frequently used to identify catchment runoff processes responsible for downstream transport or sources of various solutes, including studies of DOC transport in northern landscapes (Carey and Quinton, 2005; Ladouche et al., 2001; McNamara et al., 1997; Petrone et al., 2007). By using information of the chemical signature of potential end-members and stream water it is possible to estimate the relative contribution of each end-member to stream flow. Most often, mixing models are applied to short time-scales, e.g. storm events or during snowmelt, but models can also be used at the annual timescale (Uhlenbrook et al., 2002) when the assumptions of the mixing model can be met (Hoeg et al., 2000).

Sources of DOC within a catchment can differ greatly in their bulk chemical composition (Roehm et al., 2009; Wickland et al., 2007). Indices that are commonly used to characterize the DOC bulk composition include specific UV absorbance at 254 nm ($SUVA_{254}$), which can be used as an estimate of DOC aromaticity (Weishaar et al., 2003), and a_{250}/a_{365}, an absorbance ratio that is linked to the average DOC molecular size (Peuravuori and Pihlaja, 1997). Both increased aromaticity and molecular weight of soil extracts have been linked to decreased bioavailability (Kalbitz et al., 2003a; Marschner and Kalbitz, 2003), but the link between DOC composition and bioavailability at the catchment scale is not clear (Spencer et al., 2008). The lack of clarity could be due to secondary processes such as microbial degradation (Kalbitz et al., 2003b), photodegradation (Bertilsson and Tranvik, 2000) and selective soil sorption (Kaiser and Zech, 1998). While the link between composition and bioavailability is unclear, DOC

composition has recently started to be used as an indicator of DOC source in catchment studies (Ågren et al., 2008b; Hood et al., 2006).

The peatlands in our study catchment are currently undergoing permafrost thaw, leading to the partial conversion of palsa type peatland into fen (Malmer et al., 2005). Our research question is "what is the influence of different types of peatlands on the timing, the amount and the composition of catchment DOC export?". We will answer this question by using a combination of an end-member mixing model, runoff hydrographs and measured DOC fluxes and composition over three different time scales: a year, a season and individual storm events.

6.3 METHODS

6.3.1 SITE DESCRIPTION

The Stordalen catchment is a 15 km^2 catchment located within the Scandinavian Caledonides in northernmost Sweden (68.20N, 19.03E) (Fig 6.1). The average annual temperature measured at Abisko Scientific research station located 10 km west of the study catchment has increased over the last three decades from -0.7 ±1.0 °C (mean ±SD) (1913-1979) to 0.0 ±0.9 °C (1980-2009) (NORDKLIM, data available at http://www.smhi.se/hfa_coord/nordklim). The average daily temperature is currently above 0°C from mid April until late October. Annual precipitation has increased from 292 ±50 mm (1913-1979) to 335 ±67 mm (1980-2009). Snow-fall represents 40% of the annual precipitation, and the maximum snow-depth has increased by 10% per decade since the 1930s (Kohler et al., 2006) while the period of permanent snow cover has decreased by one month since 1986 (Malmer et al., 2005).

The geology of Stordalen catchment contains thrusted quartzite, shales and carbonate bedrock including dolomite (Andersson et al., 1996). Soils are poorly developed, dominated by tills and glaciofluvial sands. The catchment has a distinct break in slope, dividing the catchment into a mountainous and a low-land part. Scree slopes, comprising unconsolidated rock of unknown thickness with overlying poorly developed soils are common just upslope of this mountain –

lowland transition. Stordalen catchment is dominated by an open canopy mountain birch woodland (*Betula pubescens* ssp. *czerepanovii*) with a heath ground layer of *Empetrum nigrum* ssp. *hermaphroditum, Vaccinium vitis-idaea*, *V. myrtillus* and *Arctostaphylos uva-ursi.* Vegetation above the treeline (above ~700 m) is sparse with occurrence of *Salix spp*. and *Betula nana* stands. Peatland complexes have developed in lowlands parts of the catchment, and they are underlain by silt deposits. The peatland complexes are composed of fen and palsa areas. The palsas are the only parts of the catchment that contain permafrost. Ice lenses at the interface between the silt and peat cause the palsas to be lifted above the surrounding fens and lead to ombrotrophic conditions. Vegetation composition on the palsas includes dwarf shrubs (*E. nigrum* ssp *hermaphroditum*), mosses (*Sphagnum fuscum*, *Dicranum elongatum*), lichens (*Cetaria* spp. and *Cladonia* spp.) and sedges (*Eriophorum vaginatum*). The fens receive water from their upland catchments and are characterized by a water table at or above the peat surface and a vegetation composition consisting mainly of *Carex rostrata, Eriophorum augustifolium* and *E. vaginatum*. Ongoing permafrost thaw is transforming peripheral parts of the palsas into fen (Åkerman and Johansson, 2008; Malmer et al., 2005).

This study focuses on two separate sub-catchments within the Stordalen catchment (A5 and B2) (Fig. 6.1 and Table 6.1). Of the two, only catchment A5 contains peatlands, with a large proportion of its runoff passing through two fens in the lower parts of the sub-catchment before reaching the sampling point. Both sampling locations are located just below the break in the topography, but catchment B2 has a more concave catchment structure that is associated with more extensive scree slopes. A high resolution digital elevation map (DEM) derived from light detection and ranging (LIDAR) data was produced for the whole area (Fig. 6.1). The LIDAR precision was approximately ± 5 cm. The spatial resolution chosen to estimate the hydrological divides and catchment surface areas was a pixel size of 10 m^2. Sink removal and flow accumulation calculations were performed using a form-based model (Pilesjo et al., 2006) prior to locating water courses and catchment delineations. Water courses and

catchment delineations were estimated with hydro tools in the ESRI ArcGIS 9.3 package (ArcINFO version), and confirmed through ground observations. Surface areas of peatlands, further divided into palsa and fen, were determined from aerial photographs. Data is also presented from a smaller palsa catchment (P1) located outside either catchment A5 or B2. Catchment delineation of the P1 catchment was estimated through a plane survey of the topography of the palsa.

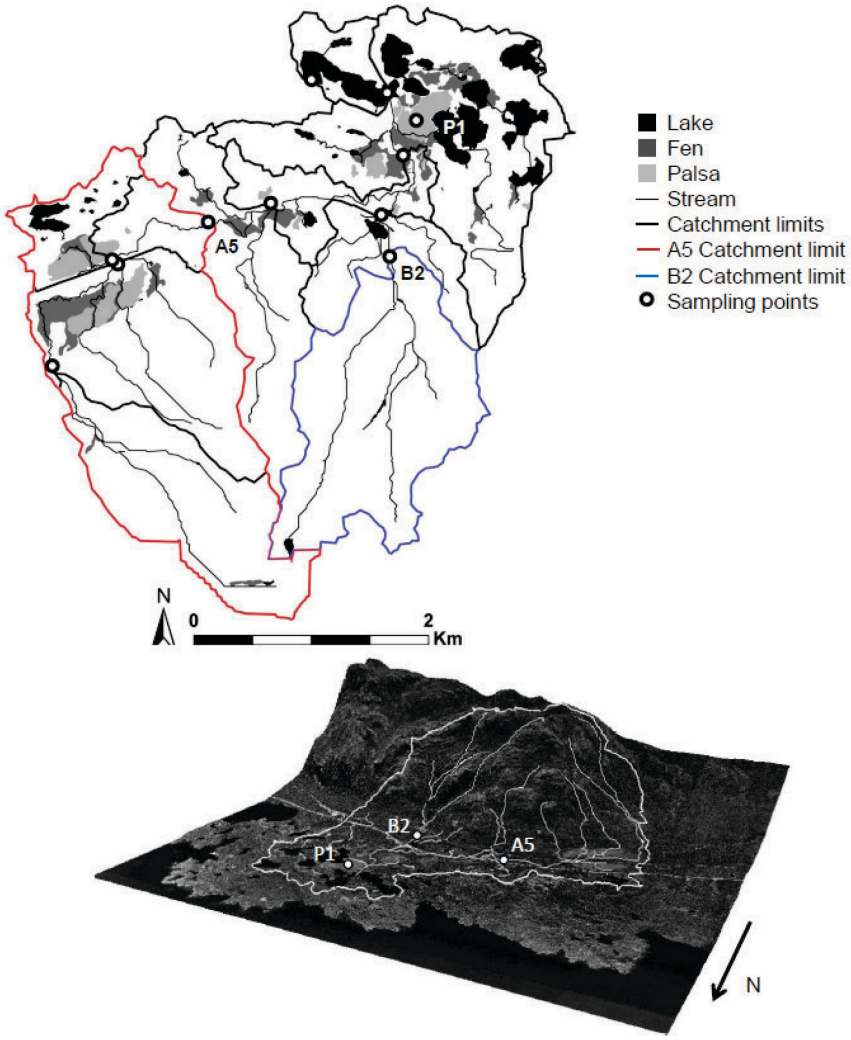

Figure 6.1. Images of Stordalen catchment (68.20N, 19.03E). Upper image highlights the studied sub-catchments of this study (A5, B2 and P1) and study sampling points, along with main streams and lake, fen and palsa areas in the full catchment. The lower aerial photograph is draped over a digital elevation map (elevation enhanced three times) with the full catchment limits delimited, along with sampling points and main streams. The two-color infrared aerial photographs (CIR, wavelengths 500-900 nm) was taken on the 29th of July 2000 from a height of 4600 m (image available at Abisko Scientific Research station).

Table 6.1. Physical characteristics of studied catchments within Stordalen catchment.

Catchment	Area (ha)	Elevation (m)	Aspect	Peatland coverage - Total (Fen/Palsa), (%)
B2	284	352-805	N	0 (0/0)
A5	617	373-791	WNW	7.2 (3.3/3.9)
P1	3.9	350-351	None	100 (0/100)

6.3.2 PRECIPITATION AND RUNOFF MEASUREMENTS

Precipitation was measured during the frost free season with a tipping bucket gauge located at Stordalen peatland in the lower part of Stordalen catchment (close to P1 catchment). Frost season precipitation at Stordalen peatland was estimated using daily precipitation measurements from Abisko research station (located 10 km west of Stordalen), calibrated for the systematic difference between the two locations. Synchronous precipitation measurements during the frost-free season found that precipitation at Stordalen peatland was 15.5% greater than at Abisko research station (range 8-18% annually, measured over 3 years), and was the factor used to adjust frost season precipitation. In addition, bulk rain gauges were set up at five different elevations within Stordalen catchment, between 351 and 756 m above sea level along the hydrological divide of sub-catchments A5 and B2. The cumulative rainfall was sampled every two weeks during May to September in 2008 and 2009. The total precipitation from the bulk rain gauges increased by 6.5% for every 100 m of altitude (linear correlation, r^2=0.93 $p<0.05$). Precipitation for each catchment was estimated based on the relationship between precipitation and elevation, using the average elevation of each catchment as derived from the DEM. Annual precipitation in catchment A5 was thus assumed to be 11% greater than the precipitation at P1, while B2 had 14% greater precipitation.

Hourly discharge for each sampling site was estimated from the onset of spring thaw in mid-April until late October in 2008 and 2009. Discharge was estimated from rating curves based on stage and discharge measurements. Water stage at sampling points was recorded continuously using Odyssey capacitance probes (resolution <1 mm, accuracy ±5mm), that were calibrated using manual stage

measurements from each water sampling. Discharge at sites A5 and B2 were estimated by velocity-area method where cross-sectional stream velocity was measured with an Aqua Data Sensa Electromagnetic Current Meter (resolution 0.01 m s^{-1}). A thin metal plated 20° weir was installed at the P1 outflow and its discharge was verified by volume bucket sampling. Rating curves for all sites were constructed using exponential equations where n ranged between 10 and 27 pairs and the r^2 of all curves was >0.98, with p values <0.001. Rating curves could not be applied to estimate discharge during early snowmelt at A5 and B2 due to ice conditions in the streams, so discharge was measured by velocity-area method every 1-3 days. Discharge between these measurements occasions was linearly interpolated. Less than 5% of the annual runoff for any site and year was estimated to occur in spring before the rating curves could be implemented.

6.3.3 WATER SAMPLING AND ANALYSIS

Water samples were both taken as grab samples, while higher sampling frequency was done by autosamplers (Hach, Sigma 900) installed at all sites. Sampling in 2008 and 2009 was initiated before snowmelt and ended in mid-October. Sampling frequency depended on discharge, with 1-3 samples/day during snowmelt, 1-3 samples/week during summer low flow periods, and an additional 10 to 25 samples taken during and for three days following a storm event. Autosamplers collected water every 2 hr (B2 and P1) or 3 hr (A5) from the start of storm events, followed by decreased frequency during stormflow recession. Water samples from the autosamplers were collected within 48 h. Only pH was noticeably affected by the storage period in the autosampler compared to chemistry of grab samples, and therefore this data was discarded. A total of 161 to 208 samples were taken in each year from sites A5 and B2, while P1 was sampled between 105 and 123 times.

Electrical conductivity (Ec) (adjusted to 20°C), and pH was measured with a hand held Oakton pH/Con 10 on each sampling occasion. In addition, Ec was measured hourly by AquiStar CT2X loggers at sampling sites A5 and B2. Water samples were filtered through 0.45 μm glass fibre filters and kept in 25 ml airtight bubble-

free vials in a dark refrigerator at 5°C. Samples for DOC analysis were acidified to pH 2 with 0.5 M HCl on the day of collection, and analyzed for DOC concentration on a Shimadzu TOC-V CPH analyzer within 3 weeks of collection. All samples were analyzed for absorbance at 250, 254 and 365 nm (a_{250}, a_{254} and a_{365}) with a Shimadzu UV-160A through a 1 cm quarts cuvette on the same day as collection. Absorbance measurements were used to calculate $SUVA_{254}$ and a_{250}/a_{365}. We also report a_{254} on its own, using it as a non-calibrated measure of the absolute concentration of aromatic DOC. A sub-set of the water samples (60-125 samples per year from A5 and B2, 43-49 samples from P1) were analyzed for ion concentrations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, NO_3^-, PO_4^-, SO_4^{2-}) by ion chromatography (Dionex ICS-1600).

6.3.4 HYDROGRAPH SEPARATION

Hydrograph separation using a mixing model method produces estimates of contributions to catchment runoff from identified water sources, - i.e. end-members (Carey and Quinton, 2005; Christophersen et al., 1990). The method is based on the mass conservation of water and geochemical tracers, allowing streamflow to be separated into n end-members by using n-1 observed tracers ($t_1, t_2, ..., t_{n-1}$):

$$R_T = R_1 + R_2 + \ldots + R_n \quad (1)$$

$$C^{t_i}{}_T R_T = C^{t_i}{}_1 R_1 + C^{t_i}{}_2 R_2 + \ldots + C^{t_i}{}_n R_n \quad (2)$$

where R_T is total stream runoff, R_1 to R_n is contributing runoff from end-member 1 to n, $C^{t_i}{}_T$ is the observed tracer concentration in streamflow and $C^{t_i}{}_1$ to $C^{t_i}{}_n$ are tracer i concentrations of end-members 1 to n. Equations 1 and 2 can be combined to solve for the fractional contribution of individual end-members at each sampling occasion, with the resulting equation dependent on the number of end-members included in the model:

$$f_1 = \frac{R_1}{R_T} = \frac{C_T^{t_1} - C_1^{t_1}}{C_2^{t_1} - C_T^{t_1}} \quad (3)$$

$$f_1 = \frac{R_1}{R_T} = \frac{\left(C_T^{t_1} - C_3^{t_1}\right) - \left(C_T^{t_2} - C_3^{t_2}\right) \times \left(C_2^{t_1} - C_3^{t_1}\right) / \left(C_2^{t_2} - C_3^{t_2}\right)}{\left(C_1^{t_1} - C_3^{t_1}\right) - \left(C_1^{t_2} - C_3^{t_2}\right) \times \left(C_2^{t_1} - C_3^{t_1}\right) / \left(C_2^{t_2} - C_3^{t_2}\right)} \quad (4)$$

where eq. 3 is the solution to a one tracer - two end-member mixing model and eq. 4 is the solution to a two tracer – three end-member mixing model. Fractional contributions of additional end-members (f_1 through f_n) can be solved analogously.

Several assumptions need to be fulfilled for mixing models to yield accurate results; (1) tracers must mix conservatively, (2) end-members must have statistically different tracer concentrations, (3) tracer concentrations of end-members must be spatially and temporally constant (or changes must be taken into account) and (4) runoff contribution of end-members not included in the analysis must be negligible or have similar tracer concentrations as an included end-member. If all these assumptions are fulfilled, then observed stream water concentrations of used tracers will fit into the mixing space created from the chosen end-members. However, stream observations within the defined mixing space are conversely not a guarantee that the mixing model assumptions are fulfilled. Evaluation of the mixing model can be performed by testing its ability to reproduce observed concentrations of solutes that are not included as tracers. Projected concentrations, which are compared to observed concentrations, are calculated by rearranging Eq. 2 to solve for an unknown stream concentration of the chosen solute (not a tracer) – using estimated end-member contribution to stream-flow and their characterization with regards to the chosen solute.

We used a three end-member mixing model with a_{254} and Ec as tracers for catchments A5 and B2 and a two end-member mixing model with a_{254} as the sole tracer was used for P1. We chose to use a_{254} and Ec as conservative tracers in the mixing models for catchment B2 and A5, since they were assumed to best meet the criteria of the mixing model. Ec can be assumed to mix conservatively in situations where acid-base reactions are negligible (pH close to neutral) and ion concentrations are low to moderate (Schleppi et al., 2006), criteria that both are fulfilled in catchments B2 and A5. An alternative to Ec would have been the

concentrations of base cations, e.g. Ca^{2+} or Mg^{2+}, but continuous Ec measurements allowed for a higher temporal resolution of the mixing model. Previous studies have used DOC concentration successfully as a tracer in mixing models (Carey and Quinton, 2005; Ladouche et al., 2001; Petrone et al., 2007), but instead we choose to use a_{254} as our second tracer – with a_{254} being a measure of the concentration of aromatic DOC (Weishaar et al., 2003). We did not want to use DOC concentration as a tracer in the mixing model because it is specifically the stream DOC patterns and differences thereof between catchments that we wish to explain. Instead we have later evaluated the ability of the mixing model to reproduce the observed DOC concentrations. Further, a_{254} is a suitable tracer to identify water which originates from organic soils and has had little interaction with mineral soils, where aromatic DOC is rapidly absorbed (Peichl et al., 2007). Ec and a_{254} were also chosen as tracers since end-member sampling had relatively low variability over the season (Table 6.2), a criteria that prohibited the use e.g. of K^+ and Cl^- as conservative tracers.

The three end-members used in the mixing models were precipitation (*Pr*), forest O-horizon water (*O-h*) and groundwater (*Gw*), with the *Gw* end-member omitted in the mixing model for catchment P1. Rain samples for *Pr* characterization were collected during the storm events of 2008 and 2009 (Table 6.2). Since surface area of the stream is <1% of the A5 and B2 catchments, contribution of direct precipitation can only represent a tiny fraction of streamflow. Instead the *Pr* contribution to streamflow needs to be characterized as water that reaches the stream through quickflow and therefore retains the chemical signature of precipitation or snowmelt. For the *O-h* end-member, two 1.5 m troughs were inserted between the ground layer and the mineral soil in the birch forest to collect throughfall and *O-h* drainage during storm events. Samples from sampling sites A5 and B2 taken prior to snowmelt and during the late 2009 summer low flow period were used for *Gw* characterization. A fourth potential end-member, palsa porewater (*Pp*), was sampled in four wells inserted on the palsa in catchment P1. However, the *Pp* end-member Ec and a_{254} range overlapped with the *O-h* end-member, and was therefore not explicitly included in the mixing model but rather

assumed to be a part of *O-h* streamflow contribution - in accordance with the fourth assumption of the mixing model as stated above. Thus the three end-member mixing model for A5 and B2 gave estimates of $f_{O\text{-}h}$, f_{Pr} and f_{Gw} and the two component mixing model for P1 yielded f_{Pr} and $f_{O\text{-}h}$.

To remove the influence of a few outlier samples we used median values of measured tracer concentrations in the mixing models. Uncertainty of the mixing model was assessed by exchanging the median end-member tracer concentrations with that of the 1st and 3rd quartile and reporting the maximum and minimum estimates of end-member contribution to stream flow. The mixing model uncertainty analysis yielded results where the estimated contribution of each end-member in most cases were significantly separated and contained within the mixing space, and showed that the uncertainty of f_{Pr} and f_{Gw} was primarily associated with the *Gw* end-member variability of Ec while it was the variability in a_{254} of the *O-h* end-member that caused uncertainty of $f_{O\text{-}h}$.

Table 6.2. General properties of the potential end-members used in this study. Median values along with the 1st and 3rd quartile values in parenthesis.

	Groundwater (*Gw*)	Precipitation (*Pr*)	Organic water (*O-h*)	Palsa porewater (*Pp*)
Sample size (n)	20	19	14	26
Ec (µS cm^{-1})	90 (70-115)	6.0 (4.5-12)	51 (45-75)	45 (38-56)
a_{254} (cm^{-1})	0.03 (0.02-0.06)	0.01 (0.01-0.02)	2.25 (1.8-3.3)	2.25 (1.5-2.8)
DOC (mg l^{-1})	5.0 (4.0-7.0)	1.0 (0.5-1.9)	72 (59-105)	64 (46-84)
$SUVA_{254}$ (l mg^{-1} m^{-1})	0.6 (0.5-1.0)	2.0 (0.5-3.3)	3.1 (2.7-3.6)	3.5 (3.1-3.9)
a_{250}/a_{365} (-)	6.1 (5.8-6.5)	4.7 (4.0-5.7)	5.4 (5.1-5.5)	4.6 (4.3-5.0)
Ca^{2+} (mg l^{-1})	19 (14-22)	0.75 (0.52-0.95)	6.7 (6.2-9.7)	0.9 (0.7-1.3)
SO_4^{2-} (mg l^{-1})	10 (9-12)	0.61 (0.43-0.86)	1.3 (1.1-2.2)	0.45 (0.2-0.6)

6.3.5 SOLUTE TRANSPORT

Estimates of solute export rates were calculated by multiplying discharge and linearly interpolated solute concentrations between sampling occasions. Both observed and predicted solute concentrations from the mixing model were used to estimate total annual exports. Uncertainties of annual export estimates from observed solute concentrations for the included catchments have in a previous study been estimated at 17% (Chapter 5), through Monte Carlo simulations that take into account the uncertainty of runoff, analytical precision and interpolation of solute concentrations.

6.4 RESULTS

The objective of the study is to assess the influence of fens and palsas on catchment waterborne transport of DOC, with regards to DOC quantity, timing and composition. To attain this objective we compare the stream chemistry of catchments A5 and B2, while using the results from palsa catchment P1 to represent the reference behavior of palsa DOC export patterns.

6.4.1 CLIMATE

The three catchments were monitored during 2008 and 2009, including two snowmelt periods and seven storm events that were sampled at higher frequency. The hydrological year in Stordalen was chosen to start on Nov 1st, as this approximates when snow accumulation starts and stream discharge enters a winter low-flow period. Annual precipitation at Stordalen peatland (close to sampling site P1) was estimated to be 320 and 290 mm respectively in 2008 and 2009 (1st Nov- 31st Oct) – based on frost free season measurements at Stordalen catchment supplemented with frost season precipitation measured at Abisko Research station located 10 km west of Stordalen peatland. The annual precipitation was in both years below the estimated long term (1913-2009) average of 350 mm. The summer of 2009 had 132 mm of precipitation between June 1st and Oct 30th, and this is more than a standard deviation lower than the long term average of 180 mm for the same period.

6.4.2 OBSERVED DOC EXPORT

Runoff, DOC concentrations and DOC composition for the three catchments included in this study have been presented in accompanying studies (Chapters 3 and 5), with relevant data for this study presented here in Table 6.3. Catchment B2 had significantly greater runoff than catchment A5 in both years, particularly during summers. The greater runoff from B2 led to greater total DOC export than from A5, despite lower average DOC concentrations. Export of DOC from the palsa P1 catchment was of similar magnitude to that of B2 and A5 despite much higher DOC concentrations because of a much more restricted period with runoff compared to that of the other two catchments. Catchments B2 and A5 also differed in DOC composition, with lower $SUVA_{254}$ and higher a_{250}/a_{365} in catchment B2, especially during summers.

Table 6.3. Precipitation, runoff, flow-weighted average DOC concentrations, DOC export and flow-weighted average $SUVA_{254}$ and a_{250}/a_{365} from catchments B2, A5 and P1 within Stordalen catchment. Values in parenthesis in the body of the table indicate the partitioning of the annual values between spring (1 Nov-20 Jun) and summer (21 Jun-31 Oct). Summary based on results from Chapters 3 and 5.

	B2 (0% peatland)	A5 (7.2% peatland)	P1 (100% peatland)
Precipitation -08 (mm)	376 (184/192)	357 (174/182)	320 (156/163)
Precipitation -09 (mm)	340 (209/130)	322 (198/124)	290 (178/112)
Runoff -08 (mm)	350 (162/188)	237 (134/103)	123 (84/38)
Runoff -09 (mm)	248 (190/58)	159 (139/20)	101 (101/0)
[DOC] -08 (mg l^{-1})	8.0 (8.5/7.6)	11.6 (11.5/11.8)	29.1 (22.5/43.9)
[DOC] -09 (mg l^{-1})	10.7 (11.7/7.6)	14.6 (14.8/12.9)	27.2 (27.2/-)
DOC export -08 (g m^{-2})	2.80 (1.37/1.43)	2.75 (1.53/1.22)	3.56 (1.89/1.67)
DOC export -09 (g m^{-2})	2.66 (1.71/0.94)	2.31 (2.06/0.25)	2.76 (2.76/0)
$SUVA_{254}$ -08 (l mg^{-1} m^{-1})	2.30 (2.65/1.97)	3.08 (3.16/2.97)	3.29 (3.19/3.41)
$SUVA_{254}$ -09 (l mg^{-1} m^{-1})	2.46 (2.71/1.18)	2.86 (2.88/2.71)	2.73 (2.73/-)
a_{250}/a_{365} -08 (N/A)	5.13 (4.89/5.34)	4.65 (4.73/4.55)	4.60 (4.51/4.79)
a_{250}/a_{365} -09 (N/A)	5.26 (5.06/5.94)	4.81 (4.92/4.00)	3.41 (3.41/-)

6.4.3 MIXING MODEL IMPLEMENTATION AND HYDROGRAPH SEPARATION

Ec and a_{254} from catchments A5 and B2 varied considerably in stream water over the year (Fig. 6.2 and 6.3), but very few samples fell outside the mixing space defined by the selected end-members (Fig. 6.4). These outliers were all from periods of very low flow, either before snowmelt or during very dry summer of 2009. Observations of Ec and a_{254} in catchment P1 primarily fell along the boundary between the *Pr* and *O-h* end-members in the mixing diagram (Fig. 6.4), which provides the justification for only using a two end-member mixing model for catchment P1 with a_{254} as the sole tracer. The P1 samples that diverge from the *O-h – Pr* boundary were mainly samples from early snowmelt that were also characterized by much higher ion concentrations (primarily Na^+ and Cl^-) than during the remainder of the frost-free season (data not shown).

In both A5 and B2, f_{Gw} was lowest during snowmelt and exhibited decreased importance during storm events (Fig. 6.2 and 6.3). However, the R_{Gw}/P ratio (i.e. the *Gw* end-member runoff ratio) varied both between catchments and years of the study, with higher ratios in catchment B2 and in 2008 (Table 6.3). Catchments A5 and B2 also had similar seasonal pattern for f_{Pr} which mirrored the pattern of f_{Gw}, with the greatest contribution during late snowmelt ($f_{Pr} > 0.6$) followed by decreasing importance over the summer (Fig. 6.2 and 6.3). The R_{Pr}/P ratio was stable between 0.27 and 0.35 for both between catchments and years (Table 6.3). Catchment A5 had higher $f_{O\text{-}h}$ than catchment B2 throughout the study, especially during summers (Fig. 6.2 and 6.3). This led both to higher total $R_{O\text{-}h}$ contribution to streamflow and $R_{O\text{-}h}$/P ratios in catchment A5 compared to B2 (Table 6.3), but the difference was just below significance (e.g. the $R_{O\text{-}h}$/P ratio of 2008 and 2009 was 0.09 ±0.03 for A5 and 0.07 ±0.02 for B2, further compared to 0.13 ±0.05 for the P1 palsa catchment).

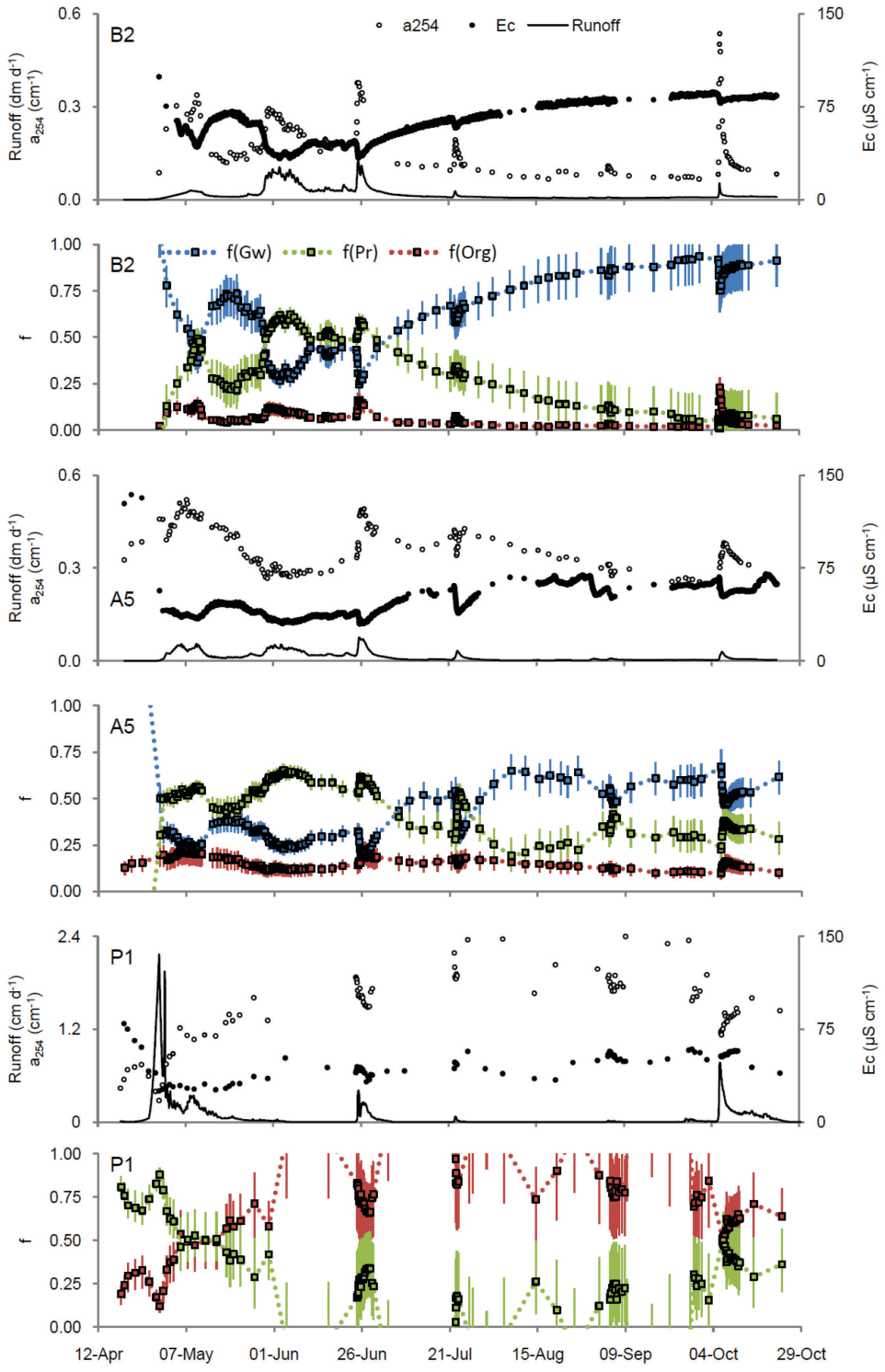

Figure 6.2. Hydrographs, observed tracer concentrations (a_{254} and Ec) used in mixing model and mixing model derived fractional contributions of identified end-members to streamflow in 2009. Data shown for three catchments; B2 (no peatland in catchment), A5 (7.8% peatland in catchment) and P1 (100% palsa peatland in catchment). The uncertainty of the estimates for fractional contributions is indicated by whiskers (see methods). Note the altered vertical scale used for the P1 catchment.

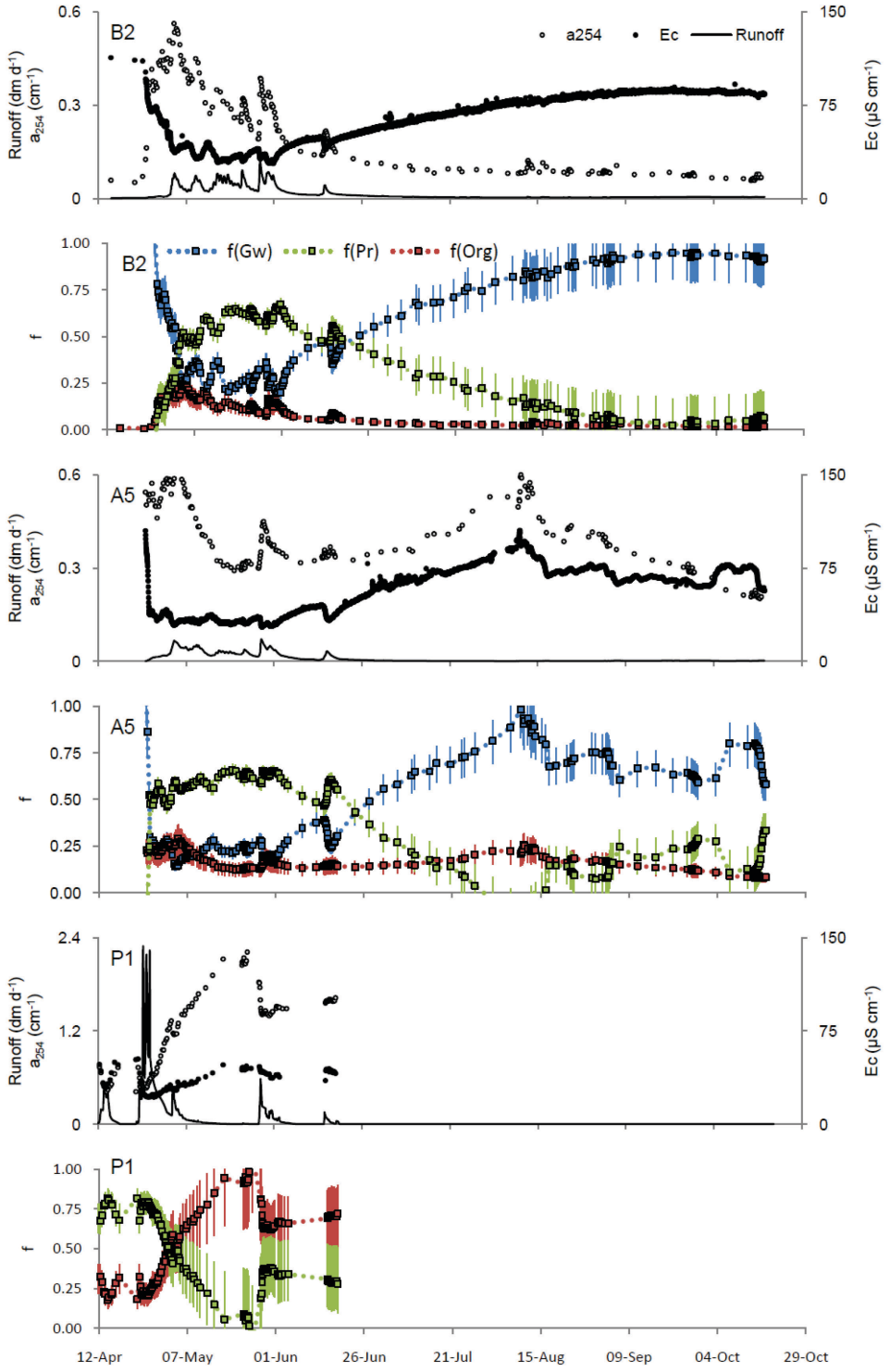

Figure 6.3. Hydrographs, observed tracer concentrations (a_{254} and Ec) used in mixing model and mixing model derived fractional contributions of identified end-members to streamflow in 2009. Data shown for three catchments; B2 (no peatland in catchment), A5 (7.8% peatland in catchment) and P1 (100% palsa peatland in catchment). The

uncertainty of the estimates for fractional contributions is indicated by whiskers (see methods). Note the altered vertical scale used for the P1 catchment.

The response of $f_{O\text{-}h}$ to runoff varied between catchments (Fig. 6.4), with generally high $f_{O\text{-}h}$ estimated during periods with high runoff for catchment B2, while catchment P1 had the opposite pattern and catchment A5 had no apparent relationship. For catchment B2 there were two periods during the study when estimated $f_{O\text{-}h}$ was greater than expected from an otherwise strong relationship between runoff and $f_{O\text{-}h}$; early snowmelt during both years and during the storm event that started on the 5th of October in 2008. Conversely, it was found for catchment P1 that early snowmelt had a lower $f_{O\text{-}h}$ than would be expected from the general relationship between $f_{O\text{-}h}$ and runoff.

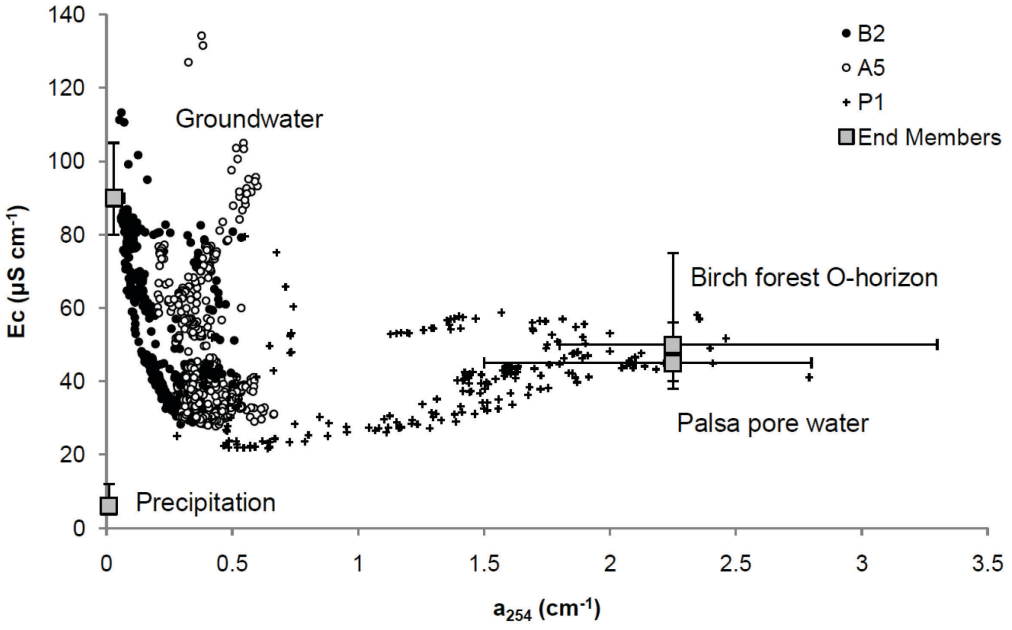

Figure 6.4. Mixing diagram of samples taken at the outflow of the three catchments (A5, B2 and P1), using Ec and a_{254} as conservative tracers. Squares represent median end-member measurements with error bars representing the 1st and 3rd quartile measurements.

Table 6.4. Measured runoff and DOC export, with estimated partitioning from the end-member analysis. The range of uncertainty follows in parentheses, see text for method. Second parenthesis under runoff estimates indicate the runoff ratios of each end-member, while the second parenthesis under DOC export estimates indicate the fractional contribution of each end-member to total DOC export.

	A5 Runoff (mm)	B2 Runoff (mm)	A5 DOC Export (g m^{-2})	B2 DOC Export (g m^{-2})
2008				
Total	222 (0.62)	315 (0.84)	2.62	2.60
Groundwater (*Gw*)	73 (58-89) (0.20)	162 (135-188) (0.43)	0.37 (0.23-0.62) (14%)	0.81 (0.54-1.31) (31%)
Precipitation (*Pr*)	115 (109-121) (0.32)	128 (111-149) (0.34)	0.11 (0.05-0.23) (4%)	0.13 (0.06-0.28) (5%)
Organic (*O-h*)	34 (24-44) (0.10)	25 (17-31) (0.07)	*2.15 (1.77-2.33) (82%)*[a]	*1.66 (1.00-2.00) (64%)*[a]
2009				
Total	159 (0.49)	248 (0.71)	2.30	2.65
Groundwater (*Gw*)	43 (34-55) (0.13)	102 (84-119) (0.30)	0.22 (0.14-0.39) (10%)	0.51 (0.34-0.83) (20%)
Precipitation (*Pr*)	87 (84-89) (0.27)	118 (110-130) (0.35)	0.09 (0.04-0.17) (4%)	0.11 (0.06-0.25) (4%)
Organic (*O-h*)	28 (19-35) (0.09)	27 (18-34) (0.08)	*1.99 (1.75-2.12) (87%)*[a]	*2.03 (1.57-2.26) (77%)*[a]

[a]The *O-h* end-member DOC export was calculated as a residual, see text for details.

The contribution of *Gw* and *Pr* end-members to annual catchment DOC export can be estimated through multiplication of respective end-member annual runoff and median DOC concentration (Table 6.3). The uncertainty of end-member DOC exports were estimated by using the uncertainty of end-member runoff (see text above) and the 1st and 3rd quartile of end-member DOC concentration (Table 6.2). For catchment B2 it was found that together *Gw* and *Pr* were responsible for 30% of the total DOC export, while they were responsible for 16% in catchment A5 (Table 6.3). Because the estimated *O-h* end-member runoff is assumed to include an unknown runoff contribution from the *Pp* end-member, this causes the *O-h* end-member DOC concentration to be unknown. Hence we estimate the *O-h* end-member DOC export as the residual DOC export after removing the *Pr* and *Gw* contribution from the total DOC export (Table 6.3). The uncertainty of the *O-h* DOC export estimate is achieved by using the lowest and highest DOC export contributions from the *Pp* and *Gw* end-members. A test of this approach is done by comparing the measured *O-h* and *Pp* end-member DOC concentration (Table

6.2) and inferred *O-h* concentrations derived from estimated *O-h* runoff and DOC export (Table 6.3). Using data from both 2008 and 2009, the average DOC concentration of the *O-h* end-member in catchment B2 was 72 mg l^{-1} (range of uncertainty 40-122 mg l^{-1}). This is identical to the measured *O-h* end-member median concentration, while the estimated DOC concentration of the *O-h* end-member for catchment A5 is 66 mg l^{-1} (range 44-104 mg l^{-1}), which is identical to the measured *Pp* median DOC concentration. While these estimates are not significantly different, they indicate a palsa influence for DOC export in catchment A5.

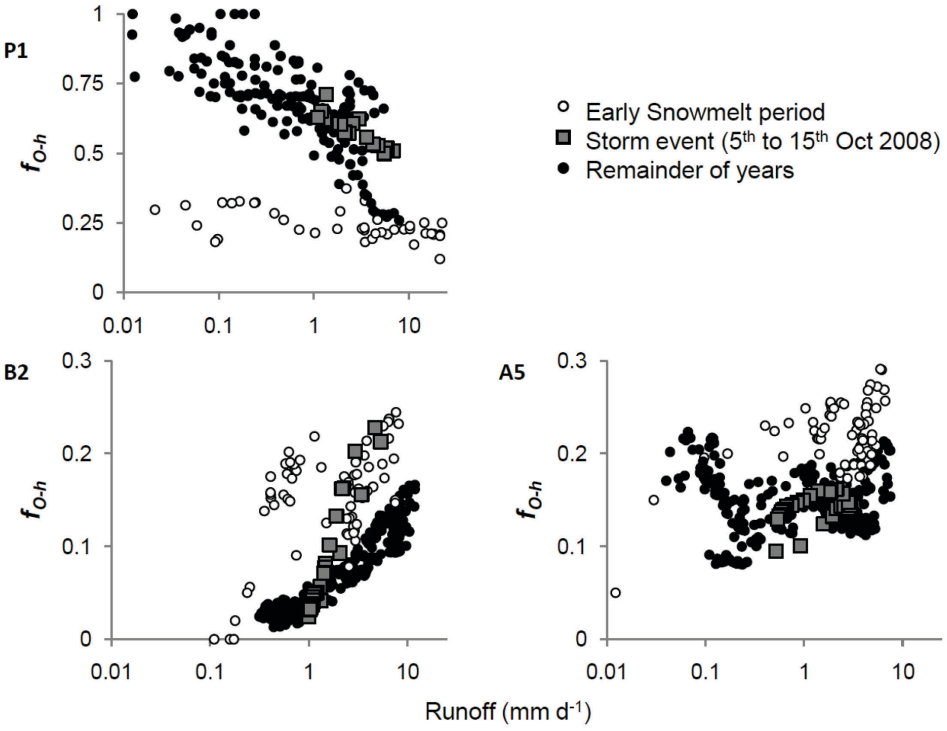

Figure 6.4. Plot of f_{O-h} and runoff for each of the three sampled catchments (P1: 100% peatland coverage, B2: 0% peatland coverage, A5: 7.8% peatland coverage). The plots combine measurements from both 2008 and 2009. Two periods of the study period have been highlighted – early snowmelt runoff and a large storm event (42 mm precipitation) which was sampled between the 5th and 15th of October in 2008. The end date of early snowmelt runoff was defined differently between the catchments. For catchment P1 it was defined by peak daily runoff during snowmelt, which occurred on the 2nd of May in 2008 and on the 28th of April in 2009. For catchments A5 and B2 the end of early snowmelt was defined a postperiori based on when B2 measurements diverged from the general relationship between f_{O-h} and runoff, which occurred on the 12th of May in 2008 and on the 16th of May in 2009.

6.4.4 SNOWMELT RUNOFF PERIOD

Over the two years of the study, the spring period from snowmelt initiation until the 20th of June was responsible for >55% of the total DOC export from catchments A5 and B2, and 75% of the P1 catchment export (Table 6.2). The importance of snowmelt runoff warrants a closer look at its patterns.

The timing of snowmelt runoff differed between the catchments in the study (Fig. 6.5). Catchment P1 had the earliest snowmelt runoff period, with nearly all snowmelt runoff occurring before snowmelt runoff started in catchments A5 and B2. The palsas are located at low elevations in Stordalen catchment and they are exposed which leads to a thin snow cover by the end of winter. Snowmelt from catchment B2 is slightly delayed in comparison to catchment A5, probably due to differences in aspect between the two catchments, with the slope of B2 facing northwards and A5 sloping westwards.

In order to assess the contribution of palsa runoff for total runoff from catchment A5, we scaled the measured runoff from palsa catchment P1 to apply to the palsa runoff in catchment A5 assuming all else being equal (palsas cover 3.9% of catchment A5) (scaling of P1 runoff used in Fig. 6.5, and also in Fig. 6.6). The scaled runoff demonstrates the palsas contributed significantly to catchment A5 runoff only during the first few days of snowmelt runoff.

While both catchment A5 and B2 exhibited seasonally high $f_{O\text{-}h}$ during the early snowmelt runoff period (Fig. 6.4), there was an additional trend in both years where $f_{O\text{-}h}$ was higher in catchment A5 than in B2 during early snowmelt runoff but the $f_{O\text{-}h}$ estimates for the two catchments converged to a similar fraction during the later stage of snowmelt runoff (Fig. 6.5). This A5 and B2 convergence also occurs in the DOC composition over the snowmelt runoff period (both for $SUVA_{254}$ and a_{250}/a_{365}), where the DOC composition in runoff from catchment A5 during early snowmelt was more similar to that of the palsa P1 catchment (Fig. 6.5).

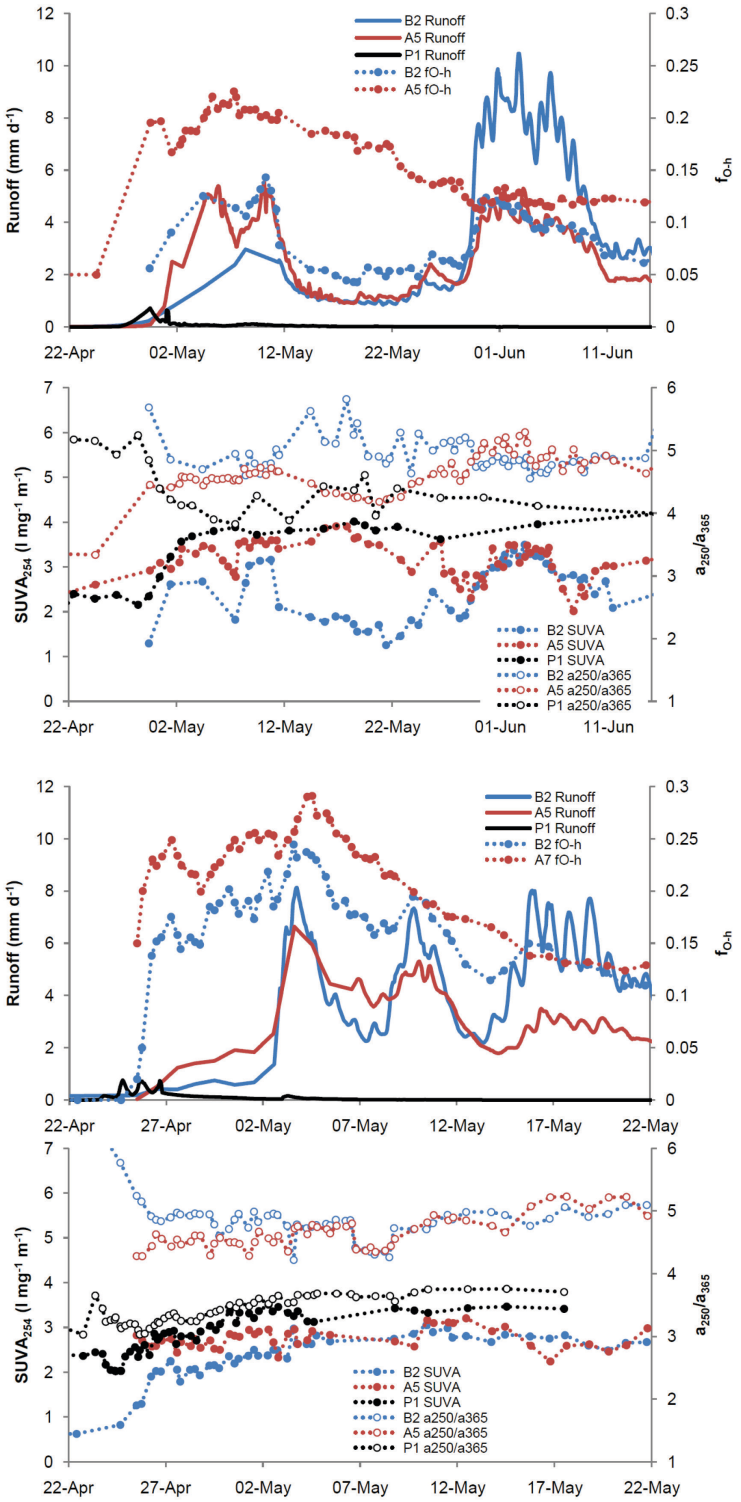

Figure 6.5. Snowmelt period of 2008 (top 2 graphs) and 2009 (bottom 2 graphs), showing runoff, $f_{O\text{-}h}$, $SUVA_{254}$ and a_{250}/a_{365}. Runoff from the P1 catchment scaled to represent the runoff of palsas present in catchment A5, in order to evaluate the possible influence of palsa runoff to catchment patterns.

6.4.5 STORM EVENTS

There were only seven storm events outside the snowmelt runoff period of 2008 and 2009 that caused more than minimal increase in runoff from catchments A5 and B2 (Fig. 6.2. and 6.3), and these were all sampled at high frequency (Fig. 6.6). The storm event precipitation for included storm events ranged between 9 and 42 mm, indicating that at least ~10 mm of daily precipitation was needed for a hydrological response. Conversely there was only one period during the study period when the daily precipitation exceeded 10 mm but did not yield significantly increased runoff – an event which occurred after a long drought period on the 11th of August in 2009. Total precipitation associated with the seven sampled storm events was 174 mm, representing 28% of the total precipitation for the two years, or ~60% of the total rain fall (i.e. removing frost season snow fall).

We defined the start of individual storm events as when runoff started to increase following or during precipitation associated with the storm events, and the end of the storm event was defined as the point in time when catchment runoff returned to the pre-event rate (or came within 5% of the runoff for events when runoff did not fully return to pre-event rates). The total duration of the storm events, as defined above, represented 15% of the two years and were responsible for 25, 18 and 21% of annual runoff for catchments B2, A5 and P1 respectively, along with 24, 23 and 33% of their respective annual DOC exports.

Because the mixing model *O-h* end-member is responsible for the majority of catchment DOC export due to its higher DOC concentration (whether dominated by *O-h* or *Pp* water), we studied the patterns of estimated *O-h* end-member runoff during storm events and compared it among the three catchments. Cumulative *O-h* end-member runoff for individual storm events ($\sum R_{O\text{-}h}$, measured in mm), was only significantly correlated with storm event total precipitation ($\sum$P) for catchment P1 (r^2=0.71, p<0.05). The P1 catchment *O-h* end-member storm event runoff ratio ($\sum R_{O\text{-}h}$ / $\sum$P) also increased during events with greater total precipitation, with *O-h* runoff ratios <0.1 for events with <~25 mm (n=4) P and runoff ratios between 0.15 and 0.35 for events with >~25 mm P – indicating that

the importance of individual storm events for palsa DOC export is exponential with regards to storm event total precipitation.

Neither event rain amount nor antecedent runoff (a surrogate for antecedent catchment moisture conditions) could on their own explain the cumulative storm event *O-h* end-member runoff for catchments A5 and B2 (all $r^2<0.4$ and $p>0.05$). However, a compound variable of the product of runoff at the start of the storm event and total event precipitation was found to positively correlate with storm event $\sum R_{O\text{-}h}$ for both catchment A5 and B2 ($r^2>0.79$, $p<0.05$). While the controls of event $\sum R_{O\text{-}h}$ thus appear similar for catchments A5 and B2, the $\sum R_{O\text{-}h}$ relative to antecedent moisture conditions was different (Fig. 6.7). This relationship shows how A5 has greater total $\sum R_{O\text{-}h}$ than catchment B2 when the storm event is preceded by dry conditions, but how wet antecedent conditions results in equal total storm event $\sum R_{O\text{-}h}$. The only storm event that the B2 $R_{O\text{-}h}$ was greater than the A5 $\sum R_{O\text{-}h}$ was the storm event that started on the 22nd of May in 2009, i.e. when snowmelt was still occurring in B2 but was ending in catchment A5 and thus not suitable for this comparison of storm event response.

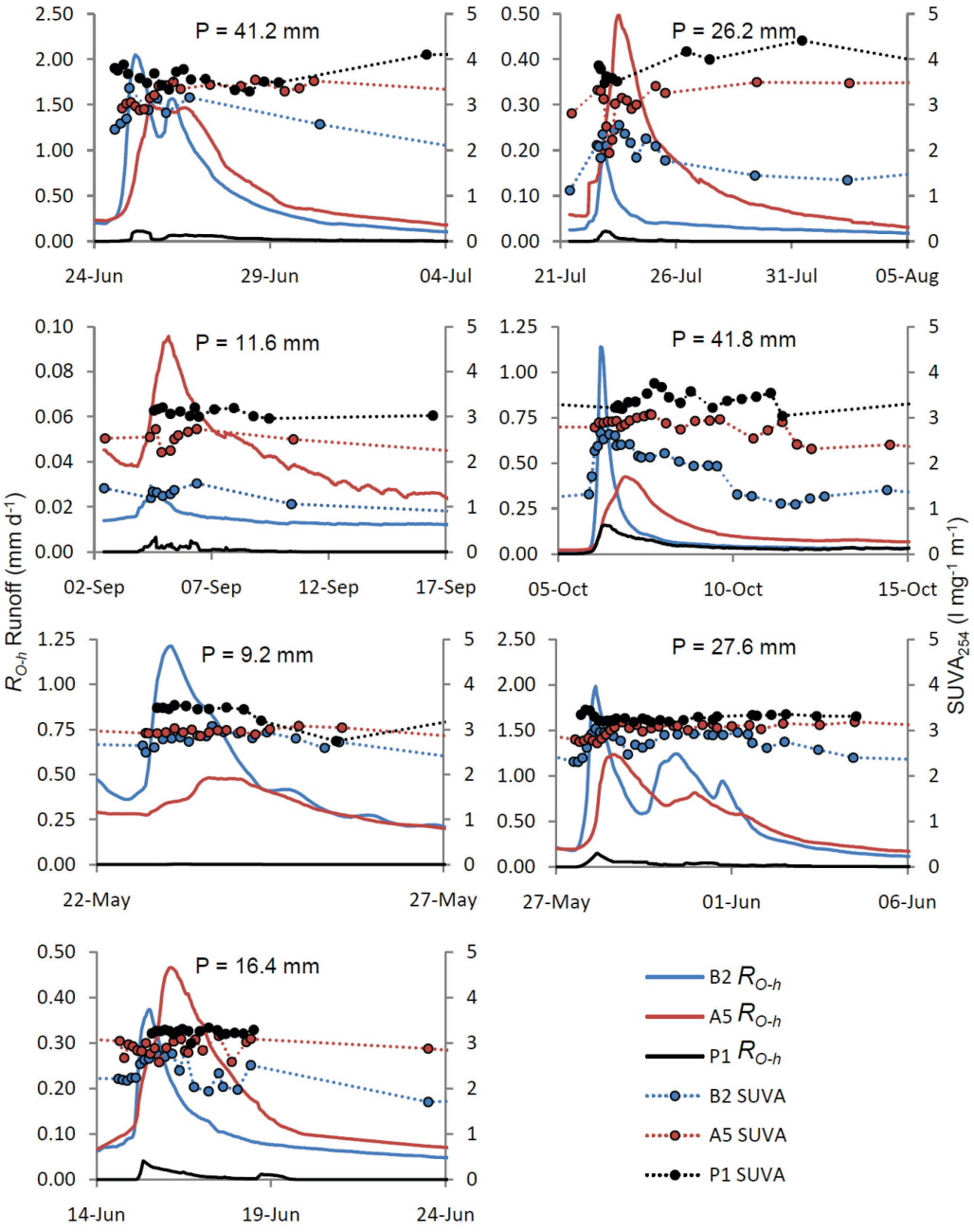

Figure 6.6. Estimates of storm event $R_{O\text{-}h}$ from catchment A5, B2 and P1 along with the measured $SUVA_{254}$ from each site. Top four events occurred in 2008, while the lower three occurred in 2009. Note the different scales for runoff for each storm event, and the differences in storm event duration (each tick represents 5 days). Total storm event precipitation indicated at the top of each graph. The P1 catchment $R_{O\text{-}h}$ is scaled to represent the runoff from palsas within the A5 catchment.

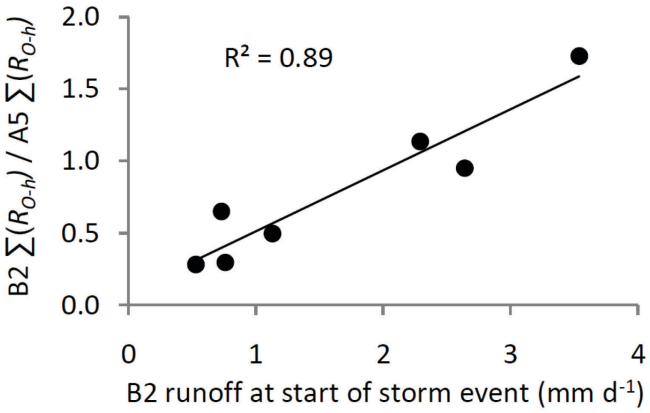

Figure 6.7. Relationship between the ratio of cumulative storm event $R_{O\text{-}h}$ runoff from catchment B2 and A5 and the B2 runoff at the start of each storm event, used as an indicator of antecedent moisture condition.

DOC composition of runoff from catchment P1 remained at high $SUVA_{254}$ (between 3 and 4 l mg^{-1} C m^{-1}) throughout all storm events, suggesting a single source of DOC in palsas during summers, regardless of hydrological conditions (Fig. 6.6). In contrast, $SUVA_{254}$ of samples from the B2 catchment outflow was positively correlated with runoff (r^2=0.78, p<0.001), with $SUVA_{254}$ values ranging between 0.5 and 3 l mg^{-1} C m^{-1} – i.e at all times lower than observed in the P1 catchment. The shift in DOC composition with changes in runoff is explained by the mixing model through increased $f_{O\text{-}h,}$ (delivering DOC with high $SUVA_{254}$, see table 6.2) and decreased f_{Gw} (delivering DOC with low $SUVA_{254}$) during periods of high runoff (Fig. 6.2 and 6.3). Lastly, $SUVA_{254}$ measured at catchment A5 outflow was intermediate between B2 and P1 for most of the time during the storm events. In several storm events there was a trend of A5 $SUVA_{254}$ measurement to approach values similar to B2 during early stages of storm events, indicating that the DOC export is less influence by *Pp* water during this period, followed by a trend of generally converging with the P1 catchment during the later stages of the events. However, the $R_{O\text{-}h}$ pattern from catchment P1 shows that the palsas are unlikely to contribute significantly to A5 $R_{O\text{-}h}$ during the later stages of storm events. In order to better explain the patterns of DOC composition and $R_{O\text{-}h}$ in catchment A5 during storm events it is necessary to assume contribution of *O-h* water from an additional source which must not be present in the B2

catchment – and an influence of the fens provides the simplest explanation, as will be discussed below.

6.4.6 MIXING MODEL PROJECTIONS OF STREAM SOLUTE CONCENTRATIONS

The fractional contribution of different end-members along with end-member characterization can be used to estimate stream chemistry of solutes not used in the development of the mixing model. A good fit between estimated and observed stream chemistry of conservative solutes can provide additional confidence in the mixing model, while a poor fit can demonstrate when the model has less explanatory power. Further, discrepancies between estimated and observed stream chemistry for solutes that are not conservative at times when the model works for conservative solutes can lead to inductive hypotheses of the processes that are of importance for catchment behavior but not taken into consideration by the mixing model.

The three end-member mixing model, using *O-h*, *Pr* and *Gw*, was able to estimate concentrations of several solutes very well for the B2 catchment, including Ca^{2+} (Fig. 6.8), Na^{+}, Mg^{2+}, SO_4^{2-} (Fig. 6.9) and DOC concentrations (Fig. 6.10). Data for Na^{+} and Mg^{2+} are not shown, but their trends are similar to Ca^{2+}. For all these ions there was an offset between estimated and observed concentrations in 2008, but not in 2009, possibly due to instrument calibration. Even after accounting for the offset, concentrations were over-estimated during the late autumn storm event starting on the 5th of Oct in 2008. The mixing model was also able to reproduce the seasonal pattern of DOC composition for B2, as measured by a_{250}/a_{365} (with low values during periods of high runoff and high values during low flow periods, see Fig. 6.11) – but not reproduce the observed values. However, a 1:1 match of estimated and observed a_{250}/a_{365} should not be expected since a_{250}/a_{365} should not mix conservatively as it is exponentially related to the average molecular weight. The mixing model was not able to estimate K^{+} and Cl^{-} very well for either catchment B2 or A5 ($r^2<0.35$ for correlations between projected and observed concentrations), while only trace concentrations of NH_4^{+}, Br^{-}, NO_3^{-}, and PO_4^{3-} were observed and they are not evaluated.

The ability of the mixing model to accurately estimate stream solute concentrations for catchment A5 was somewhat different than for catchment B2. The mixing model still was able to accurately estimate Ca^{2+} (Fig. 6.8), Mg^{2+} and Na^{+}, including the 2008 offset noted in B2. However, for catchment A5 SO_4^{2-} does not behave conservatively: there is a large mismatch between observed and mixing model estimated concentrations, particularly during summer (Fig. 6.9). The mixing model was able to reproduce the DOC concentration pattern for catchment A5, but not as well as for the B2 catchment, primarily due to the mixing model consistently overestimates the DOC concentrations during summer low flow periods (Fig. 6.10). Further, the mixing model was not able to reproduce the seasonal pattern of observed a_{250}/a_{365} for catchment A5, with observed a_{250}/a_{365} value falling outside the mixing space defined by the end-members (i.e. <4.0, Table 6.1) and a having relationship with catchment runoff that is opposite to that observed in catchment B2 (Fig. 6.11).

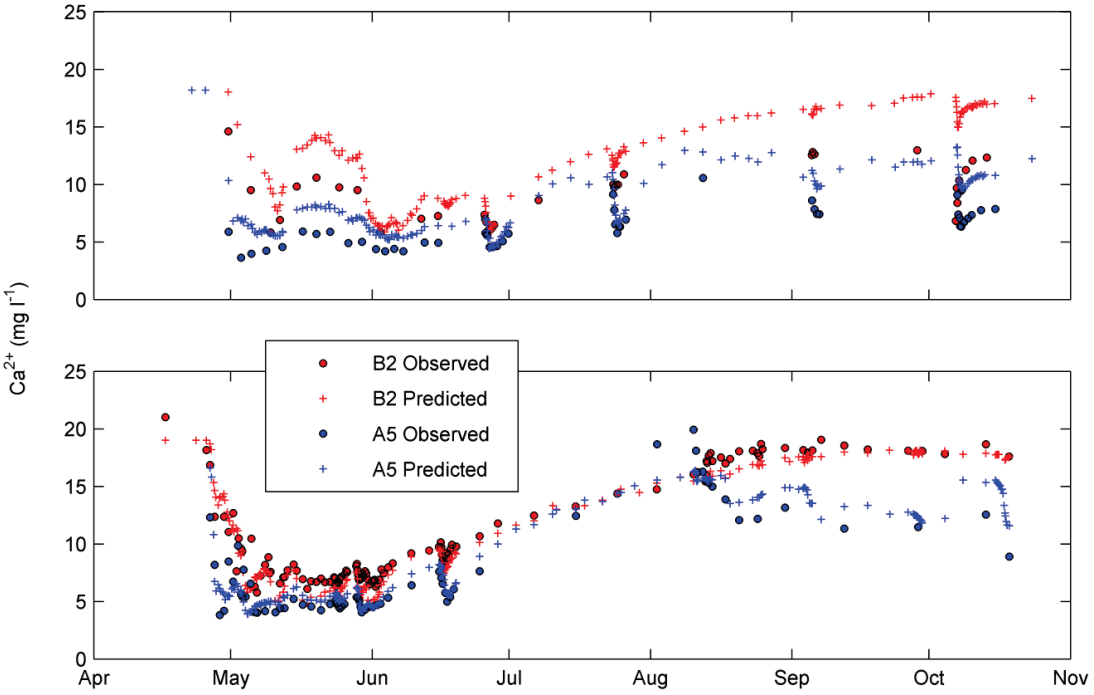

Figure 6.8. Observed and projected Ca^{2+} concentrations by the mixing model. Upper figure is data from 2008, and lower is from 2009.

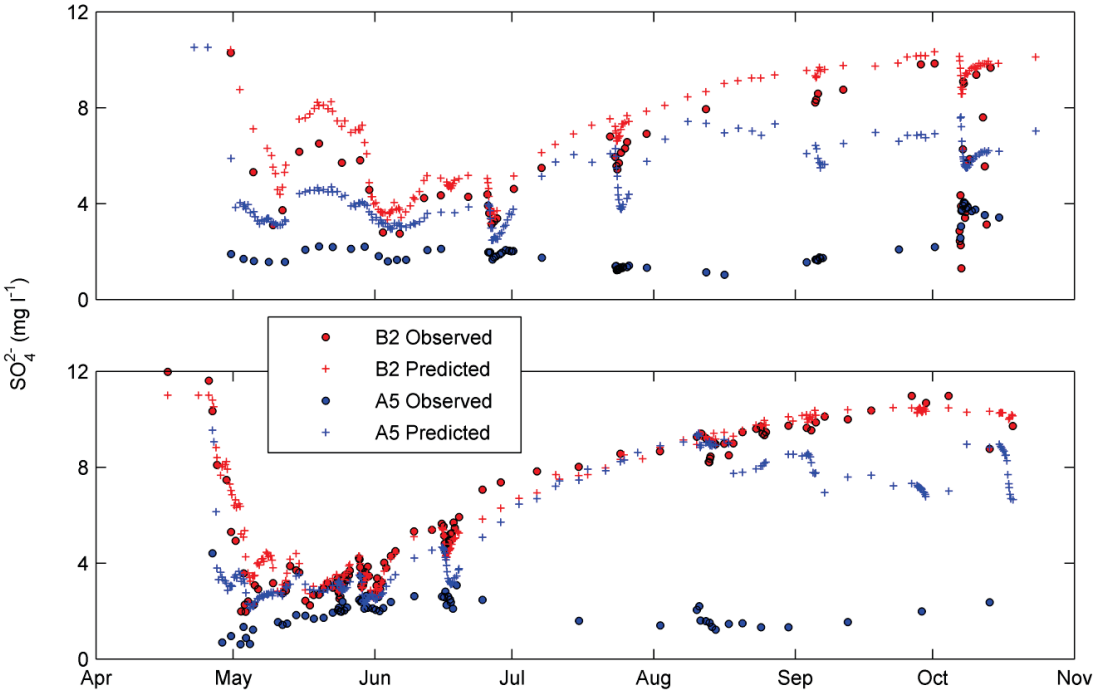

Figure 6.9. Observed and projected SO_4^{2-} concentrations by the mixing model. Upper figure is data from 2008, and lower is from 2009.

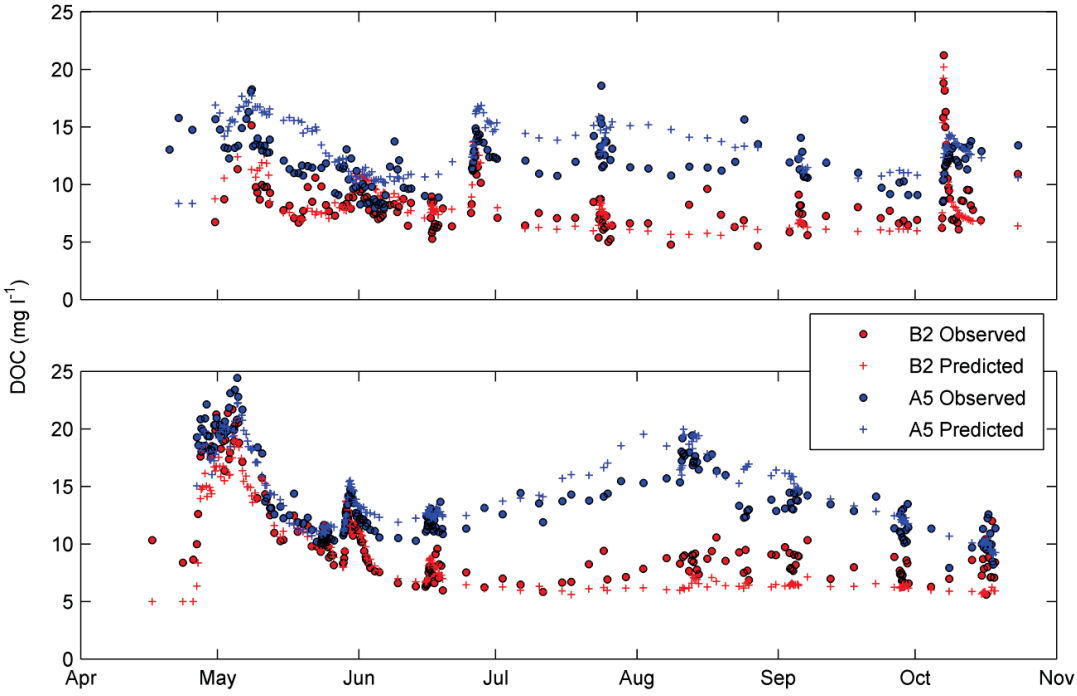

Figure 6.10. Observed and projected DOC concentrations by the mixing model. Upper figure is data from 2008, and lower is from 2009.

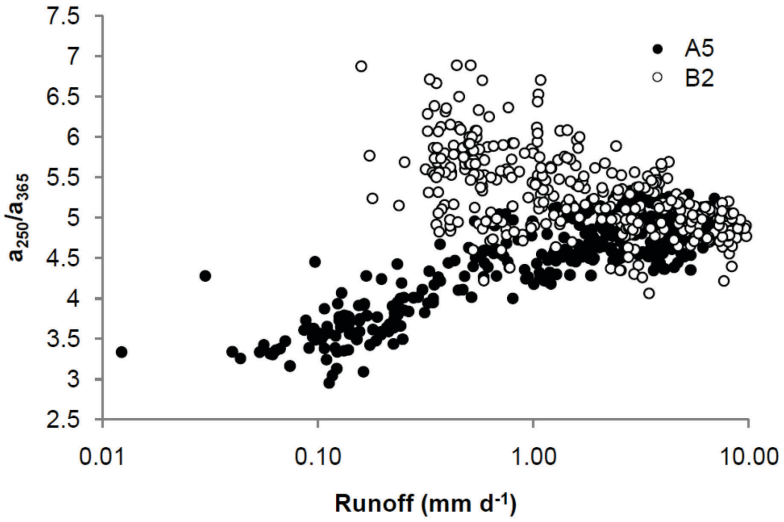

Figure 6.11. Relationship between catchment runoff rate and a_{250}/a_{365} for catchments A5 and B2.

6.5 Discussion

The purpose of this study was to separate the influence of different DOC source on the patterns of DOC quantity and composition at the catchment outflows. This discussion will focus on the influence exerted by forested areas, palsas, fens and also DOC that reaches streams through groundwater sources. The results enable the generation of hypotheses that predict the possible impacts on catchment DOC transport from continued permafrost thaw and associated conversion of palsas into fens.

6.5.1 Groundwater influence on catchment DOC transport

Our results indicated that the influence of groundwater differed between catchments A5 and B2. The hydrograph separation showed that the greater runoff from catchment B2 in comparison to A5 (182 mm greater over two years) was primarily due to greater groundwater runoff (148 mm greater for same period). An increased groundwater influence in catchment B2 is likely the result of differences in catchment geomorphology, with catchment B2 having a more concavity that contain rock debris – i.e. greater potential for groundwater storage. The outflows of the catchments are located below the break in topography between the uplands

and lowlands so the physical setting exists for groundwater emergence (Winter, 1999). Given the geology and morphology of the catchments, and the seasonal variations in flow, the groundwater influence is likely due influence of local groundwater flow, but could also be due in part to regional groundwater flow, i.e. groundwater that is derived from outside the topographic catchment (Toth, 1963b).

The groundwater end-member was characterized by stream samples taken both prior to snowmelt and during the driest periods of the 2009 summer drought. While estimated to represent between 30 and 50% of the total runoff for catchments B2 and A5, low DOC concentration of the groundwater end-member led groundwater sources to contribute an estimated 10 to 30% of the annual catchment DOC export. However, DOC from groundwater sources dominates the DOC pool in the non-peatland catchment B2 for lengthy periods during summer low flow conditions. This has been observed previously in several studies of northern forested catchments (Carey and Quinton, 2005; Hinton et al., 1994). Dominance of DOC from groundwater sources during summers was associated with low aromaticity and low average molecular weight of the DOC pool in this study, indicated by $SUVA_{254}$ and a_{250}/a_{365}, a pattern that also has been observed previously in other catchments (Hood et al., 2006; Spencer et al., 2008). Despite its low aromaticity, DOC exported from large arctic rivers during summers is a poor substrate for microbial degradation (Holmes et al., 2008). Because arctic river DOC exports have often been estimated using summer samples, this has led to poor estimates of annual DOC export rates and its composition since the groundwater dominance during summers is not a representative of the annual average DOC concentration or composition (Finlay et al., 2006; Spencer et al., 2009).

6.5.2 Birch forest influence on catchment DOC export

In the Stordalen catchments the dominant vegetation cover is an open canopy mountain birch forest with a thick ground layer of woody shrubs. For catchment B2 that contains no peatlands, runoff from the shallow forest soil (*O-h* water)

contributed only 8 to 11% of the total runoff, but this runoff contributed between 64 and 77% of the total catchment's DOC export. There were strong positive relationships between runoff and $f_{O\text{-}h}$, DOC concentration, DOC aromaticity ($SUVA_{254}$) and average molecular weight (a_{250}/a_{365}) for catchment B2. Increased DOC concentrations during snowmelt (Buffam et al., 2007) and storm events (Petrone et al., 2007) have been found for several other forested boreal and subarctic catchments, and have also been linked to increased aromaticity (van Verseveld et al., 2008). The B2 catchment relationship between $f_{O\text{-}h}$ and runoff in this study for catchment B2 suggests that increased moisture storage in the catchment is associated with a greater supply of *O-h* water to the stream. The variable source area concept, where only saturated areas contribute runoff – e.g. primarily riparian soils during low to moderate catchment moisture levels, has been used to explain the increased importance of shallow forest soil water with increased runoff (Inamdar and Mitchell, 2007). In our study there was a linear relationship between $f_{O\text{-}h}$ and runoff for catchment B2, which would be consistent with the variable source area concept, although early snowmelt and a large autumn storm event had higher $f_{O\text{-}h}$ than expected based on the B2 general relationship. Several processes could explain this pattern, including surface frost that promotes hydrological conductivity of shallow soils, reduced influence of *Gw* water during early snowmelt due to limited groundwater recharge during the preceding winter and/or altered characterization of the *O-h* end-member during this period compared to later in the season (no samples of the *O-h* end-member were taken during the early snowmelt period), but we have no evidence that can be used to discriminate among these hypotheses.

The storm events that occurred during the study period were responsible for 24% of the total DOC export for catchment B2. Thus the storm event export in the Stordalen catchments is small proportion of total export observed in other studies (Buffam et al., 2001; Hinton et al., 1997; Inamdar et al., 2006). This is primarily due to the small number of storm events that led to a hydrological response during the study period (seven storm events over two years). While the storm events in catchment B2 led to elevated DOC concentrations, the storm events did not

contribute disproportionally to the DOC export in relation to the runoff contribution of storm events (25% of annual runoff) – due to the large influence of high DOC export during snowmelt.

The strong influence of runoff for $f_{O\text{-}h}$, DOC concentrations and DOC composition in catchment B2 was not as clearly observed in catchment A5, and some relationships were even reversed as in the case of the relationship between runoff and a_{250}/a_{365} - despite catchment A5 only containing ~7% peatland cover, evenly partitioned between palsa and fen type peatlands. While some of the differences between catchment A5 and B2 can be explained by their differences in groundwater importance, several differences needs to further take into account the influence of the peatlands.

6.5.3 PALSA INFLUENCE ON CATCHMENT DOC TRANSPORT

The permafrost peatlands in Stordalen, palsas, are exclusively rain-fed and thus act as small headwater catchments. Only two end-members (*O-h* and *Pr* water) were needed to reproduce the observed DOC concentration patterns at the P1 palsa catchment outflow. In contrast to the B2 catchment, the palsa catchment $f_{O\text{-}h}$ and DOC concentrations were found to decrease during periods of higher runoff – a pattern that has been observed from other peatland catchments and it is attributed to dilution (Buffam et al., 2007), consistent with the increased importance in our study by f_{Pr} during periods of high runoff. The two end-member mixing model was not able to reproduce the observed ion concentration of the P1 catchment, primarily due to measurements of a_{254} and Ec during early snowmelt that could not be a mix of the two end-members included in the model for catchment P1. The early snowmelt period was further characterized by lower $f_{O\text{-}h}$ estimates than expected from the seasonal relationship between $f_{O\text{-}h}$ and runoff, by high Cl^- and Na^+ concentrations and by lower DOC aromaticity than for the remainder of the season (Chapter 3). These results indicate that a third, un-sampled end-member, associated with runoff generation during early snowmelt and having flow paths on or near the peat surface would be useful to explain the observed solute concentrations and DOC composition from the palsas.

The total DOC export from the palsa was found to be only 25% greater per unit area than the DOC export from the non-peatland B2 catchment (6.32 vs. 5.06 g C m^{-2} over two years). The average DOC concentration was ~2.5 higher from the P1 catchment than the B1, therefore the similar export rates arises because of differences in the amount of runoff in the two catchments, the palsas have a relatively low R/P ratio (~0.4 over two years). Assuming that the palsas in catchment A5 behave the same as the monitored P1 catchment, then the palsa contribution (covering 3.9% of the A5 catchment) to the total *O-h* runoff (62 mm over two years) would be ~3 mm or only ~5%.

Despite the limited influence of the palsas for the total A5 catchment DOC export, the palsas do affect DOC transport patterns during snowmelt. During early snowmelt catchment A5 had higher $f_{O\text{-}h}$ than catchment B2 and had DOC aromaticity observations that were closer to those observed for catchment P1 than B2. Observations of $f_{O\text{-}h}$ and aromaticity for catchments A5 and B2 converged during the second half of snowmelt, when runoff from the palsa catchment P1 had ceased. While the presence of fens could be proposed to explain the difference between catchment A5 and B2 during snowmelt, the fens have lower DOC export during the early snowmelt as frozen conditions restrict water interaction with the peat matrix (Chapter 3). Thus if the fens were responsible for the difference between catchment A5 and B2 then we would expect divergence of observations as snowmelt progressed – not convergence.

The influence of the palsas on catchment DOC during early snowmelt emphasizes that DOC transport patterns at a catchment scale are dependent on the timing of snowmelt runoff and hydrological connectivity between different landscape units (Laudon et al., 2007; Pacific et al., 2010). However, catchment B2, with no peatlands, also exhibited a large influence of *O-h* water during snowmelt. Previous studies of forested catchments have also observed patterns of a large contribution of water derived from organic sources during early snowmelt (Ågren et al., 2008a; Carey, 2003; Finlay et al., 2006). This pattern of high DOC concentrations during early snowmelt has been explained by the flushing of a

finite DOC store in the near surface soils that built up over winter or alternatively by a deepening of flow paths that route late snowmelt runoff through mineral soils before reaching the stream during the later stages of snowmelt (McNamara et al., 1997). Thus our study shows that in order to explain the observed DOC export patterns and its composition at a catchment scale, it is necessary to take into account both the internal interactions within each landscape unit as well as the timing among landscape units.

6.5.4 Fen influence on catchment DOC transport

Often peatlands are treated as a single landscape unit when assessing peatland influence on catchment DOC export (Creed et al., 2008; Kortelainen et al., 2006). However, vegetation map analysis shows that different peatland types have differing relationships with measured DOC concentrations at their catchment outflows (Johnston et al., 2008). Few studies have tried to isolate the influence of fens in particular, even though fens have a greater influence on lake acidity than bogs due to their greater flow-through (Halsey et al., 1997b), and are catchment sites for nitrogen and phosphorus retention (Prepas et al., 2001). In our study there were several discrepancies between the DOC transport patterns in catchment A5 and B2 that cannot be explained by the influence of the palsas or due to groundwater differences – but likely linked to the influence of the fens.

Although the total DOC export from the non-peatland catchment B2 was greater than that of A5, this was due to a greater groundwater discharge from catchment B2. However, over the study catchment A5 *O-h* runoff that was ~10 mm higher than that for catchment B2, representing a ~20% increase. Similarly the DOC export associated with *O-h* runoff was ~10% greater from catchment A5 than B2. While acknowledging that the estimates of *O-h* runoff and DOC export associated with the *O-h* end-member for the two catchments were not significantly different, the palsas in catchment A5 (covering 3.9%) cannot explain more than a small fraction (<10%) of the magnitude of the differences between A5 and B2 central estimates of *O-h* runoff and its associated DOC export. There were, however, certain times of the year when *O-h* runoff from catchment A5 was greater than

from B2, including a separation of their error bounds during early snowmelt, during the runoff recession following summer storm events and into the following low runoff periods. As discussed above, the additional *O-h* runoff from catchment A5 during snowmelt can be attributed to the palsas, but the palsas in catchment A5 contribute very little to the total *O-h* runoff during most storm events. We also found that the ratio between cumulative storm event *O-h* runoff between B2 and A5 depends on the runoff at the start of the storm event – indicating that there is a source of *O-h* water readily available for downstream transport in catchment A5 even during dry conditions. Based on these converging lines of evidence we hypothesize that these differences in *O-h* runoff and DOC export are due to the fens acting as DOC sources, and that their relative importance increases during summer low flow periods. We have studied two fens in Stordalen catchment, located outside the A5 and B2 catchment (Chapter 3). We found that these fens were large annual DOC sources at between 6 and 11 g C m^{-2}, and that more than half of this export occurred outside the snowmelt runoff period.

We also think our results indicate that the fens are catchment locations where DOC from upstream sources is substantially transformed and/or degraded. Firstly, DOC concentrations in catchment A5 during summer low flow periods are lower than estimated by the mixing model. While observations were within the margin of error, the pattern is consistent and contrasts with that of catchment B2 where the mixing model underestimated DOC concentrations. Because a_{254} is used as a tracer in the mixing model, an overestimation by the mixing model of DOC concentrations as for catchment A5 also implies that the mixing model estimates lower $SUVA_{254}$ (and thus lower DOC aromaticity) than observed. These discrepancies cannot be due to the palsas as they are hydrologically disconnected from the rest of the catchment for much of the summers. The difference could also have been explained by an addition of DOC produced within the fens, but then the aromaticity of DOC produced in the fens would need to be higher than that of the *O-h* end-member. However, DOC derived from fen soils in the catchment have a low $SUVA_{254}$ at 2.2 l mg^{-1} C m^{-1} (Roehm et al., 2009), meaning that including fen DOC in the mixing model would yield estimates that were yet further away from

the observed aromaticity. The observed patterns could however be explained by losses of non-aromatic DOC within the fens, e.g. through selective microbial degradation (Berggren et al., 2009a). Further indicating biological processes to be responsible for the mismatch between observed and estimated DOC concentrations is the fact that there seems to be a temperature dependence – with less mismatch during the autumn.

Additional support for transformation of DOC in the fens is in the patterns of DOC composition in A5. While a_{250}/a_{365} was found to act similar to a conservative tracer in B2, this was not true for catchment A5 where the observed values fell outside the mixing space provided by the end-members – particularly during low runoff periods. DOC with a lower molecular weight (higher a_{250}/a_{365} values) has been found to be more rapidly microbially degraded (Berggren et al., 2010; Marschner and Kalbitz, 2003), so it is possible that the observed drop in a_{250}/a_{365} values in A5 is due to selective degradation of DOC with low molecular weight within the fens. Further it was observed that measured $SUVA_{254}$ of catchments A5 and B2 diverged on the recession limb following summer storm events, with A5 values approaching those observed in the palsa catchment P1 – despite runoff from P1 contributing negligible to the total runoff. Patterns of DOC composition thus suggest that the fens acts to transform incoming DOC from upstream sources, yielding higher aromaticity and higher average molecular weight than can be explained by conservative mixing of DOC sources. Transformation and selective degradation of DOC in fens can explain how even catchments with a small fraction of fen (<5%), can exhibit DOC compositions indicating a total dominance of peatland DOC (Ågren et al., 2008b).

Sulfate was found to act conservatively in catchment B2, and the observed concentration patterns were well reproduced by the mixing model. In catchment A5 the mixing model was unable to reproduce the observed sulfate patterns, and we hypothesize that microbial sulfate reduction in the fens is the most plausible explanation for the discrepancy between the two catchments. Sulfate reduction is a reaction where organic matter is oxidized under anoxic conditions (Vile et al.,

2003), which occurs in peatlands. Using observed SO_4^{2-} concentrations to estimate the A5 catchment export in 2009 yielded an estimate of 0.29 g m^{-2} yr^{-1}, while using the projected SO_4^{2-} concentrations from the mixing model yielded 0.55 g m^{-2}. The difference between observed and estimated SO_4^{2-} export by the mixing model can be considered the net result of sulfate reduction in the fens. Stoichiometrically a mole of biologically reduced SO_4^{2-} yields two moles of CO_2, and it is thus possible to estimate that the fens in catchment A5 release 1.9 g CO_2-C m^{-2} yr^{-1} derived from sulfate reduction, equivalent to 2.9% of the A5 catchment total DOC export if the sulfate reduction is assumed to act upon DOC. No similar estimates were done for 2008 due to the offset in the match between observed and predicted SO_4^{2-} in catchment B2, but the general patterns were similar. Sulfate reduction is part of a succession of pathways for microbial degradation of organic C, starting with aerobic processes and then moving through reduction processes of nitrate, manganese, ferric iron, sulfate and on to methanogenesis that uses acetate or CO_2 as electron acceptors. Emissions of CH_4 from a fen in Stordalen catchment has been estimated at 25-30 g C m^{-2} yr^{-1} (Bäckstrand et al., 2008; Jackowicz-Korczynski et al., 2010), indicating that all electron acceptors for organic C oxidation other than those involved in methanogenesis are fully utilized. This shows that there are internal processes in the fens that link DOC with the atmospheric C exchange, and it can be hypothesized that these processes affect DOC transport to a greater degree during the summer low flow periods when water temperatures are high and water residence time within the fen are long.

While the lines of evidence are circumstantial, taken together they do strongly suggest that the fens act as strong catchment sources of DOC and that they degrade and transform DOC from upstream sources. We have proposed a number of hypotheses that could be tested in subsequent studies that could tentatively confirm or clearly reject the proposed role of fens for catchment DOC mass transport and composition.

6.6 CONCLUSIONS

This research shows that different peatland types affect catchment DOC transport patterns differently, both with respect to DOC quantity and composition. It is important to understand the different roles of peatlands for catchment DOC transport since permafrost thaw is expected to alter the relative abundance of peatland types, which in Stordalen catchments has led to a conversion of palsas into fens. The annual DOC export from the palsas was not much higher than from a non-peatland catchment, but its DOC export was concentrated to early snowmelt and was characterized by high aromaticity. The fens were found to be larger DOC sources, but also indicated as locations in the catchment where degradation and transformation of DOC from upstream sources occur - thus acting as regulators for the catchment DOC transport. This study shows that even a small catchment coverage of peatlands, and fens in particular, can significantly affect catchment DOC mass export and composition.

7. SUMMARY, CONCLUSIONS AND DIRECTIONS FOR FUTURE RESEARCH

In this thesis I have shown that different peatland types within the same peatland complex can have very different patterns of DOC mass export and composition. Permafrost thaw in subarctic peatlands alters the landscape makeup of peatland types within peatland complexes and thus the complex's DOC export, which in turn alters the catchment DOC export and composition to downstream aquatic ecosystems. My research in the Stordalen catchment (northern Sweden) provides examples of processes that need to be considered when assessing the impacts of peatland permafrost thaw on the waterborne C transport from northern catchments.

The DOC export from the palsa peatland was found to range between 2.8 and 3.6 g C m^{-2} yr^{-1}. This was a similar range of DOC export as from non-peatland sub-catchments in Stordalen: 2.5 to 4.1 g C m^{-2} yr^{-1}. The low runoff from the palsa constrained its DOC export, while peat pore water DOC concentrations were similar to that of other studied peatlands. Palsa DOC export occurred primarily during the early snowmelt period prior to when runoff commenced in the forested parts of the catchment. Significant DOC export from the palsas outside the snowmelt period only occurred following large storm events and only if the palsa's antecedent moisture condition was relatively wet. While the DOC composition of palsa runoff was of high aromaticity for most of the season, early snowmelt DOC had significantly lower aromaticity than the rest of the year. This indicates that there were two primary sources of DOC in the palsa, one associated with a shallow flow path through more recent litter and one associated with deeper flow paths through stored peat that dominated outside the snowmelt period. This conclusion was also supported by the results from the mixing model analysis.

The bog, which represents one of two possible end-states or a transitional peatland state between palsa and fen end-state following palsa surface permafrost thaw in Stordalen, is characterized by a higher water table and increased abundance of

Sphagnum mosses than found in the palsas but is still mainly rain-fed, receiving only lateral runoff from the surrounding palsas. The bog had a similar total DOC export as the palsa, but DOC composition was shifted towards lower aromaticity (although still higher than observed in streams draining non-peatland catchments). Because DOC leached from thawed palsa peat has a very high aromaticity, it is speculated that the compositional shift is due to changes in vegetation rather than greater hydrological interactions of the recently thawed peat.

The study of the NECB of the palsa and bog of Stordalen peatland complex showed the net balance was very similar to other non-permafrost peatlands, despite having a much lower gross ecosystem productivity. The permafrost restricts ecosystem respiration by confining decomposition to a relatively thin active layer. The DOC export from the palsa and bog are equivalent to 6% of the net ecosystem productivity, a much smaller proportion than found in other studied peatlands.

While fens can be assumed to have always been present in Stordalen regardless of permafrost conditions because they convey runoff from much larger upstream catchments, they have expanded as increased permafrost thaw in the palsas has taken place. The fens in the Stordalen catchment are catchment hotspots for DOC export at between 6 and 11 g C m^{-2} yr^{-1}. The majority of this export occurred outside the snowmelt period as the frozen fen interacted very little with the water flowing through them during snowmelt. While no ^{14}C dating of DOC was performed in our studies, there were no indications in our data that suggest that the higher DOC export from the fens was a result of increased access to recently thawed palsa peat, rather it is hypothesized to be a result of an altered hydrological setting and associated changes in vegetation composition, nutrient availability and hence ecosystem productivity.

The DOC export pattern from a sub-catchment in Stordalen that did not contain any peatlands was reproduced well by a three end-member mixing model with the end-members being forest O-horizon water, groundwater and precipitation. DOC from the forest O-horizon dominated the DOC export, particularly during

snowmelt and large storm events, and was characterized by an aromaticity intermediate between the palsa DOC and groundwater DOC. Groundwater sources were responsible for up to 30% of the total DOC export (up to 0.8 g C m^{-2} yr^{-1}), and had a DOC composition that was characterized by very low aromaticity and average molecular weight – possibly a result of sorption processes in mineral soils. Groundwater sources were also associated with catchment DIC export that reached export rates of between 0.5 and 3.0 g C m^{-2} yr^{-1} – a substantial contribution to the total waterborne C transport that is a result of the Stordalen catchment having carbonate bedrock. Years with lower runoff led to both decreased DOC and DIC export, but DIC export decreased relatively more, indicating that the magnitude of groundwater discharge was more sensitive than runoff associated with shallower flow paths to inter-annual variations in precipitation magnitude.

Of the studied Stordalen sub-catchments all but one had a peatland cover of less than 8%, and differing groundwater contribution among the catchments had a greater impact on the total DOC export than amount of peatland coverage did. However, even a small amount of coverage by peatlands significantly altered the catchment DOC export patterns and particularly its DOC composition. Early snowmelt runoff from the palsas could be seen in the catchment scale runoff, causing increased DOC concentrations and aromaticity compared to the catchment without palsas. Contrastingly, in the summer the fens influenced the DOC concentrations and composition. The magnitude of the fen's influence was greater than expected from the magnitude of its net DOC export, and several inferential lines of evidence suggest that the fens are both sources and sites for loss and transformation of DOC from upstream sources. Fen can thus be thought of as regulators for catchment DOC export. This functional attribute of the fens was dependent on magnitude of the fen flow-through, indicating that the location of fens in the catchment is a significant factor for the catchment's DOC export and composition. Additional research is needed to test several of the hypotheses put forward on the role the fens play and to see if there are any links between fen DOC degradation/production/transformation processes and the atmospheric C

exchange of the fens, including both CO_2 and CH_4 balances. Such research could be done both along appropriate transects in the field, e.g. along a fen from inflow to outflow, or in a laboratory setting that provides a more controlled environment, e.g. through peat monolith experiments.

While DOC indices were useful in identifying different DOC sources, I believe the use of simple DOC composition indices such as $SUVA_{254}$, a_{250}/a_{365} or FI as indicators of DOC lability at the catchment scale is of somewhat limited utility. Processes such as mineral soil sorption, photodegradation and microbial degradation alters the composition of DOC from terrestrial sources as it moves to a catchment outflow, and these processes can affect composition and lability in different ways. This makes it hard to infer impacts of peatland permafrost thaw on C turnover in downstream aquatic environments based solely on the observed differences in DOC composition among peatland types. Further, an increased coverage of fen type peatlands can be hypothesized to alter both the fen capacity to transform and degrade DOC from upstream sources but also cause increased total peatland DOC export – and thus downstream aquatic ecosystems will experience both changes in quantity and composition of DOC. Changes in DOC export from northern peatlands is likely to have cascading effects on catchment C balances. The effects of altered DOC quantity and composition reaching northern aquatic ecosystem were beyond the scope of this thesis, but need to be considered when assessing the impact of climate change on the C balance of northern aquatic environments.

In the Stordalen catchment peatland permafrost thaw leads to the conversion of palsa to bog or fen with minor respectively significant changes to the peatland and catchment DOC export. In different geographical settings, other end-states following peatland permafrost thaw have been reported, e.g. collapse scars and thermokarst erosion along rivers, and these can be expected to produce different responses for the DOC export and composition. My research shows however that the greatest impact of permafrost thaw in peatlands on catchment DOC export can be expected when peatlands end up in a minerotrophic setting, both due to an

increase in DOC transport potential but also to the role of fens as catchment regulator for DOC export.

8. REFERENCES

Admiral, S.W., Lafleur, P.M., 2007. Partitioning of latent heat flux at a northern peatland. Aquat Bot, 86(2): 107-116.

Ågren, A., Buffam, I., Jansson, M., Laudon, H., 2007. Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. J Geophys Res-Biogeo, 112(G3): G03003.

Ågren, A., Berggren, M., Laudon, H., Jansson, M., 2008a. Terrestrial export of highly bioavailable carbon from small boreal catchments in spring floods. Freshwater Biol, 53(5): 964-972.

Ågren, A. et al., 2008b. Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer. J Geophys Res-Biogeo, 113(G3): G03031.

Åkerman, H.J., Johansson, M., 2008. Thawing permafrost and thicker active layers in sub-arctic Sweden. Permafrost Periglac, 19(3): 279-292.

Algesten, G. et al., 2004. Role of lakes for organic carbon cycling in the boreal zone. Global Change Biology, 10(1): 141-147.

Andersson, N.Å., Callaghan, T.V., Karlsson, P.S., 1996. The Abisko Scientific Research Station. Ecological Bulletins(45): 11-5.

Anesio, A.M., Graneli, W., 2003. Increased photoreactivity of DOC by acidification: Implications for the carbon cycle in humic lakes. Limnol Oceanogr, 48(2): 735-744.

Bäckstrand, K., Crill, P.M., Mastepanov, M., Christensen, T.R., Bastviken, D., 2008. Total hydrocarbon flux dynamics at a subarctic mire in northern Sweden. J Geophys Res-Biogeo, 113(G3): G03026.

Bäckstrand, K. et al., 2010. Annual carbon gas budget for a subarctic peatland, Northern Sweden. Biogeosciences, 7(1): 95-108.

Balcarczyk, K.L., Jones, J.B., Jaffe, R., Maie, N., 2009. Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost. Biogeochemistry, 94(3): 255-270.

Ball, D.F., 1964. Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. Journal of Soil Science, 15(1): 84-92.

Barr, A.G. et al., 2004. Inter-annual variability in the leaf area index of a boreal aspen-hazelnut forest in relation to net ecosystem production. Agr Forest Meteorol, 126(3-4): 237-255.

Barr, A.G., Morgenstern, K., Black, T.A., McCaughey, J.H., Nesic, Z., 2006. Surface energy balance closure by the eddy-covariance method above three boreal forest stands and implications for the measurement of the CO_2 flux. Agr Forest Meteorol, 140(1-4): 322-337.

Bengtsson, G., Torneman, N., 2004. Dissolved organic carbon dynamics in the peat-streamwater interface. Biogeochemistry, 70(1): 93-116.

Bergeron, O., Strachan, I.B., submitted. Year-round CO_2 fluxes over Montreal, Canada residential areas. Atmospheric Environment.

Berggren, M., Laudon, H., Jansson, M., 2009a. Aging of allochthonous organic carbon regulates bacterial production in unproductive boreal lakes. Limnol Oceanogr, 54(4): 1333-1342.

Berggren, M., Laudon, H., Jansson, M., 2009b. Hydrological Control of Organic Carbon Support for Bacterial Growth in Boreal Headwater Streams. Microb Ecol, 57(1): 170-178.

Berggren, M. et al., 2010. Lake secondary production fueled by rapid transfer of low molecular weight organic carbon from terrestrial sources to aquatic consumers. Ecol Lett, 13(7): 870-880.

Bertilsson, S., Tranvik, L.J., 2000. Photochemical transformation of dissolved organic matter in lakes. Limnol Oceanogr, 45(4): 753-762.

Billett, M.F. et al., 2004. Linking land-atmosphere-stream carbon fluxes in a lowland peatland system. Global Biogeochemical Cycles, 18(1): GB1024.

Billett, M.F., Deacon, C.M., Palmer, S.M., Dawson, J.J.C., Hope, D., 2006. Connecting organic carbon in stream water and soils in a peatland catchment. J Geophys Res-Biogeo, 111(G2): G03026.

Billett, M.F., Garnett, M.H., Harvey, F., 2007. UK peatland streams release old carbon dioxide to the atmosphere and young dissolved organic carbon to rivers. Geophys Res Lett, 34(23): L23401.

Buffam, I., Galloway, J.N., Blum, L.K., McGlathery, K.J., 2001. A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. Biogeochemistry, 53(3): 269-306.

Buffam, I., Laudon, H., Temnerud, J., Morth, C.M., Bishop, K., 2007. Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network. J Geophys Res-Biogeo, 112(G1): G01022.

Camill, P., Lynch, J.A., Clark, J.S., Adams, J.B., Jordan, B., 2001. Changes in biomass, aboveground net primary production, and peat accumulation following permafrost thaw in the boreal peatlands of Manitoba, Canada. Ecosystems, 4(5): 461-478.

Camill, P., 2005. Permafrost thaw accelerates in boreal peatlands during late-20th century climate warming. Climatic Change, 68(1-2): 135-152.

Carey, S.K., Woo, M.K., 2001. Slope runoff processes and flow generation in a subarctic, subalpine catchment. Journal of Hydrology, 253(1-4): 110-129.

Carey, S.K., 2003. Dissolved organic carbon fluxes in a discontinuous permafrost subarctic alpine catchment. Permafrost Periglac, 14(2): 161-171.

Carey, S.K., Quinton, W.L., 2005. Evaluating runoff generation during summer using hydrometric, stable isotope and hydrochemical methods in a discontinuous permafrost alpine catchment. Hydrol Process, 19(1): 95-114.

Chapin, F.S. et al., 2006. Reconciling carbon-cycle concepts, terminology, and methods. Ecosystems, 9(7): 1041-1050.

Chapman, P.J., Clark, J.M., Heathwaite, A.L., Adamson, J.K., Lane, S.N., 2005. Sulphate controls on dissolved organic carbon dynamics in blanket peat: Linking field and laboratory evidence. Iahs-Aish P, 294: 3-9.

Christensen, T.R. et al., 2003. Factors controlling large scale variations in methane emissions from wetlands. Geophys Res Lett, 30(7): 1414.

Christensen, T.R. et al., 2004. Thawing sub-arctic permafrost: Effects on vegetation and methane emissions. Geophys Res Lett, 31(4): L04501.

Christensen, T.R. et al., 2007. A catchment-scale carbon and greenhouse gas budget of a subarctic landscape. Philos T R Soc A, 365(1856): 1643-1656.

Christophersen, N., Neal, C., Hooper, R.P., Vogt, R.D., Andersen, S., 1990. Modeling Streamwater Chemistry as a Mixture of Soilwater End-Members - a Step Towards 2nd-Generation Acidification Models. Journal of Hydrology, 116(1-4): 307-320.

Clark, J.M., Lane, S.N., Chapman, P.J., Adamson, J.K., 2007. Export of dissolved organic carbon from an upland peatland during storm events: Implications for flux estimates. Journal of Hydrology, 347(3-4): 438-447.

Clymo, R.S., 2004. Hydraulic conductivity of peat at Ellergower Moss, Scotland. Hydrol Process, 18(2): 261-274.

Cole, J.J. et al., 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems, 10(1): 171-184.

Creed, I.F., Beall, F.D., Clair, T.A., Dillon, P.J., Hesslein, R.H., 2008. Predicting export of dissolved organic carbon from forested catchments in glaciated landscapes with shallow soils. Global Biogeochemical Cycles, 22(4).

Curtis, P.J., Schindler, D.W., 1997. Hydrologic control of dissolved organic matter in low-order Precambrian Shield Lakes. Biogeochemistry, 36(1): 125-138.

Dawson, J.J.C., Billett, M.F., Neal, C., Hill, S., 2002. A comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK. Journal of Hydrology, 257(1-4): 226-246.

Dawson, J.J.C., Billett, M.F., Hope, D., Palmer, S.M., Deacon, C.M., 2004. Sources and sinks of aquatic carbon in a peatland stream continuum. Biogeochemistry, 70(1): 71-92.

Dillon, P.J., Molot, L.A., 1997. Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. Water Resour Res, 33(11): 2591-2600.

Dinsmore, K.J., Billett, M.F., 2008. Continuous measurement and modeling of CO2 losses from a peatland stream during stormflow events. Water Resour Res, 44(12): W12417.

Dinsmore, K.J. et al., 2010. Role of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland catchment. Global Change Biology, 16(10): 2750-2762.

Dorrepaal, E. et al., 2009. Carbon respiration from subsurface peat accelerated by climate warming in the subarctic. Nature, 460(7255): 616-U79.

Eimers, M.C., Buttle, J., Watmough, S.A., 2008. Influence of seasonal changes in runoff and extreme events on dissolved organic carbon trends in wetland- and upland-draining streams. Can J Fish Aquat Sci, 65(5): 796-808.

Elder, J.F., Rybicki, N.B., Carter, V., Weintraub, V., 2000. Sources and yields of dissolved carbon in northern Wisconsin stream catchments with differing amounts of peatland. Wetlands, 20(1): 113-125.

Evans, C.D., Monteith, D.T., Cooper, D.M., 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. Environ Pollut, 137(1): 55-71.

Fellman, J.B., D'Amore, D.V., Hood, E., Boone, R.D., 2008. Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska. Biogeochemistry, 88(2): 169-184.

Fellman, J.B., Hood, E., Edwards, R.T., D'Amore, D.V., 2009. Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. J Geophys Res-Biogeo, 114: G01021.

Fenner, N., Ostle, N., Freeman, C., Sleep, D., Reynolds, B., 2004. Peatland carbon afflux partitioning reveals that *Sphagnum* photosynthate contributes to the DOC pool. Plant Soil, 259(1-2): 345-354.

Fenner, N., Freeman, C., Reynolds, B., 2005. Hydrological effects on the diversity of phenolic degrading bacteria in a peatland: implications for carbon cycling. Soil Biology & Biochemistry, 37(7): 1277-1287.

Fenner, N. et al., 2007. Interactions between elevated CO_2 and warming could amplify DOC exports from peatland catchments. Environ Sci Technol, 41(9): 3146-3152.

Finlay, J., Neff, J., Zimov, S., Davydova, A., Davydov, S., 2006. Snowmelt dominance of dissolved organic carbon in high-latitude watersheds: Implications for characterization and flux of river DOC. Geophys Res Lett, 33(10): L10401.

Fletcher, S.E.M., Tans, P.P., Bruhwiler, L.M., Miller, J.B., Heimann, M., 2004. CH4 sources estimated from atmospheric observations of CH4 and its C-13/C-12 isotopic ratios: 1. Inverse modeling of source processes. Global Biogeochemical Cycles, 18(4): GB4005.

Fox, A.M., Huntley, B., Lloyd, C.R., Williams, M., Baxter, R., 2008. Net ecosystem exchange over heterogeneous Arctic tundra: Scaling between chamber and eddy covariance measurements. Global Biogeochemical Cycles, 22(2): GB2027.

Fraser, C.J.D., Roulet, N.T., Moore, T.R., 2001. Hydrology and dissolved organic carbon biogeochemistry in an ombrotrophic bog. Hydrol Process, 15(16): 3151-3166.

Freeman, C., Ostle, N., Kang, H., 2001. An enzymic 'latch' on a global carbon store - A shortage of oxygen locks up carbon in peatlands by restraining a single enzyme. Nature, 409(6817): 149-149.

Frey, K.E., Smith, L.C., 2005. Amplified carbon release from vast West Siberian peatlands by 2100. Geophys Res Lett, 32(9): L09401.

Frey, K.E., McClelland, J.W., 2009. Impacts of permafrost degradation on arctic river biogeochemistry. Hydrol Process, 23(1): 169-182.

Friborg, T., Soegaard, H., Christensen, T.R., Lloyd, C.R., Panikov, N.S., 2003. Siberian wetlands: Where a sink is a source. Geophys Res Lett, 30(21): 2129.

Frolking, S., Roulet, N., Fuglestvedt, J., 2006. How northern peatlands influence the Earth's radiative budget: Sustained methane emission versus sustained carbon sequestration. J Geophys Res-Biogeo, 111(G1): G01008.

Gorham, E., 1991. Northern Peatlands - Role in the Carbon-Cycle and Probable Responses to Climatic Warming. Ecol Appl, 1(2): 182-195.

Guggenberger, G., Zech, W., 1994. Dissolved Organic-Carbon in Forest Floor Leachates - Simple Degradation Products or Humic Substances. Sci Total Environ, 152(1): 37-47.

Guggenberger, G., Zech, W., Schulten, H.R., 1994. Formation and mobilization pathways of dissolved organic matter - evidence from chemical structural studies of organic matter fractions in acid forest florr solutions. Org. Geochem., 21(1): 51-66.

Guo, L.D., Macdonald, R.W., 2006. Source and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope (delta C-13, Delta C-14, and delta N-15) composition of dissolved, colloidal, and particulate phases. Global Biogeochemical Cycles, 20(2): GB2011.

Guo, L.D., Ping, C.L., Macdonald, R.W., 2007. Mobilization pathways of organic carbon from permafrost to arctic rivers in a changing climate. Geophys Res Lett, 34(13): L13603.

Halsey, L., Vitt, D., Zoltai, S., 1997a. Climatic and physiographic controls on wetland type and distribution in Manitoba, Canada. Wetlands, 17(2): 243-262.

Halsey, L.A., Vitt, D.H., Trew, D.O., 1997b. Influence of peatlands on the acidity of lakes in northeastern Alberta, Canada. Water Air Soil Poll, 96(1-4): 17-38.

Hinton, M.J., Schiff, S.L., English, M.C., 1994. Examining the Contributions of Glacial Till Water to Storm Runoff Using 2-Component and 3-Component Hydrograph Separations. Water Resour Res, 30(4): 983-993.

Hinton, M.J., Schiff, S.L., English, M.C., 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochemistry, 36(1): 67-88.

Hoeg, S., Uhlenbrook, S., Leibundgut, C., 2000. Hydrograph separation in a mountainous catchment - combining hydrochemical and isotopic tracers. Hydrol Process, 14(7): 1199-1216.

Holmes, R.M. et al., 2008. Lability of DOC transported by Alaskan rivers to the arctic ocean. Geophys Res Lett, 35(3): L03402.

Hood, E., Gooseff, M.N., Johnson, S.L., 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. J Geophys Res-Biogeo, 111(G1): G01007.

Humphreys, E.R. et al., 2006. Summer carbon dioxide and water vapor fluxes across a range of northern peatlands. J Geophys Res-Biogeo, 111(G4): G04011.

Inamdar, S.P., O'Leary, N., Mitchell, M.J., Riley, J.T., 2006. The impact of storm events on solute exports from a glaciated forested watershed in western New York, USA. Hydrol Process, 20(16): 3423-3439.

Inamdar, S.P., Mitchell, M.J., 2007. Storm event exports of dissolved organic nitrogen (DON) across multiple catchments in a glaciated forested watershed. J Geophys Res-Biogeo, 112(G2): G02014.

Inamdar, S., Rupp, J., Mitchell, M., 2009. Groundwater flushing of solutes at wetland and hillslope positions during storm events in a small glaciated catchment in western New York, USA. Hydrol Process, 23(13): 1912-1926.

Jackowicz-Korczynski, M. et al., 2010. Annual cycle of methane emission from a subarctic peatland. J Geophys Res-Biogeo, 115: G02009.

Jager, D.F., Wilmking, M., Kukkonen, J.V.K., 2009. The influence of summer seasonal extremes on dissolved organic carbon export from a boreal peatland catchment: Evidence from one dry and one wet growing season. Sci Total Environ, 407(4): 1373-1382.

Johansson, M., Christensen, T.R., Åkerman, H.J., Callaghan, T.V., 2006a. What determines the current presence or absence of permafrost in the Tornetrask region, a sub-arctic landscape in Northern Sweden? Ambio, 35(4): 190-197.

Johansson, T. et al., 2006b. Decadal vegetation changes in a northern peatland, greenhouse gas fluxes and net radiative forcing. Global Change Biology, 12(12): 2352-2369.

Johnston, C.A. et al., 2008. Wetland types and wetland maps differ in ability to predict dissolved organic carbon concentrations in streams. Sci Total Environ, 404(2-3): 326-334.

Jonsson, A. et al., 2007. Integrating aquatic carbon fluxes in a boreal catchment carbon budget. Journal of Hydrology, 334(1-2): 141-150.

Kaiser, K., Zech, W., 1998. Rates of dissolved organic matter release and sorption in forest soils. Soil Sci, 163(9): 714-725.

Kalbitz, K., Wennrich, R., 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. Sci Total Environ, 209(1): 27-39.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: A review. Soil Sci, 165(4): 277-304.

Kalbitz, K., Schmerwitz, J., Schwesig, D., Matzner, E., 2003a. Biodegradation of soil-derived dissolved organic matter as related to its properties. Geoderma, 113(3-4): 273-291.

Kalbitz, K. et al., 2003b. Changes in properties of soil-derived dissolved organic matter induced by biodegradation. Soil Biology & Biochemistry, 35(8): 1129-1142.

Karlsson, J. et al., 2010. Quantifying the relative importance of lake emissions in the carbon budget of a subarctic catchment. J Geophys Res-Biogeo, 115: G03006.

Kawahigashi, M., Kaiser, K., Kalbitz, K., Rodionov, A., Guggenberger, G., 2004. Dissolved organic matter in small streams along a gradient from discontinuous to continuous permafrost. Global Change Biology, 10(9): 1576-1586.

Kellner, E., Halldin, S., 2002. Water budget and surface-layer water storage in a *Sphagnum* bog in central Sweden. Hydrol Process, 16(1): 87-103.

Kling, G.W., Kipphut, G.W., Miller, M.C., 1991. Arctic Lakes and Streams as Gas Conduits to the Atmosphere - Implications for Tundra Carbon Budgets. Science, 251(4991): 298-301.

Koehler, A.K., Murphy, K., Kiely, G., Sottocornola, M., 2009. Seasonal variation of DOC concentration and annual loss of DOC from an Atlantic blanket bog in South Western Ireland. Biogeochemistry, 95(2-3): 231-242.

Koelbener, A., Strom, L., Edwards, P.J., Venterink, H.O., 2010. Plant species from mesotrophic wetlands cause relatively high methane emissions from peat soil. Plant Soil, 326(1-2): 147-158.

Kohler, J., Brandt, O., Johansson, M., Callaghan, T., 2006. A long-term Arctic snow depth record from Abisko, northern Sweden, 1913-2004. Polar Res, 25(2): 91-113.

Kohler, S.J., Buffam, I., Laudon, H., Bishop, K.H., 2008. Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements. J Geophys Res-Biogeo, 113(G3): G03012.

Kohler, S.J., Buffam, I., Seibert, J., Bishop, K.H., Laudon, H., 2009. Dynamics of stream water TOC concentrations in a boreal headwater catchment: Controlling factors and implications for climate scenarios. J Hydrol, 373(1-2): 44-56.

Kokfelt, U. et al., 2009. Ecosystem responses to increased precipitation and permafrost decay in subarctic Sweden inferred from peat and lake sediments. Global Change Biology, 15(7): 1652-1663.

Kokfelt, U. et al., 2010. Wetland development, permafrost history and nutrient cycling inferred from late Holocene peat and lake sediment records in subarctic Sweden. J. Paleolimn., 44(1): 327-342.

Kortelainen, P. et al., 2006. Controls on the export of C, N, P and Fe from undisturbed boreal catchments, Finland. Aquatic Sciences, 68(4): 453-468.

Kuhry, P., 2008. Palsa and peat plateau development in the Hudson Bay Lowlands, Canada: timing, pathways and causes. Boreas, 37(2): 316-327.

Ladouche, B. et al., 2001. Hydrograph separation using isotopic, chemical and hydrological approaches (Strengbach catchment, France). Journal of Hydrology, 242(3-4): 255-274.

Lafleur, P.M., Roulet, N.T., 1992. A Comparison of Evaporation Rates from 2 Fens of the Hudson-Bay Lowland. Aquat Bot, 44(1): 59-69.

Laine, A. et al., 2006. Estimating net ecosystem exchange in a patterned ecosystem: Example from blanket bog. Agr Forest Meteorol, 138(1-4): 231-243.

Laudon, H., Kohler, S., Buffam, I., 2004. Seasonal TOC export from seven boreal catchments in northern Sweden. Aquatic Sciences, 66(2): 223-230.

Laudon, H., Sjoblom, V., Buffam, I., Seibert, J., Morth, M., 2007. The role of catchment scale and landscape characteristics for runoff generation of boreal streams. Journal of Hydrology, 344(3-4): 198-209.

Lawrence, D.M., Slater, A.G., Romanovsky, V.E., Nicolsky, D.J., 2008. Sensitivity of a model projection of near-surface permafrost degradation to soil column depth and representation of soil organic matter. J Geophys Res-Earth, 113(F2): F02011.

Limpens, J. et al., 2008. Peatlands and the carbon cycle: from local processes to global implications - a synthesis. Biogeosciences, 5(5): 1475-1491.

Lindroth, A. et al., 2007. Environmental controls on the CO2 exchange in north European mires. Tellus B, 59(5): 812-825.

Lloyd, J., Taylor, J.A., 1994. On the Temperature-Dependence of Soil Respiration. Funct Ecol, 8(3): 315-323.

Lou, T., Xie, H.X., 2006. Photochemical alteration of the molecular weight of dissolved organic matter. Chemosphere, 65(11): 2333-2342.

Lundström, U.S. et al., 2000. Advances in understanding the podzolization process resulting from a multidisciplinary study of three coniferous forest soils in the Nordic Countries. Geoderma, 94(2-4): 335-353.

Malmer, N., Wallén, B., 1996. Peat Formation and Mass Balance in Subarctic Ombrotrophic Peatland around Abisko, Northern Scandinavia. Ecological Bulletins(45): 79-92.

Malmer, N., Johansson, T., Olsrud, M., Christensen, T.R., 2005. Vegetation, climatic changes and net carbon sequestration in a North-Scandinavian subarctic mire over 30 years. Global Change Biol, 11(11): 1895-1909.

Marschner, B., Kalbitz, K., 2003. Controls of bioavailability and biodegradability of dissolved organic matter in soils. Geoderma, 113(3-4): 211-235.

Masing, V., Botch, M., Laanelaid, A., 2010. Mires of the former Soviet Union. Wetl Ecol Manag, 18(4): 397-433.

Mattsson, T., Kortelainen, P., Raike, A., 2005. Export of DOM from boreal catchments: impacts of land use cover and climate. Biogeochemistry, 76(2): 373-394.

McClain, M.E. et al., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems, 6(4): 301-312.

McDowell, W.H. et al., 2006. A comparison of methods to determine the biodegradable dissolved organic carbon from different terrestrial sources. Soil Biol Biochem, 38(7): 1933-1942.

McGuire, A.D. et al., 2009. Sensitivity of the carbon cycle in the Arctic to climate change. Ecological Monographs, 79(4): 523-555.

McGuire, A.D. et al., 2010. The carbon budget of the northern cryosphere region. Curr. Opin. Environ. Sustain., 2(4): 231-236.

McKnight, D.M. et al., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol Oceanogr, 46(1): 38-48.

McNamara, J.P., Kane, D.L., Hinzman, L.D., 1997. Hydrograph separations in an Arctic watershed using mixing model and graphical techniques. Water Resour Res, 33(7): 1707-1719.

McNamara, J.P., Kane, D.L., Hinzman, L.D., 1998. An analysis of streamflow hydrology in the Kuparuk River basin, Arctic Alaska: A nested watershed approach. Journal of Hydrology, 206(1-2): 39-57.

Meybeck, M., 1993. Riverine Transport of Atmospheric Carbon - Sources, Global Typology and Budget. Water Air Soil Poll, 70(1-4): 443-463.

Michalzik, B., Kalbitz, K., Park, J.H., Solinger, S., Matzner, E., 2001. Fluxes and concentrations of dissolved organic carbon and nitrogen - a synthesis for temperate forests. Biogeochemistry, 52(2): 173-205.

Molot, L.A., Dillon, P.J., 1997. Photolytic regulation of dissolved organic carbon in northern lakes. Global Biogeochemical Cycles, 11(3): 357-365.

Moore, T.R., Dalva, M., 2001. Some controls on the release of dissolved organic carbon by plant tissues and soils. Soil Sci, 166(1): 38-47.

Moore, T.R., 2003. Dissolved organic carbon in a northern boreal landscape. Global Biogeochemical Cycles, 17(4): 1109.

Neff, J.C. et al., 2006. Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams. Geophys Res Lett, 33(23): L23401.

Nilsson, M. et al., 2008. Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire - a significant sink after accounting for all C-fluxes. Global Change Biol, 14(10): 2317-2332.

Öquist, M.G., Wallin, M., Seibert, J., Bishop, K., Laudon, H., 2009. Dissolved Inorganic Carbon Export Across the Soil/Stream Interface and Its Fate in a Boreal Headwater Stream. Environ Sci Technol, 43(19): 7364-7369.

Pacific, V.J., Jencso, K.G., McGlynn, B.L., 2010. Variable flushing mechanisms and landscape structure control stream DOC export during snowmelt in a set of nested catchments. Biogeochemistry, 99(1-3): 193-211.

Pastor, J. et al., 2003. Global warming and the export of dissolved organic carbon from boreal peatlands. Oikos, 100(2): 380-386.

Payette, S., Delwaide, A., Caccianiga, M., Beauchemin, M., 2004. Accelerated thawing of subarctic peatland permafrost over the last 50 years. Geophys Res Lett, 31(18): L18208.

Peichl, M. et al., 2007. Concentrations and fluxes of dissolved organic carbon in an age-sequence of white pine forests in Southern Ontario, Canada. Biogeochemistry, 86(1): 1-17.

Petrone, K.C., Hinzman, L.D., Shibata, H., Jones, J.B., Boone, R.D., 2007. The influence of fire and permafrost on sub-arctic stream chemistry during storms. Hydrol Process, 21(4): 423-434.

Peuravuori, J., Pihlaja, K., 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Anal Chim Acta, 337(2): 133-149.

Pilesjö, P., Persson, A., Harrie, L., 2006. Digital elevation data for estimation of potential wetness in ridged fields - Comparison of two different methods. Agricultural Water Management, 79(3): 225-247.

Prepas, E.E. et al., 2001. Landscape variables influencing nutrients and phytoplankton communities in Boreal Plain lakes of northern Alberta: a comparison of wetland- and upland-dominated catchments. Can J Fish Aquat Sci, 58(7): 1286-1299.

Prokushkin, A.S., Gleixner, G., McDowell, W.H., Ruehlow, S., Schulze, E.D., 2007. Source- and substrate-specific export of dissolved organic matter from permafrost-dominated forested watershed in central Siberia. Global Biogeochemical Cycles, 21(4): GB4003.

Quinton, W.L., Marsh, P., 1999. A conceptual framework for runoff generation in a permafrost environment. Hydrol Process, 13(16): 2563-2581.

Raulund-Rasmussen, K., Borggaard, O.K., Hansen, H.C.B., Olsson, M., 1998. Effect of natural organic soil solutes on weathering rates of soil minerals. Eur J Soil Sci, 49(3): 397-406.

Raymond, P.A. et al., 2007. Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. Global Biogeochemical Cycles, 21(4): GB4011.

Robinson, S.D., 2006. Carbon accumulation in peatlands, southwestern Northwest Territories, Canada. Can J Soil Sci, 86(2): 305-319.

Roehm, C.L., Giesler, R., Karlsson, J., 2009. Bioavailability of terrestrial organic carbon to lake bacteria: The case of a degrading subarctic permafrost mire complex. J Geophys Res-Biogeo, 114: G03006.

Roulet, N.T. et al., 2007. Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland. Global Change Biology, 13(2): 397-411.

Rydén, B.E., Fors, L., Kostov, L., 1980. Physical Properties of the Tundra Soil-Water System at Stordalen, Abisko. Ecological Bulletins(30): 27-54.

Rydén, B.E., Kostov, L., 1980. Thawing and Freezing in Tundra Soils. Ecological Bulletins(30): 251-281.

Sagerfors, J. et al., 2008. Annual CO2 exchange between a nutrient-poor, minerotrophic, boreal mire and the atmosphere. J Geophys Res-Biogeo, 113(G1): G01001.

Sannel, A.B.K., Kuhry, P., 2009. Holocene peat growth and decay dynamics in sub-arctic peat plateaus, west-central Canada. Boreas, 38(1): 13-24.

Saraceno, J.F. et al., 2009. High-frequency in situ optical measurements during a storm event: Assessing relationships between dissolved organic matter, sediment concentrations, and hydrologic processes. J Geophys Res-Biogeo, 114: G00F09.

Schindler, D.W. et al., 1997. Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. Biogeochemistry, 36(1): 9-28.

Schleppi, P., Waldner, P.A., Fritschi, B., 2006. Accuracy and precision of different sampling strategies and flux integration methods for runoff water: comparisons based on measurements of the electrical conductivity. Hydrol Process, 20(2): 395-410.

Schuur, E.A.G. et al., 2008. Vulnerability of permafrost carbon to climate change: Implications for the global carbon cycle. Bioscience, 58(8): 701-714.

Schuur, E.A.G. et al., 2009. The effect of permafrost thaw on old carbon release and net carbon exchange from tundra. Nature, 459(7246): 556-559.

Seppälä, M., 1988. Palsas and related forms. In: Clark, J.M. (Ed.), Advances in Periglacial Geomorphology. John Wiley, Chichester, pp. 247-278.

Seppälä, M., 1994. Snow Depth Controls Palsa Growth. Permafrost Periglac, 5(4): 283-288.

Sobek, S., Tranvik, L.J., Cole, J.J., 2005. Temperature independence of carbon dioxide supersaturation in global lakes. Global Biogeochemical Cycles, 19(2).

Sonesson, M. (Ed.), 1980. Ecology of a Subarctic Mire. Ecological Bulletins. Oikos Editorial Office, 3 pp.

Sonesson, M., Kvillner, E., 1980. Plant Communities of the Stordalen Mire: A Comparison between Numerical and Non-Numerical Classification Methods. Ecological Bulletins(30): 113-125.

Spence, C., Woo, M.K., 2006. Hydrology of subarctic Canadian Shield: heterogeneous headwater basins. J Hydrol, 317(1-2): 138-154.

Spencer, R.G.M., Aiken, G.R., Wickland, K.P., Striegl, R.G., Hernes, P.J., 2008. Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon River basin, Alaska. Global Biogeochemical Cycles, 22(4): GB4002.

Spencer, R.G.M. et al., 2009. Utilizing chromophoric dissolved organic matter measurements to derive export and reactivity of dissolved organic carbon exported to the Arctic Ocean: A case study of the Yukon River, Alaska. Geophys Res Lett, 36: L06401.

Stedmon, C.A., Markager, S., 2005. Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis. Limnol Oceanogr, 50(5): 1415-1426.

Strack, M., Waddington, J.M., Lucchese, M.C., Cagampan, J.P., 2009. Moisture controls on CO2 exchange in a *Sphagnum*-dominated peatland: results from an extreme drought field experiment. Ecohydrology, 2(4): 454-461.

Striegl, R.G., Aiken, G.R., Dornblaser, M.M., Raymond, P.A., Wickland, K.P., 2005. A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. Geophys Res Lett, 32(21): L21413.

Striegl, R.G., Dornblaser, M.M., Aiken, G.R., Wickland, K.P., Raymond, P.A., 2007. Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001-2005. Water Resour Res, 43(2): W02411.

Ström, L., Ekberg, A., Mastepanov, M., Christensen, T.R., 2003. The effect of vascular plants on carbon turnover and methane emissions from a tundra wetland. Global Change Biology, 9(8): 1185-1192.

Ström, L., Mastepanov, M., Christensen, T.R., 2005. Species-specific effects of vascular plants on carbon turnover and methane emissions from wetlands. Biogeochemistry, 75(1): 65-82.

Sulman, B.N. et al., 2010. CO2 fluxes at northern fens and bogs have opposite responses to inter-annual fluctuations in water table. Geophys Res Lett, 37: L19702.

Suyker, A.E., Verma, S.B., Clement, R.J., Billesbach, D.P., 1996. Methane flux in a boreal fen: Season-long measurement by eddy correlation. J Geophys Res-Atmos, 101(D22): 28637-28647.

Tarnocai, C., 2009. The Impact of Climate Change on Canadian Peatlands. Can Water Resour J, 34(4): 453-466.

Tarnocai, C. et al., 2009. Soil organic carbon pools in the northern circumpolar permafrost region. Global Biogeochemical Cycles, 23: GB2023.

Toth, J., 1963a. A Theoretical Analysis of Groundwater Flow in Small Drainage Basins. J Geophys Res, 68(16): 4795.

Toth, J., 1963b. A Theoretical Analysis of Groundwater Flow in Small Drainage Basins. J Geophys Res, 68(16): 4795.

Tranvik, L.J. et al., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol Oceanogr, 54(6): 2298-2314.

Turetsky, M.R., Wieder, R.K., Vitt, D.H., Evans, R.J., Scott, K.D., 2007. The disappearance of relict permafrost in boreal north America: Effects on peatland carbon storage and fluxes. Global Change Biology, 13(9): 1922-1934.

Turunen, J., Tomppo, E., Tolonen, K., Reinikainen, A., 2002. Estimating carbon accumulation rates of undrained mires in Finland - application to boreal and subarctic regions. Holocene, 12(1): 69-80.

Uhlenbrook, S., Frey, M., Leibundgut, C., Maloszewski, P., 2002. Hydrograph separations in a mesoscale mountainous basin at event and seasonal timescales. Water Resour Res, 38(6): 1096.

van Hees, P.A.W., Jones, D.L., Finlay, R., Godbold, D.L., Lundstomd, U.S., 2005. The carbon we do not see - the impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: a review. Soil Biology & Biochemistry, 37(1): 1-13.

van Verseveld, W.J., McDonnell, J.J., Lajtha, K., 2008. A mechanistic assessment of nutrient flushing at the catchment scale. Journal of Hydrology, 358(3-4): 268-287.

Vardy, S.R., Warner, B.G., Turunen, J., Aravena, R., 2000. Carbon accumulation in permafrost peatlands in the Northwest Territories and Nunavut, Canada. Holocene, 10(2): 273-280.

Vile, M.A., Bridgham, S.D., Wieder, R.K., Novak, M., 2003. Atmospheric sulfur deposition alters pathways of gaseous carbon production in peatlands. Global Biogeochemical Cycles, 17(2): 1058.

Volk, C. et al., 2000. Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water. Water Res, 34(12): 3247-3257.

von Wachenfeldt, E., Tranvik, L.J., 2008. Sedimentation in boreal lakes - The role of flocculation of allochthonous dissolved organic matter in the water column. Ecosystems, 11(5): 803-814.

Wallin, M., Buffam, I., Öquist, M., Laudon, H., Bishop, K., 2010. Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes. J Geophys Res-Biogeo, 115: G02014.

Walvoord, M.A., Striegl, R.G., 2007. Increased groundwater to stream discharge from permafrost thawing in the Yukon River basin: Potential impacts on lateral export of carbon and nitrogen. Geophys Res Lett, 34(12): L12402.

Weishaar, J.L. et al., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol, 37(20): 4702-4708.

Wessel, D.A., Rouse, W.R., 1994. Modeling Evaporation from Wetland Tundra. Bound-Lay Meteorol, 68(1-2): 109-130.

Wheeler, B.D., Proctor, M.C.F., 2000. Ecological gradients, subdivisions and terminology of north-west European mires. J Ecol, 88(2): 187-203.

White, D., Autier, V., Yoshikawa, K., Jones, J., Seelen, S., 2008. Using DOC to better understand local hydrology in a subarctic watershed. Cold Reg. Sci. Tech., 51(1): 68-75.

Wickland, K.P., Neff, J.C., Aiken, G.R., 2007. Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability. Ecosystems, 10(8): 1323-1340.

Winter, T.C., 1999. Relation of streams, lakes, and wetlands to groundwater flow systems. Hydrogeol J, 7(1): 28-45.

Woo, M.K., Guan, X.J., 2006. Hydrological connectivity and seasonal storage change of tundra ponds in a polar oasis environment, Canadian High Arctic. Permafrost Periglac, 17(4): 309-323.

Woo, M.K., Mielko, C., 2007. An integrated framework of lake-stream connectivity for a semi-arid, subarctic environment. Hydrol Process, 21(19): 2668-2674.

Woo, M.K., Thorne, R., Szeto, K., Yang, D.Q., 2008. Streamflow hydrology in the boreal region under the influences of climate and human interference. Philos T R Soc B, 363(1501): 2251-2260.

Worrall, F., Burt, T.P., Jaeban, R.Y., Warburton, J., Shedden, R., 2002. Release of dissolved organic carbon from upland peat. Hydrol Process, 16(17): 3487-3504.

Worrall, F., Burt, T.P., 2007. Flux of dissolved organic carbon from UK rivers. Global Biogeochemical Cycles, 21(1): GB1013.

Worrall, F., Gibson, H.S., Burt, T.P., 2008. Production vs. solubility in controlling runoff of DOC from peat soils - The use of an event analysis. Journal of Hydrology, 358(1-2): 84-95.

Wright, N., Quinton, W.L., Hayashi, M., 2008. Hillslope runoff from an ice-cored peat plateau in a discontinuous permafrost basin, Northwest Territories, Canada. Hydrol Process, 22(15): 2816-2828.

Wright, N., Hayashi, M., Quinton, W.L., 2009. Spatial and temporal variations in active layer thawing and their implication on runoff generation in peat-covered permafrost terrain. Water Resour Res, 45: W05414.

Yamazaki, Y., Kubota, J., Ohata, T., Vuglinsky, V., Mizuyama, T., 2006. Seasonal changes in runoff characteristics on a permafrost watershed in

the southern mountainous region of eastern Siberia. Hydrol Process, 20(3): 453-467.

Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B., Saccomandi, F., 1999. Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. Chemosphere, 38(1): 45-50.