

**Spatial variability and seasonal dynamics of dissolved
organic matter in surface and soil pore waters in mire-forest
landscapes in the Komi Republic, Northwest-Russia.**

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I Summary and structure

The overarching aim of this thesis is to describe and contribute to the still rather sparse data on the small-scale spatial variability and seasonal dynamics of dissolved organic matter (DOM) in the surface and soil pore waters in mire-forest landscapes in the Komi Republic of Northwest Russia. This study stands out because it estimates the DOC flux during the snowmelt and identifies the main ecohydrological units that contribute to the flux. Furthermore, this study aims to bridge the gap between the knowledge of DOM fluxes and different size fractions of organic carbon (truly dissolved and colloidal) in a boreal mire-forest landscape. It also provides comparative analyses of different portable DOC measurement methods, which is important for evaluating DOC dynamics in remote sites.

This thesis consists of eight chapters. **Chapter 1** presents the Introduction, which highlights the current gaps in our knowledge of DOM dynamics. Additionally, it presents the motivations, principle objectives and scope of the investigation. **Chapter 2** provides a literature review of the importance of peatlands as carbon sinks and highlights the role of dissolved organic carbon (DOC), the main component of lateral carbon fluxes, in predicting the possible responses to global change and other effects on biochemical cycles. In addition, **Chapter 2** describes the structural characteristics of DOM and the primary regulatory factors that cause changes in DOM concentrations. **Chapter 3** provides detailed information about the study site for the conducted research that is described in Chapters 4-7. The description includes information about the location, geology, climatic data and vegetation of the site.

The main findings of this thesis are presented in **Chapters 4-7**. Each of these chapters consists of separate sections: abstract, introduction, materials and methods, results, discussion and conclusions. The primary objective of **Chapter 4** is to provide a comparative study of innovative methods for measuring DOC under remote field conditions. The chapter evaluates the application of automated DOC measurements using portable UV-Vis probes. The secondary objective is to establish the link between absorbance and DOC concentrations for different landscape subunits and fractions. This chapter also stresses the importance of quality assurance and quality control when using

absorbance values as proxies for quantifying DOM. This chapter shows that the UV-Vis submersible probe facilitates the rapid, robust and continuous measurement of DOC contents under field conditions. This chapter also demonstrates that studies that use absorbance values as a proxy for DOC content determination should include more than one wavelength in their absorbance-concentration models.

The main objective of **Chapter 5** is to describe the hydrochemical gradients in the surface and pore waters with respect to DOM and vegetation changes across the mire complex. Specifically, it assesses the qualitative and quantitative variations in DOC and the major ion dynamics during the active vegetation growth and senescence periods. Furthermore, this chapter describes another goal of the study, which is to determine the location of hot spots for DOC production and export. The results of **Chapter 5** demonstrate that the DOC content within the boreal mire complex ranged from 20-54 mg L⁻¹. The diverging hydrochemistry and DOC content indicated a high heterogeneity between different ecohydrological subunits within one mire complex. The current study also shows that, in terms of hydrochemistry, the lagg zone may act as a hotspot within the mire and that due to the high nutrient and DOC contents, the lagg zone can potentially act as a major CO₂ and CH₄ emitter. Furthermore, the hydrochemical parameters demonstrated that the lagg site was the primary contributor to the outflow streams.

The goals of **Chapter 6** are to quantify the DOC export during snowmelt, which is a major hydrological event, and to explain the main factors that regulate the DOC export. In addition, it identifies the flow paths of runoff water during the period of snowmelt and provides a conceptual understanding of the spatial and temporal dynamics of the surface chemistry along the lagg-fen-bog gradient after snowmelt. This chapter demonstrates that during the snowmelt period, 1.7 g C m⁻² in the form of DOC was transferred in the 74 mm of runoff from the catchment into the river. The ecohydrological units differ with the mire thaw at different times as a result of differences in the exposure to the sunlight, vegetation cover, and soil structures. Different thawing periods lead to variation in the inputs and relative contribution of variable sub-units to the outflow DOC content change over a short period of time.

Chapter 7 presents, for the first time, a detailed quantitative and qualitative analysis of truly dissolved and colloidal organic compound variation in the boreal mire-river

complex over the course of one annual cycle. This chapter focuses on the use of DOC content and stable isotope data from different size fractions to identify qualitative variations in the DOM within the mire complex and to trace the water flow pathways. The study demonstrates that the proportion of truly dissolved and colloidal organic carbon varies temporally and spatially. The highest proportion of the truly dissolved organic carbon fraction was detected at all sites during the summer. Based on the seasonal changes in the fraction distribution, increased vegetation growth and water residence times, high temperatures, and stronger photodegradation can be suggested to lead to a higher proportion of the truly dissolved organic carbon fraction during the summer period. Furthermore, a significant difference was detected in the $\delta^{13}\text{C}$ values for all fractions. The $\delta^{13}\text{C}$ values were the lowest during the summer period and increased during the fall and snowmelt periods. However, interpretation with respect to decomposition based solely on $\delta^{13}\text{C}$ should be performed with caution because the $\delta^{13}\text{C}$ values can vary due to the presence of different molecular compounds, vegetation cover and climatic factors. $\delta^{13}\text{C}$ can also be used as a tracer for detecting organic matter transport. In the current study, the $\delta^{13}\text{C}$ signatures reveal that the outflow waters were hydrochemically closely related to the surface waters of the lagg zone. Finally, **Chapter 8** summarizes the main findings and proposes recommendations for further studies. It highlights that to predict how peatlands will respond to climate change, an integrated approach to the process-level understanding of carbon cycle, especially DOM studies, should be not neglected and included in the total carbon budget estimations.

II Zusammenfassung

Das übergreifende Ziel dieser Doktorarbeit ist es, das noch immer spärliche Datenmaterial dazustellen und zu ergänzen, welches kleinmaßstäbliche, räumliche Variabilität und saisonale Dynamiken von gelöster organischer Substanz (DOM) in Oberflächen- und Bodenporenwassern in Sumpf-Wald Landschaften der Komi Republik von Nordwest Russland beschreibt. Diese Studie hebt sich außerdem ab, indem sie den gelösten organischen Kohlenstoff (DOC) Fluss während der Schneeschmelze berechnet und die beitragenden ökohydrologischen Einheiten dieses Flusses identifiziert. Desweiteren beabsichtigt diese Studie, die Wissenslücke zwischen DOM Flüssen und unterschiedlichen Korngrößenanteilen von organischem Kohlenstoff (gelöst - d.h. niedermolekulare Masse - und kolloidal) in einer borealen Sumpf-Wald Landschaft zu schließen. Sie liefert darüber hinaus Vergleichsanalysen verschiedener transportabler Methoden zur DOC Messung.

Diese Doktorarbeit umfasst acht Kapitel. **Kapitel 1** bildet die Einleitung, welche momentanen Wissenslücken im Gebiet der DOM Dynamiken aufzeigt. Außerdem werden die Motivation, die Zielsetzung und der Untersuchungsrahmen dargestellt. **Kapitel 2** beinhaltet eine Literaturlauswertung mit Bezug auf die Bedeutung von Mooren als Kohlenstoffsinken. Außerdem wird die Rolle des DOC, dem Hauptbestandteil des lateralen Kohlenstoffflusses, in der Prognose potenzieller Reaktionen von biogeochemischen Kreisläufen auf globalen Wandel und andere Einwirkungen unterstrichen. Zusätzlich beschreibt Kapitel 2 die strukturellen Charakteristiken des DOM und primäre Regulationsfaktoren welche Veränderungen der DOM Konzentrationen verursachen können. **Kapitel 3** bietet eine detaillierte Übersicht des Versuchsstandorts und enthält Informationen über Lage, Geologie, Klimadaten und Vegetation des Standortes.

Die wesentlichen Erkenntnisse dieser Doktorarbeit sind in Kapitel 4-7 dargelegt. Jedes dieser Kapitel besteht aus separaten Abschnitten: Zusammenfassung, Einleitung, Material und Methodik, Ergebnisse, Diskussion und Schlussfolgerung. Das Hauptziel des **Kapitels 4** ist es, eine Vergleichsstudie innovativer Methoden für die DOC-Messung unter entlegenen Feldbedingungen zu liefern. Dazu wertet das Kapitel die Anwendung

von automatisierten DOC-Messungen mittels tragbarer UV-Vis-Sensoren aus. Das weitere Ziel ist es die Verbindung zwischen Absorption und DOC-Konzentrationen in unterschiedlichen Landschaftsteilen und -abschnitten herzustellen. Außerdem verdeutlicht dieses Kapitel die Wichtigkeit der Qualitätssicherung und -kontrolle bei der Nutzung von indirekten Anzeigern (Proxys) zur DOM-Quantifizierung. Im Kapitel wird aufgezeigt, dass der tauchfeste UV-Vis-Sensor die schnelle, stabile und fortlaufende Messung von DOC-Gehalt unter Feldbedingungen ermöglicht. Diese Studie demonstriert des Weiteren, dass Studien welche den Gebrauch von Absorptionswerten als Proxys für DOC-Gehalt anwenden, mehr als eine Wellenlänge in ihr Absorptions-Konzentrations Modell miteinbeziehen sollten.

Die Zielsetzung von **Kapitel 5** ist die Beschreibung der hydrochemischen Gradienten in Oberflächen- und Porenwassern bezogen auf DOM und Vegetationsveränderungen über den Sumpf-Komplex. Insbesondere sind die qualitativen und quantitativen DOC-Schwankungen ausgewertet, sowie die Veränderungen der wesentlichen Ionen während des aktiven Vegetationswachstums und der Seneszenz-Phase. Überdies beschreibt dieses Kapitel ein weiteres Ziel der Studie, welches die Ermittlung von Hotspots für DOC-Produktion und -Export darstellt. Die Ergebnisse in Kapitel 5 zeigen, dass der DOC-Gehalt in dem borealen Sumpf-Komplex zwischen 20-54 mg L⁻¹ liegt. Die divergierende Hydrochemie und die DOC-Gehalte zeigen eine hohe Heterogenität zwischen den verschiedenen ökohydrologischen Teilabschnitten innerhalb eines Sumpf-Komplexes an. Zudem zeigt die vorliegende Studie, dass die Lagg-Zone (topographische Senke) die Hydrochemie betreffend einen Hotspot innerhalb des Sumpfes darstellen kann, und aufgrund der hohen Nährstoff- und DOC-Gehalte als wesentliche CO₂- und CH₄-Emissionsquelle zu verstehen ist. Außerdem zeigen hydrochemische Parameter, dass die Lagg-Zone den Hauptanteil zum Abfluss beitrug. Die Ziele in **Kapitel 6** umfassen die Quantifizierung des DOC-Exports während der Schneeschmelze, einem wesentlichen hydrologischen Ereignis, und die Beschreibung der Hauptfaktoren, welche den DOC-Export regulieren. Zusätzlich wurden Fließwege des Abflusswassers während der Schneeschmelze identifiziert und ein konzeptuelles Verständnis der räumlichen und zeitlichen Entwicklungen der Oberflächenchemie entlang des Lagg-Marsch-Moor Gefälles nach der Schneeschmelze erstellt. Im Kapitel ist

gezeigt, dass während der Schneeschmelze 1.7 g C m^{-2} in Form von DOC über die 74 mm Abfluss vom Einzugsgebiet in den Fluss geleitet werden. Die verschiedenen ökohydrologischen Abschnitte innerhalb des Sumpfgebiets tauen zu unterschiedlichen Zeiten als Folge der unterschiedlichen Sonneneinstrahlung, der Vegetationsbedeckung und der Bodenstruktur. Die verschiedenen Tauphasen führen zu unterschiedlichen Einträgen und relativen Beiträgen der verschiedenen Gebietsabschnitte, die DOC-Gehaltsschwankungen im Abfluss bewirken.

Kapitel 7 bietet erstmals eine eingehende, quantitative und qualitative Analyse der Variabilität von gelösten und kolloidalen organischen Verbindungen in einem borealen Sumpf-Fluss- Komplex über den Jahresverlauf. Dieses Kapitel befasst sich mit der Anwendung von DOC-Gehalt und stabilen Isotopen verschiedener Größengruppen um qualitative Variationen in DOM innerhalb des Sumpf-Komplexes zu identifizieren, und den Wasserlauf nachzuverfolgen. Die Studie zeigt, dass die Proportionen des gelösten und kolloidalen organischen Kohlenstoffs zeitlich und räumlich variieren. Der höchste Anteil des gelösten organischen Kohlenstoffs war an allen Messstellen im Sommer zu finden. Aufgrund der saisonalen Veränderungen in der Anteilsverteilung kann vermutet werden, dass verstärkter Vegetationswachstum und Residenzzeit des Wassers, hohe Temperaturen, und verstärkter photooxidativer Abbau zu einer höheren Proportion des gelösten organischen Kohlenstoff Anteils während des Sommers führen. Des Weiteren wurde ein signifikanter Unterschied der $\delta^{13}\text{C}$ -Werte aller Fraktionen erfasst. Die $\delta^{13}\text{C}$ -Werte waren am niedrigsten während der Sommerphase und stiegen während Herbst und Schneeschmelze an. Dennoch sollte die Interpretation des Abbaus basierend auf $\delta^{13}\text{C}$ mit Vorsicht durchgeführt werden, weil verschiedener molekularer Verbindungen, Vegetationsbedeckung, und klimatischen Faktoren zu einer Variation der $\delta^{13}\text{C}$ -Werte führen können. $\delta^{13}\text{C}$ kann ebenfalls als Tracer genutzt werden, um organische Stoffflüsse zu verfolgen. In der vorliegenden Studie haben $\delta^{13}\text{C}$ -Werte gezeigt, dass die Abflusswasser hydrochemisch nah verwandt waren mit den Oberflächenwassern der Lagg-Zone.

Das abschließende **Kapitel 8** fasst die Hauptergebnisse zusammen und enthält Empfehlungen für zukünftige Studien. Diese Studie unterstreicht, dass eine Prognose über die Reaktion von Mooren auf den Klimawandel einer integrierten Herangehensweise

bedarf. Hierfür und für eine umfassende Gesamtkohlenstoffbilanz ist ein Verständnis der verschiedenen Prozessebenen des Kohlenstoffkreislaufes erforderlich, welches auch Studien über DOM berücksichtigen sollte.

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VI Abbreviations and symbols

C: carbon

C: concentration

CDOM: colored dissolved organic matter

DOC: dissolved organic carbon

DOM: dissolved organic matter

kDa: kilodalton

L: liter

mg: milligram

n: number

OC: organic carbon

Pg: petagram

RMSE: Root mean square error of prediction.

SD: standard deviation.

SOM: Soil organic matter

SOM: soil organic matter

T: temperature

TFF: Tangential flow filtration.

VII Definitions

Bog: An elevated portion of ombrotrophic peatland that receives water and nutrients exclusively from atmospheric deposition and is isolated from laterally moving, mineral-rich soil water.

DOC: Dissolved organic carbon: the total carbon content of the DOM fraction.

DOM: Dissolved organic matter: organic matter that passes through glass fiber filters (GF/F) with a nominal pore-size cut-off of 0.7 μm .

Fen: A minerotrophic peatland that receives water and nutrients both from the atmosphere and groundwater inputs.

Lagg: A marginal forest swamp area that is located in a topographical depression and receives water surpluses from both the mire and the surrounding mineral soils.

Mire: A wet terrain dominated by living peat-forming plants (Rydin & Jeglum, 2006).

Peatland: Any ecosystem with at least 30 cm peat thickness (includes some wetlands, drained and afforested peatlands).

Wetland: “*Wetlands are areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six meters*” (Ramsar, 1987).

1 Introduction

Even though peatlands cover only 3 % of the earth's land surface, they represent an important terrestrial carbon reserve and have functioned as carbon sinks for many centuries because the rate of plant production generally exceeds the rate of organic matter decomposition in the mires (Post et al., 1982; Clymo 1984; Gorham 1991; Frohking et al. 2011; Yu et al. 2011). In particular, northern peatlands (i.e., boreal and subarctic peatlands) are considered to be important carbon sinks because they store most of the peatland carbon stock. It has been estimated that northern peatlands store between 200 and 621 Pg of carbon (C), and the rate of C accumulation over the last six to eight thousand years has been estimated to be between 16 and 117 g C m⁻² yr⁻¹ (Gorham 1991; Vitt et al. 2000; Turunen et al. 2002, 2004; Gorham et al. 2003; 2004; Roulet et al. 2007; Yu et al. 2010). Moreover, investigation of boreal region is particularly important as this region has a stronger greenhouse gases global warming potential compared with the soils in the tropical and temperate regions (Jungkunst & Fiedler, 2007).

Currently, northern peatlands are viewed as potentially “fragile” carbon stores (Baird et al., 2009) and are considered to be carbon hotspots in terms of their potential impact on climate change (Yu et al., 2011). The coupled physical-biogeochemical soil model by Ise et al. (2008) demonstrated that a 4 °C temperature increase could potentially lead to a 86 % loss of soil organic carbon from the deep peat and a 40 % loss from the shallow peat. However, whether climate warming and other anthropogenic effects will result in changing peatlands from long-term carbon sinks to carbon sources is still a matter of debate (e.g., Gorham 1991; Limpens et al. 2008; Nilsson et al. 2008; Kayranli et al. 2010). Recent studies have suggested that peatlands can act as both sinks and sources of carbon, and the published estimates of annual carbon fluxes vary among sites (Whiting 1994; Neumann et al. 1994; Shurpali et al., 1995; Waddington & Roulet 1997; Shurpali & Verma 1998; Hobbie et al. 2000; Schneider et al., 2012). For instance, Shurpali et al. (1995) demonstrated that a boreal peatland can act as a CO₂ source during a dry year but a sink during a following wet year, while Schneider et al. (2012) showed that ombrogenous hummocks and lawns were sources of CO₂ in contrast to the hollows and minerogenous lawns that acted as CO₂ sinks within the same peatland. Thus, both

temporal and spatial variation exists in a given peatland's ability to act as a carbon sink.

Peatlands, particularly northern peatlands, are sensitive to changes in temperature and precipitation patterns, which in turn affect hydrology, biochemistry and rate of biomass accumulation (Pastor et al. 2003; Reddy & Delaune 2008; Limpens et al. 2008; Dorrepaal et al. 2009; Yu et al. 2011). In northern peatlands, the multiyear C balance measurements have shown high inter-annual variability in response to hydrological and temperature conditions, changing from weak C sources to strong C sinks, with site averages C uptake rates ranging from 20 to 30 g C m⁻² yr⁻¹ (Yu et al., 2011).

For a complete evaluation of the carbon balance of a peatland, it is necessary to combine the results of lateral and vertical carbon flux measurements. Vertical fluxes have been adequately described in many studies, but information on lateral fluxes is relatively sparse. Thus, the lack of information concerning the transport of lateral carbon species within peatlands and their release into fluvial systems represents a major obstacle to gaining a better understanding of both local and global carbon cycles (e.g., Dawson et al. 2002a; Roulet et al. 2007). The lateral carbon losses from terrestrial to fluvial systems are typically dominated by dissolved organic carbon (DOC), and most temperate and boreal catchments export between 1 and 13 g C m⁻² yr⁻¹ (Hope et al. 1994; Laudon et al. 2004; Ågren et al. 2007; Nilsson et al. 2008), which can represent a significant part of the annual net carbon uptake. The exclusion of lateral carbon losses from the carbon budget can lead to severe carbon budget miscalculations. Nilsson et al. (2008) measured losses via lateral fluxes of up to 37 % of the annual net CO₂-C uptake of a boreal oligotrophic minerogenic mire. The investigation of lateral carbon loss is particularly important because it was also demonstrated that the DOC exported from the terrestrial systems and the carbon dioxide outgassing from freshwater ecosystems are underestimated, which can lead to errors in carbon budget estimation (Worrall et al., 2007; Battin et al., 2008; Lauerwald et al., 2012). Thus, to reduce error in the estimates, the total DOC exports from the terrestrial system into streams should be monitored.

DOC is also used to quantify dissolved organic matter (DOM) because it represents the bulk of DOM (~67%) (Bolan et al., 2011). DOM is primarily produced and accumulated near the surface as a result of the decomposition of living peat surface plants and the supply of recently produced organic matter. DOM includes a small proportion of

identifiable, low-molecular-mass compounds such as carbohydrates and amino acids, and a larger proportion of complex, high-molecular-mass compounds (Thurman, 1985; Rydin & Jeglum, 2006; Koch et al., 2008; Reddy and Delaune, 2008). Peatlands are net exporters of DOM to adjacent aquatic systems and represent a major source of the terrestrial organic matter losses to rivers, lakes and oceans (Urban et al., 1989). Therefore, any alterations in DOM fluxes from peatlands will lead to a significant regional redistribution of terrestrial carbon (Limpens et al., 2008).

Apart from redistributing parts of the carbon budget between terrestrial and fluvial systems, DOM affects the solubility, transport and toxicity of heavy metals and organic pollutants because of its high cationic binding capacity (Carter & Suffet 1982; Chiou et al. 1986; Driscoll et al., 1988; McKnight et al. 1992; Haitzer et al. 2002; Scott et al., 2003; Pokrovsky et al. 2006). It can influence light attenuation (Zafiriou et al., 1984; Williamson 1994; Scott et al. 2003; Karlsson et al., 2009), the acidification of aquatic systems (Oliver et al., 1983), and ecosystem nutrient availability (Carpenter et al., 2005) as well. DOM acts also as a substrate for CH₄ and CO₂ production (Wolf 2009). High DOM content can enhance bacterial proliferation in drinking water systems (Bolan et al. 2011) and can cause the formation of toxic by-products when surface water is chlorinated for drinking (Nokes et al., 1999; Sadiq & Rodriguez, 2004; Chowdhury et al., 2009). Consequently, DOM content is used as an indicator of drinking water quality. In addition to the negative health effects of DOM, its presence gives water a yellow color, which is aesthetically unappealing and causes problems for the drinking water industry (Minear and Amy, 1996). Therefore, determining DOM concentrations is crucial for understanding and tracing geochemical, ecological and environmental processes (Aiken et al., 2002; Jaffé et al., 2008; Cory et al., 2011).

Many researchers have observed a significant increase in DOM concentrations in lakes and streams in Europe and North America in recent decades (Freeman et al. 2001a; Hejzlar et al. 2003; Worrall et al. 2004a,b; Evans et al. 2005; Skjelkvåle et al. 2005; Monteith et al. 2007). The increase in DOM has raised concerns that organic-carbon stocks in the soil are beginning to destabilize due to climate and land use changes and may eventually return to the atmosphere, strengthening the greenhouse effect (Freeman et al., 2001a). Although there have been increasing efforts to characterize peatland DOM

fluxes in the northern hemisphere, these geochemical measurements have largely been restricted to North America (Charman et al. 1994; Moore 2003), the United Kingdom (Freeman et al. 2001a; Worrall et al. 2002; Evans et al. 2005), and Fennoscandia (Ågren et al., 2008; Dyson et al., 2011). In particular, observations of DOM, the spatial and temporal variability of DOM, and other components of water chemistry are relatively scarce in the boreal regions of Russia (Inisheva & Inishev, 2001; Pokrovsky et al., 2005; Shvartsev et al., 2012), where more than 50 % of the world's boreal peatlands are located (Apps et al. 1993). It was previously demonstrated that extrapolation from thoroughly investigated boreal regions, such as Canada, can lead to the misestimation of carbon stocks in Russia (Zubrzycki et al., 2012). Thus, due to vegetative, hydrological and geological dissimilarities between sites, it is not feasible to extrapolate DOM dynamics from the well-explored regions to a global prediction of DOC flux. Furthermore, in contrast with other peatlands, such as the relatively homogenous upland peatlands in the UK, Russian peatlands demonstrate a strong heterogeneous pattern in regard to CO₂ emission rates (Schneider et al., 2012). The variation in the CO₂ emissions of heterogeneous areas of a given peatland can also vary in regard to the quantity and quality of DOM, further impacting biochemical processes. Therefore, the lack of qualitative and quantitative characteristics of DOM for remote areas, such as the boreal region of Russia, represents a major gap in our understanding of both local and global carbon cycles.

Furthermore, most of the studies do not consider the potential feedback to climate change in respect of DOM changes from different peatlands sub-units, which could vary because of geological, vegetative and hydrochemical differences. In peatlands, the importance of small-scale patterning has already been emphasized for vertical fluxes such as CH₄ variation (Baird et al., 2009; Forbrich et al., 2011). Increased methane emissions are evident in the cases of increased water table and anaerobic conditions (Kutzbach et al., 2004; Waddington & Day, 2007; Gažovič et al., 2010). Similarly, during the summer, Wolf (2009) detected a large variability in CH₄ flux that varied from 4.9 to 1,614.2 mg m⁻² d⁻¹ in ombrogenous plots (4.9-676 mg m⁻² d⁻¹ in hummocks, 88.2-1,614.2 mg m⁻² d⁻¹ in lawns) to 6.7-1,269.27 mg m⁻² d⁻¹ in the minerogenous sites (6.7-657.64 mg m⁻² d⁻¹ hummocks; 78.5-1,269.27 mg m⁻² d⁻¹ in lawns; 150.3-1038.5 mg m⁻² d⁻¹ in flarks). A

variability in DOM was also detected by Wolf (2009). However, in the study by Wolf (2009) only a limited amount of DOM samples were taken.

The seasonal variation in water chemistry over a bog-fen gradient has mostly been described with respect to the relationship between vegetation patterns and chemical gradients such as pH and ion levels (Glaser et al., 1990; Bubier, 1995; Boeye and Verheyen, 1994; Vitt et al., 1995; Bragazza & Gerdol, 1999a,b; Tahvanainen et al., 2002). Fewer studies have focused on presenting the effect of peatland spatial heterogeneity on the quantity of DOM (Moore, 1987; Marin et al., 1990; Dalva & Moore, 1991; Waddington and Roulet, 2000). Moreover, there has been little recent attention on the function of the marginal transitional (lagg) zones in regulating lateral fluxes in mire complexes. Lagg zones are located in topographic depressions and collect runoff from ombrotrophic bogs and the adjacent, often forested areas with mineral soils (Howie & Tromp-van Meerveld, 2011). Because of their location in a boundary area, lagg zones have transitional chemical properties are influenced by both ombrotrophic bogs and adjacent mineral soils (Howie & Tromp-van Meerveld, 2011). Within the mire complex, the lagg zone can be considered a biogeochemical hotspot, defined as an area exhibiting "disproportionately high reaction rates relative to the surrounding matrix" (McClain et al., 2003). Lagg zones similarly to the wet forested zones (Christiansen et al., 2010; Fiedler et al., 2005; Grunwald et al., 2012) can act as strong CH₄ producer. Thus, it can be hypothesized that during baseflow, the lagg zone may act as a hotspot and serve as the main pathway for lateral mass balance transfer across the mire. Due to biogeochemical and hydrological differences among lagg, fen and bog, it can be expected that they represent separate units with distinctively different DOM concentrations and may react differently to climate change. Appearance of these zones within a single mire complex is typical to large peatlands areas in Russia. Thus, they should be considered separately for monitoring and predicting future change in the boreal region.

In a study that quantified the long-term mineralization as well as greenhouse gas (CO₂ and CH₄) production, Knoblauch et al. (2013) demonstrated that labile pools of organic matter are mineralized faster than stable pools. Thus, to identify the future fate of DOM and evaluate its susceptibility to decomposition it is important to investigate its qualitative characteristics (Worrall et al., 2007). To quantify the terrestrial DOM

biodegradability is also important for the evaluation its influence on aquatic systems. This is particularly important because the conventional perception that terrestrial organic matter is recalcitrant and contributes little to the aquatic metabolism was contradicted (Battin et al., 2008). Thus, it can be hypothesized that due to the heterogeneous nature of peatlands, the DOM they produce may vary in structure among sites and exhibit different proportions of compounds with different molecular sizes. Molecular size is the primary determinant of the chemical, physical and biological characteristics of DOM (Lou and Xie, 2006). Thus, molecular weight and size are very important characteristics for determining the chemical activity and future fate of DOM.

The processes and factors that control the transport of organic carbon within peatlands and the hydrological processes that deliver organic carbon to fluvial systems are not well understood (Holden 2005; Limpens et al. 2008). Thus, it is particularly important to study the hydrologic pathways that link the different components of the catchment and play a key role in governing the DOC flux (Dalva & Moore, 1991). However, tracing lateral carbon fluxes can be particularly challenging in northern peatlands due to the diffuse and indistinct streams and outflows (Waddington & Roulet, 1997), which require complex measurements strategies.

The foregoing identifies several important knowledge gaps. Hence, this study has following objectives:

- (1) To evaluate the methods for rapid, accurate and portable DOC measurements to monitor DOM dynamics in remote areas (see Chapter 4).
- (2) To obtain a better understanding of the spatial and temporal variability of DOM in the heterogeneous landscape of a typical boreal mire in Northwest Russia. Specifically, differentiate the hydrochemical gradients that drive DOM production at different sub-units of the mire, and improve our understanding of important reservoirs of terrestrial organic carbon in remote boreal mires and better anticipate potential responses to climate change and its influence on aquatic systems (see Chapter 5).
- (3) To quantify DOM concentrations and export during the most important annual hydrological event, which is the period of snowmelt. Additionally, determine the main hydrological pathways in the studied boreal mire-forest-river landscape and

investigate the regulating factors that control DOM concentrations and export during snowmelt (see Chapter 6).

- (4) To characterize the relative proportion and nature of two pools of organic compounds, the truly dissolved and colloidal fractions. These contribute to the seasonal and annual DOM concentrations in the river, bog, fen, forest and outflow waters and are needed to evaluate the fate of DOM and gain new insights into the processes that control the generation, transport and transformation of DOM in boreal mires (see Chapter 7).

2 State-of-the-art

2.1 Peatlands and Mires

2.1.1 General characteristics

Peatlands include any ecosystem with at least 30 cm of peat thickness (Gorham 1991). Peat consists of partially decomposed plant matter, and the carbon (C) density per unit area is within the range of ~50 - >500 kg C m⁻² (Frolking et al., 2011). Therefore, peatlands are also considered 'organic wetlands' and are probably the most widespread group of wetlands (Charman, 2002). In addition to wetlands with 30 cm or more of peat, peatlands can include drained and afforested peatlands. Alternatively, where wet terrain is dominated by living peat-forming plants, the ecosystem may be classified as a mire (Rydin & Jeglum, 2006). Peatlands are characterized not only by their high soil organic matter (SOM) content but also by water logging, low oxygen, alkalinity, nutrient content, and low decomposition rates due to decreased microbiological activity, which favors peat accumulation. Peatlands support many rare and unique species and have educational and recreational value. Moreover, because of their slow decomposition rates, peatlands conserve information about past cultures and climatic and environmental conditions (Steinmann et al., 2006; Kaislahti et al., 2010).

2.1.2 Peatland structure: Acrotelm and catotelm

Peatlands generally consist of two vertical layers, acrotelm and catotelm, which differ considerably in their physical, hydrological and biological characteristics (Clymo, 1984; Charman, 2002). The acrotelm is an upper (10-50 cm deep), mostly aerobic layer (i.e., aerated at least seasonally) that has both a high hydraulic conductivity and a high soil organic matter decomposition rate (Clymo, 1984). The catotelm is a lower anaerobic layer that is generally more humid and darker. Compared with the upper layer, the catotelm is much thicker and has a lower conductivity and much lower decomposition rates (Clymo, 1984). The higher rate of microbial activity and decomposition in the upper layers is supported by the high activity of specific enzymes. For example, the 3-glucosidase, phosphatase and sulphatas enzymes were found to exhibit the highest activities at depths of less than 10 cm (Freeman et al., 1995).

2.1.3 Peatland types

Peatlands are not homogenous ecosystems and can include a mosaic of different landscapes. Generally, peatlands can be separated into two main types: bogs and fens. Bogs are isolated from groundwater and obtain all their water from atmospheric precipitation, while fens are fed both from the atmosphere and groundwater and/or overland runoff. The pH at fen sites is generally higher because it is influenced by the groundwater, and the underlying geology makes this influence highly variable (Charman, 2002). Compared with fens, bogs are more acidic and contain fewer nutrients, because they are nourished only through precipitation (Charman, 2002; Rydin & Jeglum, 2006). Due to their nutrient and hydrological differences, bogs and fens have distinctively different plant community compositions. Bogs and poor fens are typically dominated by *Sphagnum* moss and ericaceous dwarf shrubs, in contrast with rich fens, where herbaceous and graminoid vascular plants and brown mosses (Bryidae) are abundant (Tahvanainen, 2004). It has also been suggested that the bog term should refer to peatlands with low alkalinity, dominated by *Sphagna*, conifers and/or various ericaceous shrubs, while fen term for peatlands which are less acidic, more alkaline and dominated by graminoids, brown mosses, taller shrubs, and coniferous and /or deciduous trees (Bridgham et al., 1996).

Based on their water source, sites can also be separated into minerogenous (water enters the peatland from the surrounding mineral soil) and ombrogenous (receives water only from precipitation) peatlands (Rydin & Jeglum, 2006). Based on the source of nutrients, two trophic classes can be differentiated: minerotrophic (nourished by mineral soil groundwater) and ombrotrophic (nourished by precipitation and airborne dust) (Rydin & Jeglum, 2006).

2.1.4 Peatlands and climate change

Peatlands are currently considered carbon sinks and have been contributing to global cooling (Frolking & Roulet, 2007). However, there are many uncertainties in both the stocks and fluxes of peatlands, and it is still unclear whether they will continue to function as carbon sinks under future climate change and anthropogenic influences (e.g. Gorham, 1991; Limpens et al., 2008; Nilsson et al., 2008; Kayranli et al., 2010). Despite their importance in the carbon cycle and their potential positive feedback on climate change, peatlands are not explicitly included in global climate

models (IPCC 2007). Recent studies have suggested that peatlands can act as both sinks and sources of carbon, and estimates of the annual carbon fluxes vary among sites (Neumann et al., 1994; Whiting, 1994; Waddington & Roulet, 1997; Shurpali & Verma, 1998; Hobbie et al., 2000).

Peatlands are particularly sensitive to changes in temperature and precipitation patterns, which, in turn, affect their hydrology, biochemistry and biomass accumulation rates (Limpens et al., 2008; Reddy and Delaune, 2008; Yu et al., 2011). For instance, if the water table drops and the peatland surface dries (e.g., through drainage or climate change), then a greater percentage of the peat is available for oxidation, which, consequently, can become a net source of carbon dioxide (CO₂) and will release more DOC (Charman, 2002; Holden, 2005). In the case of an increased water table and anaerobic conditions the peatlands act as a net source of methane emissions (CH₄) (Kutzbach et al., 2004; Waddington & Day, 2007; Gažovič et al., 2010).

Northern peatlands are especially vulnerable to climate change because greater than average predicted temperature increases are anticipated at higher latitudes in most global change models over the next several decades (Dorrepaal et al., 2009; Pastor et al., 2003). Northern regions may also experience decrease in soil moisture (IPCC 2007). Dorrepaal et al. (2009) reported that in a subarctic peatland, approximately 1 °C of warming increased the total ecosystem respiration rates, on average, by 60 % in spring and 52 % in summer. It has been acknowledged that the net effect of climate warming on northern peatland carbon stocks will depend not only on carbon losses but also on carbon gains from new plant production (Dorrepaal et al., 2009).

To evaluate the response of peatlands to climate change, it is important to estimate the complete carbon budget. There are several pathways for carbon uptake and release from peatlands (Figure 2.1). Uptake includes sequestration from the atmosphere through photosynthesis, inputs of dissolved organic and inorganic carbon from rainwater and the intake of inorganic carbon from the weathering of underlying strata and lateral inflows. Carbon release proceeds along lateral and vertical pathways.

Vertical pathways include respiration of CO₂ and CH₄ through organic matter decomposition; while laterally carbon is transported from peatland to stream waters in the form of particulate organic matter (POC), dissolved organic carbon (DOC), or dissolved inorganic carbon (DIC), which is composed of CO₂ and CH₄ as well as

bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions (Cory et al., 2011). DIC content in the surface and pore-waters of peatlands is generally low due to low pH, thus DIC tends to contribute a smaller proportion of the total carbon content (Neal & Hill, 1994). In contrast to DIC, DOC is the main component of the lateral carbon fluxes (e.g. Dawson et al., 2002a; Roulet et al., 2007). DOC also constitutes the bulk of the DOM (~67 %). Therefore, DOM is often quantified by its carbon content and is referred to as dissolved organic carbon (DOC) (Bolan et al., 2011).

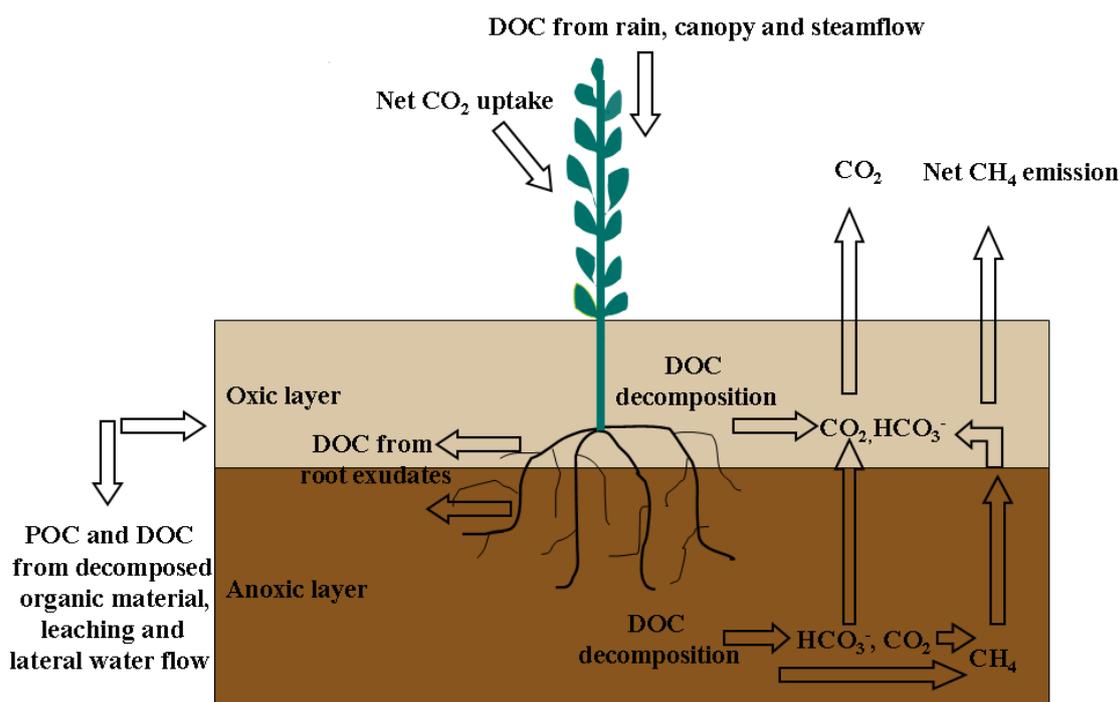


Figure 2.1 A schematic representation of the carbon cycle in peatlands. The main component of the lateral carbon fluxes is in the form of DOC. Under a high water table, CH_4 emissions increase, whereas under a low water table, CO_2 emissions increase.

Vertical fluxes have been adequately described in many studies, but there is a relative lack of information concerning lateral fluxes. In particular, quantitative information concerning DOC, the main carbon component in the lateral carbon flux, is missing, which can lead to significant errors in carbon budget estimates (e.g. Dawson et al., 2002a; Roulet et al., 2007). Therefore, estimating DOC fluxes and understanding the regulating factors that control DOC production and quality are essential for the prediction of possible responses to global change and further effects on biochemical cycles.

2.2 Dissolved organic matter (DOM)

2.2.1 Operational definition and origin of DOM

The operational distinction of DOM is based on the filter pore cutoff size, which, according to standard classification, is 0.2-0.45 μm (e.g. Evans et al., 2005; Koehler et al., 2009; Olefeldt and Roulet, 2012). In practice, however, this separation is commonly performed with carbon-free glass fiber filters (GF/F) that have a nominal pore-size cut-off of 0.7 μm (Rostan & Cellot, 1995; Yacobi et al., 2003; Retamal et al., 2007; Cory et al., 2011; Griffin et al., 2011). GF/F filters are widely preferred for filtration because they are binder-free and do not add any contamination to the sample (Cory et al., 2011). The amount of particulate organic matter (POM) that passes through the filter has been identified as a minor source of error in studies focusing on the quantity and quality of the bulk-carbon content (Cory et al., 2011). In natural systems, the main sources of DOM are the partial decomposition and/or exudation of soil organic matter and living organisms, including plants, animals, and soil microorganisms (Thurman 1985; Moore & Dalva 2001; Charman 2002; Wilson & Xenopoulos 2008).

2.2.2 Importance of DOM

The importance of DOM is presented in a schematic diagram (Figure 2.2). Fluxes of DOM not only redistribute carbon between terrestrial and fluvial systems but can also affect biogeochemical cycles and influence the physical and chemical characteristics of an aquatic ecosystem. For instance, DOM affects the solubility, transport and toxicity of heavy metals and organic pollutants (Carter & Suffet 1982; Thurman 1985; Chiou et al. 1986; Driscoll et al., 1988; McKnight et al. 1992; Haitzer et al. 2002; Scott et al. 2003; Pokrovsky et al. 2006); it controls downstream bacterial production (Wetzel, 1992) and aquatic net primary production (Carpenter & Pace, 1997); and it regulates the photochemistry of natural waters (by absorbing visible and ultraviolet radiation) (Zafiriou et al., 1984), the acidification of fluvial systems (Oliver et al., 1983), and ecosystem nutrient availability (Stewart & Wetzel 1981; Qualls & Haines 1992; Carpenter et al. 2005). The partially retained DOM is a source of CO_2 and CH_4 and as Pastor et al. (2003) have demonstrated an exponential increase in CO_2 and CH_4 emissions coincides with an increased retention (inputs > outputs) of DOC from boreal peatlands.

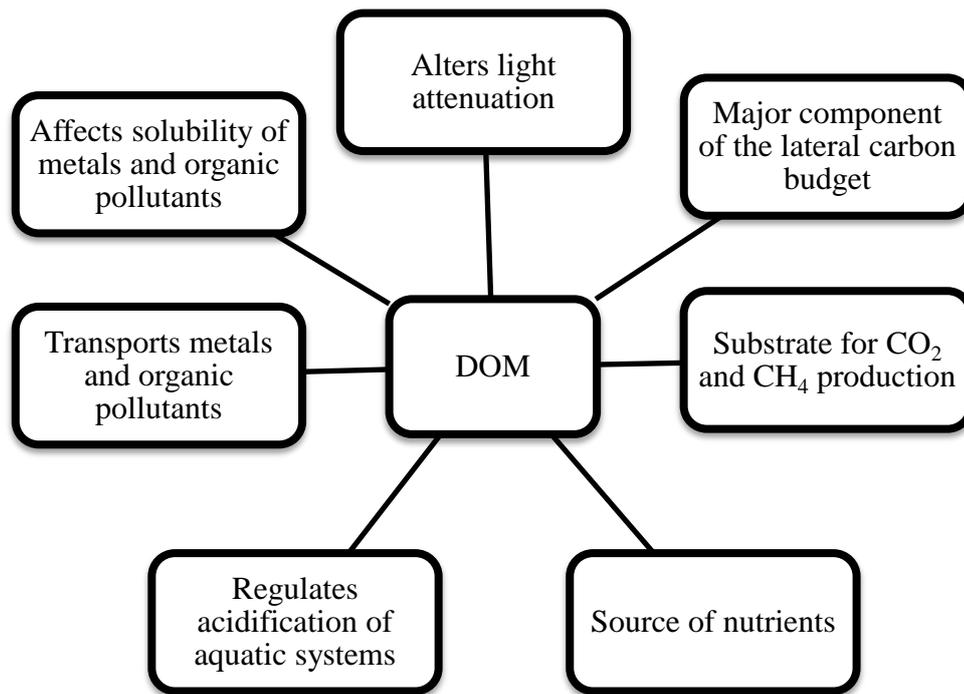


Figure 2.2 Schematic representation of importance of dissolved organic matter.

DOM can lead to bacterial proliferation within drinking water distribution systems (Bolan et al., 2011). The removal of DOM is a major expense for water distribution systems because, in addition to resulting in low aesthetic quality and bacterial proliferation, it leads to formation of potential carcinogens when it reacts with disinfectants (such as chlorine) during water treatment (Nokes et al., 1999; Sadiq & Rodriguez, 2004).

2.2.3 Structure of DOM

DOM is composed of a heterogeneous, complex mixture of organic compounds with variable molecular sizes, masses, and reactivity (Thurman 1985; Cory et al. 2011), and there is no defined structure for DOM because many different colloids and ions with variable characteristics pass through the filters. Therefore, the DOM samples from different locations vary in their relative distributions of molecular size fractions. Figure 2.3 provides a schematic structure of DOM.

DOM constituents can be roughly separated into two main groups: humic and non-humic substances. Non-humic substances include carbohydrates in the form of simple sugars, hemicellulose, cellulose, proteins, or other low molecular mass

compounds (Reddy and Delaune, 2008). Non-humic substances are more labile and degrade faster than humic substances (Marschner & Kalbitz, 2003).

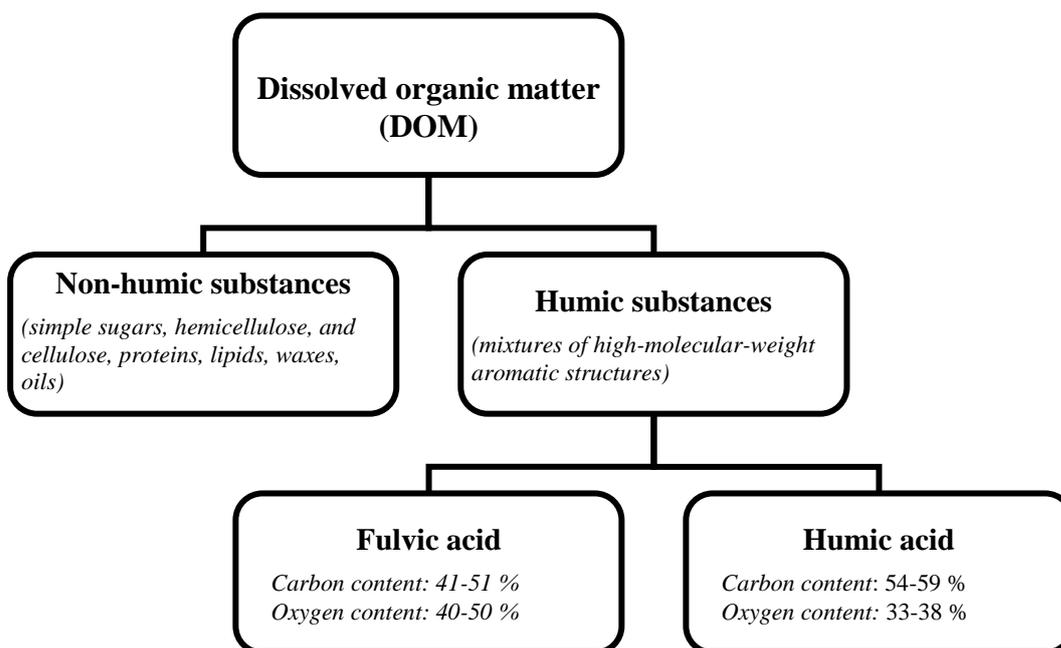


Figure 2.3 Schematic representation of DOM structure. Humic substances are a major component of DOM. Non-humic substances are more bioavailable than humic substances. Humic acids are predominatly consist of humic and fulvic acids. Humic acids are more mature than fulvic acids (Rydin & Jeglum, 2006; Reddy and Delaune, 2008).

Humic substances are heterogeneously colored complexes and are products of the decomposition of plant and animal material that include a large number of different molecules, such as aromatics, acid functional groups, and several oxygenated functional groups, such as carboxyl, phenolic hydroxyl, and carbonyl structures (Reddy and Delaune, 2008). The COOH group of humic substances contributes to most of the acidity, compared to other functional groups (Reddy and Delaune, 2008). Humic substances are a major component of DOM and POM (Rydin & Jeglum, 2006). Humic substances can be divided into two classes: humic and fulvic acids, which are the two dominant components of DOM (Thurman, 1985; Rydin & Jeglum, 2006). It is estimated that 50-75 % of the dissolved fraction is comprised of fulvic and humic acids, which, in turn, represent 5-10 % of the total anion load in streams and rivers (Thurman, 1985). The elemental composition of both groups is similar, with oxygen and carbon as their major elements, but they differ in their molecular mass range, with fulvic acids having lower molecular mass (Barreto et al., 2003; Yacobi et al., 2003). The carbon content of fulvic acid is lower (41-51 %) than that of humic acid (54-59 %) (Reddy and Delaune, 2008). In contrast, the oxygen content of fulvic acid is higher (40-50 %) than that of humic acid (33-38 %) (Reddy

and Delaune, 2008). Humic acids are the result of a more advanced stage of decomposition and are more mature than fulvic acids (Reddy & Delaune 2008; Grayson & Holden 2012). The specific light absorption of humic acid is higher than that of fulvic acid (Carder et al., 1989). Based on its chemical characteristics, bulk DOM can be also separated into hydrophobic and hydrophilic fractions (Qualls & Haines, 1991). Hydrophobic fractions include humic and aromatic substances, tannins, polyphenols, and complex amino acids, while hydrophilic fractions include small carboxylic acids, carbohydrates, free proteins, fats, and peptides (Qualls & Haines, 1991).

There are structural differences between terrestrially vegetation derived and microbially derived DOM. Humic substances of terrestrial origin are derived from lignin and have relatively large amounts of aromatic carbons with a high phenolic content. Because lignin does not contain nitrogen, terrestrially vegetation derived DOM has high C/N ratios. Alternatively, microbially derived humic substances have relatively high N contents and low aromatic carbon and phenol concentrations.

Measurements of the qualitative properties of DOM, such as molecular mass and light absorption characteristics can yield important information about the chemical reactivity and mobility within a sample (Chin et al., 1994). DOM with low humic and aromatic content is more bioavailable (Kaushal and Lewis, 2005). Low molecular mass and high molecular mass fractions exhibit different biogeochemical properties. Low molecular mass compounds are generally considered more easily degradable by bacteria than more complex high molecular mass compounds (Tranvik & Jørgensen, 1995).

2.2.4 Current level of knowledge on DOM dynamics

During the last decades, many researchers have reported a significant increase in DOM concentrations in lakes and streams in Europe and North America (Freeman et al. 2001; Hejzlar et al. 2003; Worrall et al. 2004a,b; Evans et al. 2005; Skjelkvåle et al. 2005; Monteith et al. 2007). The increase in DOM raises concerns that carbon stocks are beginning to destabilize and may eventually return to the atmosphere and strengthen the greenhouse effect (Freeman et al., 2001a).

Several studies have attributed the alterations in DOM concentrations to several large-scale environmental trends: increasing air temperature (Freeman et al.,

2001a), changes in acidification (Clark et al. 2005; Evans et al. 2006; de Wit et al. 2007; Monteith et al. 2007) and discharge rates (Pastor et al. 2003), elevated CO₂ levels (Freeman et al., 2004), nitrogen deposition (Findlay, 2005), and land use changes (Garnett et al., 2010). A schematic representation presented in Figure 2.4 summarizes the main factors that affect DOM dynamics.

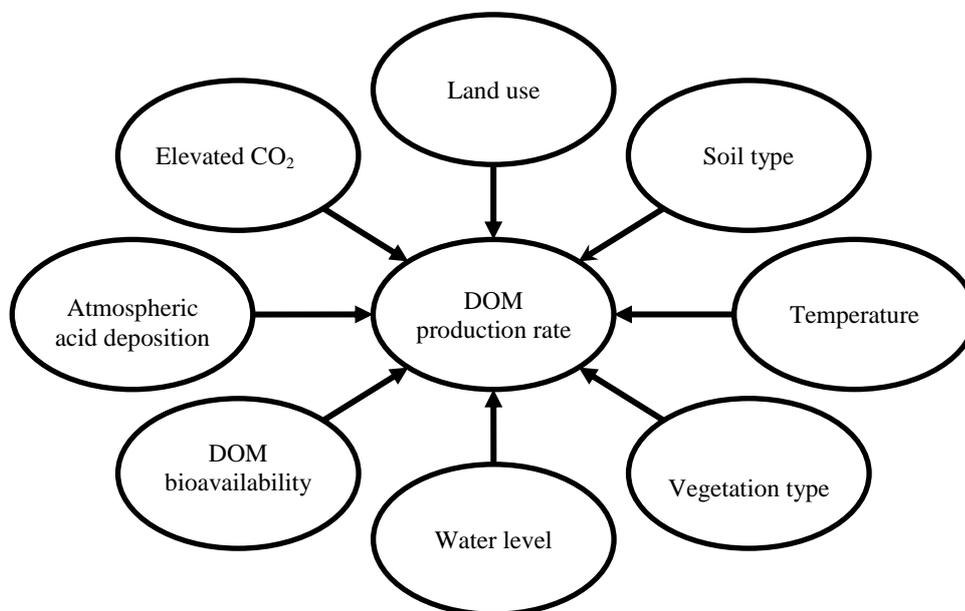


Figure 2.4 Summary of the main factors affecting DOM production rate.

Several factors may result in quantitative DOM changes. Higher temperatures increase the rate of organic matter decomposition, which, in turn, may increase DOM production. Laboratory trials observed 1.3-1.7-fold increase in the DOC concentration under Q10 conditions (i.e., an increase in the net DOC production rate as a consequence of increasing the temperature by 10 °C) (Christ & David, 1996; Freeman et al., 2001a; Moore & Dalva, 2001). Clark et al. (2009) differentiated between oxic and anoxic DOC releases and recorded an increased rate of net DOC production as a consequence of Q10 of 1.84- and 3.53-fold under anaerobic and aerobic conditions, respectively. However, temperature alone did not fully explain the DOM changes (Worrall et al., 2004a, 2004b; Clark et al., 2005; Evans et al., 2006).

Freeman et al. (2004) proposed that rising atmospheric CO₂ may be driving increased DOC due to elevated net primary productivity and an increased root exudation of DOC, which may be connected to increased vascular plant cover as opposed to mosses. Alternatively, Evans et al. (2006) argued that the current increase in atmospheric CO₂ could only account for a 1.2 %, 4.2 % and 5.2 % increase in the

DOC release from a bog, fen and riparian peatland, respectively, in the UK (Evans et al., 2006). Worrall & Burt, (2004) demonstrated that the observed upward trend in DOC can only be explained by changes in biogeochemical processes that are triggered by drought, which may be accentuated by local factors such as land management.

Another mechanism, the “enzymatic latch”, was proposed to explain the increased DOM concentrations following periods of drought (Freeman et al., 2001b). Under high water table conditions, organic matter decomposition is inhibited because the activity of phenol oxidase is strongly restricted in the absence of oxygen (Freeman et al., 2001b). Therefore, if the water table drops, the enzyme activity increases, which, in turn, destroys the phenolic compounds that repress the hydrolase activity (Freeman et al., 2001b). After the destruction of the phenolic compounds, decomposition can continue even after the water table increases (Freeman et al., 2001b). Because drought stimulates pre-existing enzymes, it is possible to observe decomposition and DOC increases without significantly increased microbial activity (Freeman et al., 1996). In contrast, Preston et al. (2011) found that drought caused a decrease in DOC concentrations and pH and an increase in sulfate (SO_4^{2-}) and base cation concentrations. Clark et al. (2005) explained the decrease in DOC concentrations during droughts through the release of sulfates from the oxidation of inorganic/organic sulfur that is stored in the peat, which leads to a decrease in pH and an increase in ionic strength. It is known that DOC solubility and content increases with increasing pH because of the deprotonation of carboxylic groups (Thurman, 1985; Scheel et al., 2007). Therefore, DOC solubility is suppressed by high soil water acidity and ionic strength (Clark et al. 2005; Evans et al. 2006; de Wit et al. 2007; Hruska et al. 2009). The impact of acid deposition on DOC solubility is greatest in the pH 4-5 range (Thurman 1985), and an increase in soil water pH of 0.5 units could cause a 50 % increase in DOC (Tipping & Woof, 1990). For every twofold increase in SO_4^{2-} , DOC suppression was found to increase by a factor of 1.4 in the soil solution (Evans et al., 2006). Therefore, in contrast to assumptions that DOC increases because of climatically driven forces, several studies have suggested that DOC concentrations are trending toward preindustrial levels as a result of decrease in acid deposition (e.g., a decline in the sulfate and sea salt loads) which led to DOC solubility increase (Evans et al. 2006; Vuorenmaa et al. 2006; Monteith et al. 2007). Thus, for detecting climatically driven changes, it can be important to investigate sites without anthropogenic acid deposition.

Various alternate factors have been reported to drive changes in DOC concentrations in peatland surface waters. Worrall et al. (2008) reported that the most important variable explaining the DOC flux was the runoff from catchments. They detected no evidence of increased production after severe droughts. Similarly, Pastor et al. (2003) demonstrated that the DOC budget was controlled predominantly by changes in discharge and runoff rather than any effect of warming or the position of the water table level on DOC concentrations. The increase in DOC in response to increased nitrogen content is controversial. For example, Findlay, (2005) found that enrichment with nitrogen increased DOC production, while Evans et al. (2008) reported inconsistent responses to increased nitrogen content. In conclusion, no single factor can explain the observed trends, and it may be unreasonable to look for a common driver behind the widespread increase in DOC concentrations because studies are conducted at different scales across divergent sites (Preston et al., 2011).

2.2.5 Qualitative and quantitative characterization of DOM

Generally, the DOM content is measured through the oxidation of organic matter to CO₂, which is typically performed using high-temperature combustion or persulfate oxidation (Aiken et al. 2002; Cory et al. 2011). Chapter 4 presents detailed information concerning the available methods, including information about the rapid high-resolution spectrophotometric absorbance measurements for DOC content determination. Several methods can be used to characterize the quality of the DOM, e.g., size fractionation (see Chapter 7 for further details) and spectrophotometric and stable carbon isotope measurements.

Spectrophotometric measurements

Relatively simple absorbance measurements are used to investigate qualitative DOM changes because the optical characteristics of DOM are controlled by physical, chemical, and biological processes (Jaffé et al., 2008). Humic and fulvic acids, which are two dominant components of DOM, absorb light in different amounts at different wavelengths, as their characteristics differ.

From the absorbance values at specific wavelengths and the ratios for the qualitative description of DOM shown in the

Table 2.1, the most widely employed absorbance coefficients for qualitative DOM description are the following ratios: A_{254}/C_{DOC} (or SUVA_{254}), A_{254}/A_{365} (E2/E3), and A_{465}/A_{665} (E4/E6).

Table 2.1 List of single wavelengths and absorbance coefficients for the qualitative characterization of DOC by absorption measurements.

λ (nm), ratios	Correlating characteristics	References
260	aromaticity, hydrophobic fraction	Chen et al. 2002; Dilling & Kaiser 2002
280	aromaticity, molecular mass	Chin et al. 1994; Peuravuori & Pihlaja 1997; Hentschel et al. 2008
285	aromaticity	Kalbitz et al. 1999; Kalbitz et al. 2000
300	aromaticity	McKnight et al., 1997
365	molecular mass	Bragazza et al. 2006
400	color determination, CDOM determination	Hongve & Åkesson 1996; Hautala et al. 2000; Watts et al. 2001; Worrall et al. 2002; Wallage et al. 2006; Kallio et al. 2008; Wallage & Holden 2010
410	color determination (index of dissolved humic substances)	Hongve & Åkesson 1996; Hautala et al. 2000
420	color determination	Hongve & Åkesson 1996
436	characterize substances with ketone and quinone functional groups; color determination	Hongve & Åkesson 1996
450	color determination; aromaticity	Hongve & Åkesson 1996; McKnight et al. 1997
456	color determination	Hautala et al. 2000;
465	color determination	Hongve & Åkesson 1996; Hautala et al. 2000; Wallage et al. 2006
490	color determination	Hautala et al. 2000
665	color determination	Wallage et al. 2006
250/365 (E2/E3)	negatively correlated to the molecular size/mass of DOC	De Haan & De Boer 1987; De Haan 1993; Peuravuori & Pihlaja 1997; Helms et al. 2008; Olefeldt & Roulet 2012, Olefeldt et al., 2012
254/365	negatively correlated to the molecular size/mass of DOC positive correlation with bacterial productivity*	Dahlén et al. 1996; Berggren et al. 2007*; Ågren et al. 2008; Baker et al. 2008
254/ C_{DOC} (SUVA_{254})	aromaticity	Abbt-Braun & Frimmel 1999; Weishaar et al. 2003; Wickland et al. 2007; Ågren et al. 2008; Haei et al. 2010; Inamdar et al. 2012; Olefeldt & Roulet 2012; Olefeldt et al., 2012
254/410 (E2/E4)	negatively related to the molecular size/mass	Andersen et al. 2000; Baker et al. 2008
465/665 (E4/E6)	degree of humification; aromaticity, molecular size	Thurman 1985; Worrall et al. 2002; Wallage et al. 2006; Zaccone et al. 2009; Helms et al. 2008; Grayson & Holden 2012
275-295nm /350-400nm	negatively correlated to the average molecular mass	Helms et al. 2008; Inamdar et al. 2012
Spectral slope	a steep spectral slope indicates low molecular mass material or decreasing aromaticity.	Blough & Vecchio 2002; Spencer et al. 2007

To measure the maximum absorbance for all aromatic structures, absorbance at 254 nm is most often used (Peuravuori & Pihlaja, 1997). Although the 280 nm wavelength may not represent the maximum absorbance for all aromatic structures present in the DOC, in some studies, it was chosen because the $\pi\text{-}\pi^*$ electron transition occurs in this UV region for phenolic arenes, benzoic acids, aniline derivatives, polyenes, and polycyclic aromatic hydrocarbons with two or more rings (Peuravuori & Pihlaja 1997).

The specific absorption coefficient at 254 nm (A_{254}/C_{DOC} or SUVA_{254} , $\text{L mg}^{-1} \text{m}^{-1}$) is calculated by dividing the absorbance at 254 nm (m^{-1}) by DOC concentration (mg L^{-1}). SUVA_{254} is positively correlated with the aromaticity of carbon (Weishaar et al., 2003) and can be used for the determination of the bioavailability of organic matter, as DOC with a high aromatic carbon content has lower bioavailability than that of aliphatic compounds. However, a similar aromatic carbon concentration does not necessarily imply a similar reactivity. For example, results from experiments involving the reactivity of DOC with specific chemical reactants, such as TMAH and NaOCL, indicate variable reactivity for samples with similar SUVA_{254} values (Weishaar et al., 2003). These results show that the chemical compositions of samples with similar average properties, as determined by absorbance or molecular mass analyses, may be very different (Weishaar et al., 2003).

The spectral slope is often used as a proxy for colored DOM (CDOM) molecular mass and to track the sources and changes (i.e., biological and chemical modification) of CDOM (Blough & Vecchio 2002, Twardowski et al. 2004). Thus, because the specific light absorption of humic acid is higher than that of fulvic acid, the slope of the line characterizing a decline of absorption with increasing wavelength is greater for fulvic than humic acid (Carder et al. 1989). Thus, A_{254}/A_{365} or A_{250}/A_{365} are inversely related to molecular mass (De Haan, 1993) because of the stronger light absorption by high-molecular-mass CDOM at longer wavelengths (Helms et al., 2008). Using the A_{254}/A_{365} absorbance ratio, researchers demonstrated that wetland-derived DOC had a higher average molecular mass than forest DOC (Ågren et al., 2008). Additionally, in boreal Sweden, bacterial productivity has been found to be positively correlated with A_{254}/A_{365} (Berggren et al., 2007). The absorbance ratio of A_{465}/A_{665} (E4/E6) is related to the molecular size of humic substances. Progressive humification is indicated by decreasing E4/E6 ratios (Peuravuori & Pihlaja, 1997), and the E4/E6 ratio for humic acids is usually <5.0 ; the ratio for fulvic acids ranges

from 6.0 to 8.5 (Thurman 1985). This ratio was also reported to be inversely related to CDOM aromaticity (Chin et al., 1994; Piccolo et al., 1992).

However, no one specific spectrophotometric measurement explains absolutely the qualitative DOM variation in fluvial systems; the measurement of multiple optical parameters is therefore recommended (Spencer et al. 2007). Additionally, absorbance values can be subject to interference from various factors. For instance, a change in pH and cation concentrations lead to structural changes in the DOM linked to solvent pH ionic strength and complexing cations of the solvent (Chin et al. 1998; Myneni et al. 1999; Weishaar et al. 2003; Baalousha 2006). Specifically, Chin et al. (1998) documented the expansion of marine DOM polymer gels across a pH gradient with an abrupt transition to a larger size at a pH of approximately 6. Pace et al. (2011) proposed that the key process causing pH-related change in DOM optical properties is shifts in the structural conformation of at least a portion of the pool. At low pH, DOM polymers and colloids are condensed with tight packing, limiting the exposure of chromophores to light, whereas at a higher (more alkaline) pH, polymers and colloids expand, exposing chromophores to light (Pace et al., 2011). This effect results in greater initial light absorption and faster photo-bleaching. In addition, Weishaar et al. (2003) observed relatively minor differences in UV absorption for most samples between pH 2.0 and 8.6, consistent with the small effect expected from the protonation of carboxyl groups with decreasing pH. Similar results were found by Spencer et al. (2007), who observed that pH has little impact on spectrophotometric measurements within natural levels typically observed in freshwaters. The low dependency of UV absorbance on pH within the range of 2-8.6 means that, within this range, it is unnecessary to adjust the pH to a constant value to compare results between samples (Weishaar et al., 2003). However, Weishaar et al. (2003) acknowledged that the preservation of DOM samples involving acidification might often result in a $\text{pH} < 2$, and it should not be assumed that acidified samples are generally appropriate for UV absorbance determinations.

Absorbance can also be affected by the presence of nitrate (NO_3^-) and iron (Fe^{3+}) (Weishaar et al. 2003). The effect of NO_3^- is significantly lower than that of Fe^{3+} . For example, an absorbance at 254 nm of 10^{-4} m^{-1} requires $> 100 \text{ mg L}^{-1} \text{ NO}_3^-$ but only $1 \text{ mg L}^{-1} \text{ Fe}^{3+}$ in solution (Weishaar et al., 2003). Therefore, interference from NO_3^- is generally limited to groundwater or samples that have been contaminated with NO_3^- , possibly by the addition of nitric acid or other compounds

containing NO_3^- (Weishaar et al., 2003). Precautions should be taken if the iron content is more than 0.5 mg L^{-1} , whereas iron concentrations within a range of $0\text{-}0.5 \text{ mg L}^{-1}$ only add $0\text{-}4 \times 10^{-4} \text{ m}^{-1}$ to the absorbance at 254 nm and, thus, do not interfere with the characterization of DOM using absorbance measurements (Weishaar et al., 2003).

Another spectrophotometric method for DOM qualitative characterization is by fluorescence measurements (excitation emission matrix-EEM) with subsequent principal component analysis and parallel factor - PARAFAC analysis, which allows the detection of different DOM components (e.g., humic and fulvic acids) based on their peaks in the EEMs (McKnight et al., 2001; Cory & McKnight, 2005; Stedmon et al., 2005).

Stable carbon isotope ($\delta^{13}\text{C}$) analysis

Isotope fractionation, which results in changes in the $\delta^{13}\text{C}$ values, can be used as a parameter to distinguish qualitatively different fractions of DOM. Isotope fractionation is termed as alterations in the partitioning of heavy and light isotopes between a source substrate and the product(s) (Dawson et al., 2002b). The isotope fractionation caused by a biological process is also called isotope discrimination (Dawson et al., 2002b). Fractionation occurs because the lighter isotope (with a lower atomic mass) develops bonds that are more easily broken (Dawson et al., 2002b). In contrast to lighter isotopes, heavy isotope bonds require more energy before the bonds can break (Fry, 2008). Thus, for a given amount of energy, more light isotope bonds will break than heavy isotope bonds, and the difference in reaction rates gives the fractionation (Fry, 2008). Many biochemical and biogeochemical processes discriminate against the heavier ^{13}C isotopic species and break slightly weaker ^{12}C - ^{12}C bonds, which leads to the production of ^{13}C -depleted organic matter (Dawson et al., 2002b; Sharp, 2006). For instance, preferential light carbon uptake by C-3 plants leads to a net fractionation of $\sim 20 \text{ ‰}$ between the atmospheric carbon dioxide and plant biomass (-28 ‰) (Fry, 2008). Generally, vegetation derived organic matter is similarly or slightly enriched in ^{13}C compared to the dominant vegetation cover (Fry, 2008). Thus, terrestrial C-3 plant-produced organic matter has a value close to -27 ‰ (Van Dongen et al., 2002).

Isotope ratios have been used as indicators of decomposition processes because changes are assumed to demonstrate the isotope fractionation by preferential microbial consumption of ^{12}C (e.g., Novák et al., 1999; Kalbitz & Geyer, 2002). Thus,

it can generally be suggested that $\delta^{13}\text{C}$ analysis may allow the degree of degradation to be determined, as degradation increases the $\delta^{13}\text{C}$ fraction of the remaining carbon due to a microbial metabolic preference for lighter isotopes. Alternatively, Ekblad et al. (2002) observed that microbial $\delta^{13}\text{C}$ discrimination during respiration is minor. Moreover, several studies have shown that $\delta^{13}\text{C}$ can be changed during peat formation because of the vegetation difference (Hornibrook et al., 2000; Pancost et al., 2003) and microhabitat conditions such as moisture (Farquhar et al., 1989; Loisel et al., 2010) and temperature (Jedrysek & Skrzypek, 2005; Skrzypek et al., 2007). Thus, relying solely on $\delta^{13}\text{C}$ results to explain decomposition is disputable.

Further details concerning the qualitative characterization of DOM by tangential flow filtration, $\delta^{13}\text{C}$ values and spectrophotometric properties are presented in Chapter 7.

3 Study site

3.1 Geographic location

The study was conducted in the Komi Republic, which is located in northwestern Russia (Figure 3.1). The republic borders the northern Urals to the east and the Timan Ridge and the upper basins of the Vychegda River to the west. The study site, the Ust-Pojeg forest-mire complex (~25 km²), is located approximately 60 km southeast of the city of Syktyvkar (61°56'N, 50°13'E), the capital of the Komi Republic, and it lies between the Pojeg River to the west, the Vychegda River to the north and forested area to the east and south (Figure 3.2).

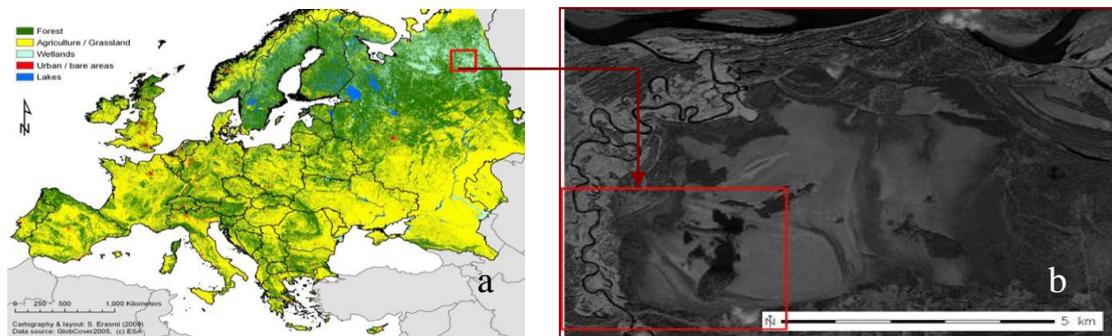
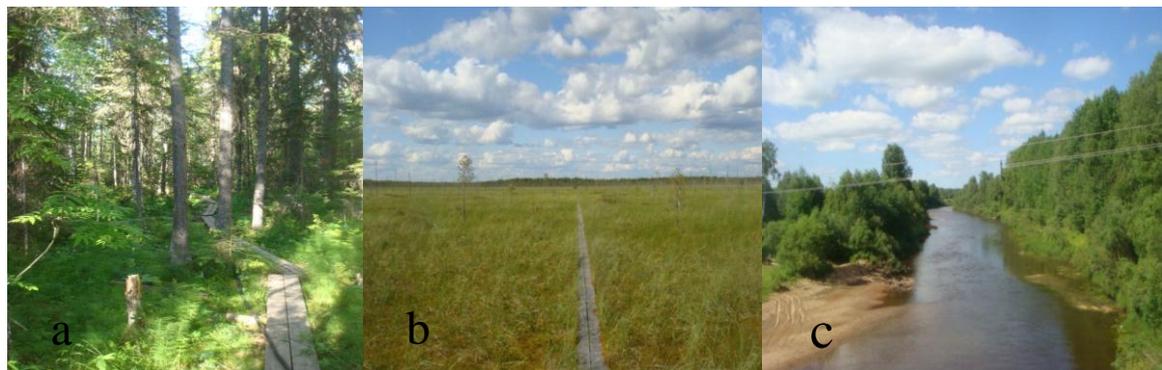


Figure 3.1 Location of the study site. The study site is located at the Ust-Pojeg forest-mire complex (61°56'N, 50°13'E) in the Komi Republic, Russia. Source: a. Globecover 2005, b. Quickbird.



3.2 Landform patterns and hydrologic gradients

This study site contains a mosaic of different landscape units based on its nutritional and hydrologic state and vegetation; it consists of forest, minerogeneous (fen), ombrogenous (bog), and transitional forest-mire (lagg) zones (Figure 3.3).

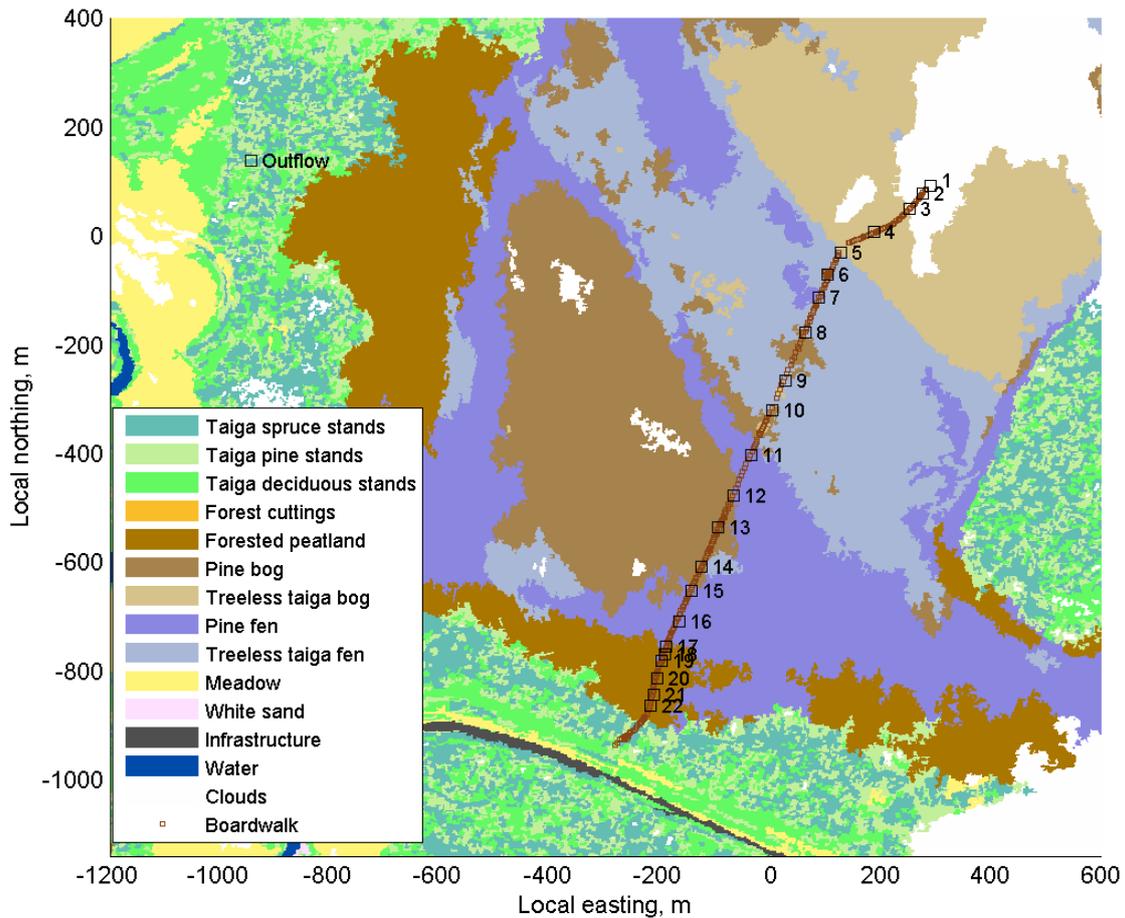


Figure 3.3 Overview of the various land classes at the study site, showing a boardwalk (~1.2 km) spanning the forest-mire complex. Based on its nutritional and hydrological state and the composition of the vegetation, the mire consisted of ombrogenous (bog: point 1-5, 12-14), minerogeous (fen: point 6-11, 15-16), and transitional forest-mire (lagg: point 17-22) zones. Map source: Susiluoto & Virtanen, unpublished data).

The forest zone slopes in the direction of the mire (Figure 3.4), thus inflow of mineral-rich ground - and surface water into the mire can be expected. The lagg zone is situated in a topographical depression that is adjacent to the forest. The lagg receives water from both the mire and the forest, and buffers the bog and fen zones from the influence of mineral-rich water inflow from the forested site. The treeless bog zone is located in the center of the mire. The treeless fen zone is located between the bog and the lagg. The surplus water from the study site drains into the Pojeg River. The water flow direction is from the southeast to the northwest. Based on water table measurements taken on July 3, the depth to groundwater at the forest's edge was greater than 42 cm, while in the forested zone the groundwater table was detected at a depth of 85 cm. All the sites within the mire zone were water saturated in July; however, the water table later dropped. For instance, at the fen site water table

decreased by 0.16 m between July 9 and August 24, 2010. After August 24 water table started to increase and in the end of November increased by 0.12 m.

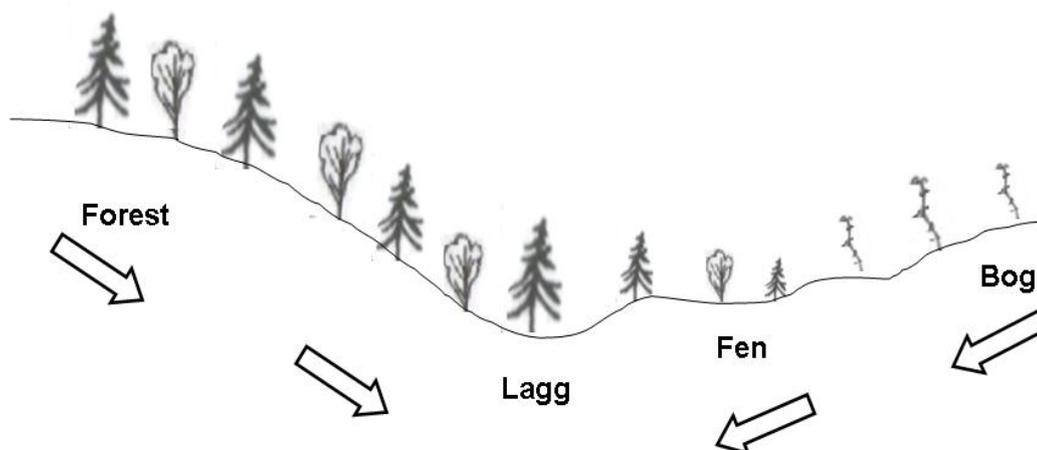


Figure 3.4. Schematic representation of the surface relief of the study site. The mire consists of minerogenous fen and lagg zones, as well as ombrogenous bog sites. The arrows show the direction of water flow. The lagg zone drains through a forested channel towards the nearby Pojæg River.

The microtopographic features at the bog site are uneven and include a well-developed pattern of hummock-lawn-hollow. Hummocks are the most elevated features in the peatland microrelief, ranging from 25 to 50 cm above the surrounding lawn surface with diameters of up to 2.5 m. The lawn areas have intermediate water table positions between the hummocks and the hollows. Hollows have the highest water table relative to the peat surface. Most of the hollows are located in the minerogenous areas rather than the ombrogenous areas due to the relatively higher water tables.

3.3 Climate data

The site's climate is boreal, humid and continental. The mean annual temperature was 1.1 °C for the period 1960 - 2011, and the mean annual precipitation at Syktyvkar for the period of 1973 - 1998 was 585 mm. The coldest month is January, and the warmest is July. The mean monthly air temperature is above 0 °C from April through October. Permanent snow cover begins at the end of October and continues until the beginning of April. The mean air temperature for 2010 and 2011 is presented in Figure 3.5.

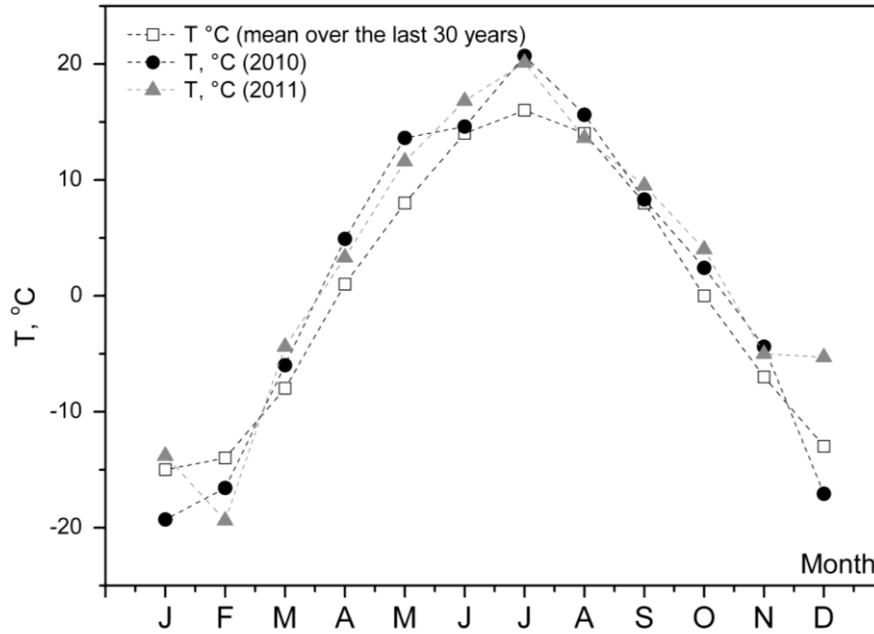


Figure 3.5. Mean air temperature during the last 30 years 2010 and 2011 at the Syktyvkar meteorological station. Sources: www.tutiempo.net and www.meteoinfospace.ru. The coldest month is January, and the warmest month is July. The mean monthly air temperature is above 0°C from April through October. The permanent snow cover period starts at the end of October and lasts until the beginning of April.

The sampling period included an extremely hot summer in 2010, which was one of the two warmest summers during last 510 years (Barriopedro et al., 2011). Extremely high daytime temperatures were recorded in many eastern European cities, including cities in this region, and Western Russia was in the center of the heat wave. Weekly to monthly anomalies exceeded the 1970-1999 mean by 10 °C (Barriopedro et al., 2011). The elevated temperatures lasted from late July until the second week of August.

3.4 Geology and soil description

The Ust Pojeg mire was formed in a former floodplain area. The inception of peat began in the flat part of the basin more than 8,000 years ago (Pluchon, 2009). Based on C¹⁴ dating of the basal peat, this mire experienced paludification, with a slow replacement of the forest by peatland at a rate of approximately 2.6 m per century over the last millennium (Pluchon, 2009). At the Ust-Pojeg mire-forest complex, six soil profiles were obtained for soil characterization and classification (Table 3.1) (Langer, 2012). According to the classification of the World Reference

Base for Soil Resources, the soils in the forest zone were classified as Folic Gleysols (Eutric, Greyic and Arenic).

Table 3.1 Soil classification across the site (Sampling date: July, 2010). Source: Langer (2012).

N	UTM coordinates	World Reference Base for Soil Resources	German classification	Soil Taxonomy of USA
1 Forest	39V 459072 6866165	<i>Folic Gleysol (Eutric, Greyic, Arenic)</i>	Podsoliger (Feuchtrohhumus) Gley (p(mr)GG)	Typic Endoaquepts
2 Forest	39V 459081 6866182	<i>Folic Gleysol (Eutric, Greyic, Arenic)</i>	Podsoliger (Feuchrohhumus) Gley(p(mr) GG)	Typic Endoaquepts
3 Forest	39V 459597 6867169	<i>Folic Gleysols (Eutric, Greyic, Arenic)</i>	Podsoliger (Feuchrohhumus) Gley (p(mr) GG)	Typic Endoaquepts
4 Lagg	39V 459088 6866257	<i>Folic Lignic Fibric Histosol</i>	Niedermoor, HN	Hydric Haplohemists
5 Fen	39V 459402 6867051	<i>Folic Fibric Histosol</i>	Hochmoor (HH)	Fabric Frasiwassits
6 Bog	39V 459461 6867100	<i>Folic, Fibric Lignic Histosol</i>	Hochmoor	Typic Haplowassists

The average depth of the peat was ca. 1.5-2 m (Langer, 2012). Carbon and nitrogen concentrations of the organic layer in the forested zone showed typical values for boreal landscape, and were within the range of 221-484 g kg⁻¹, and 13-17 g kg⁻¹, respectively (Langer, 2012). Within the mire site the peat carbon content demonstrated the following gradient lagg (350-460 g kg⁻¹) < fen (460-480 g kg⁻¹) < bog (470-580 g kg⁻¹) (Langer, 2012).

3.5 Vegetation

The Ust-Pojeg mire-forest complex had distinctively different vegetation zones (forest, lagg, fen, and bog). A vegetation survey in the forest area was completed following the Joasis Braun-Blanquet method (Braun-Blanquet, 1964). There was a strong link between water chemistry, hydrology, and vegetation across the forest-lagg-fen-bog gradient. Tall shrubs and trees occurred in the forested zone and declined in the direction of the mire. Within the mire, the tree population declined from lagg (59 %) to fen (34 %) to bog (7 %). Additionally, tree vitality declined from lagg to bog. The dominant tree species in the forest was *Picea obovata*, while in the regeneration stage, *Pinus sylvestris* dominated (Table 3.2). The tree heights in the forest were 13-17 m, considerably higher than in the mire, where the heights were

2.5-3 m. The shrub layer dominated the forest plant population, with 55 % canopy coverage per 100 m², and it was primarily composed of *Vaccinium vitris-idea*.

Table 3.2 Tree cover in the forest zone.

Trees in the forest zone			
Species	Total (n/100 m ²)	Mean height (m)	Mean circumference (cm)
<i>Betula pendula</i> , <i>Betula pubescens</i>	6	13.75	60.67
<i>Picea obovata</i>	22	17.25	59.5
<i>Pinus sylvestris</i> (Regeneration)	58	0.75	n/a
<i>Abies sibirica</i> (Regeneration)	2	1.12	n/a

The lagg zone was more afforested compared to the forest zone and was mainly covered by *Pinus sylvestris* (11 %), *Picea obovata* (14 %), *Betula pendula* (24 %) and *Alnus incana* (51 %) (Table 3.3).

Table 3.3 Tree cover in the lagg zone

Trees in the lagg zone		
Species	Total (n/100 m ²)	Mean height (m)
<i>Picea obovata</i>	8	2
<i>Betula pendula</i>	12	1.5
<i>Alnus incana</i>	27	2.1
<i>Pinus sylvestris</i>	6	4

In the forest the herb and moss layers had roughly equal coverage, at 25 % and 20 % per 100 m², respectively. The dominant herb species was *Equisetum sylvaticum* (10 %), while *Pleurozium schreberi* (20 %) was the dominant moss species. The predominant shrub, herb and moss species within the peatland zone are presented in Table 3.4.

The herb and shrub layers in the lagg zone are characterized by a dense cover of *Menyanthes trifoliata* (80 %), which indicates a greater supply of nutrients. Other abundant species included *Sphagnum magellanicum*, *Pleurozium schreberi*, *Comarum palustre* and *Ledum palustre*. The fen was mostly dominated by *Sphagnum fuscum* (45 %) and *Scheuchzeria palustris* (35 %). The dominant moss vegetation cover in the ombrogenic bog was *Sphagnum magellanicum* (hummocks) and *Sphagnum fuscum* (lawns). The transitional zone between the bog and fen was dominated by *Carex rostrata*.

Table 3.4 Species distribution in shrubs, herbs, and mosses layers across the mire.

Lagg		Fen	
<i>Menyanthes trifoliata</i>	80%	<i>Sphagnum fuscum</i>	45%
<i>Sphagnum magellanicum</i>	30%	<i>Scheuchzeria palustris</i>	45%
<i>Ledum palustre</i>	10%	<i>Andromeda polifolia</i>	5%
<i>Pleurozium schreberi</i>	10%	<i>Betula nana</i>	1%
<i>Comarum palustre</i>	5%	<i>Eriophorum vaginatum</i>	1%
<i>Carex paupercula</i>	2%	<i>Menyanthes trifoliata</i>	1%
<i>Oxycoccus microcarpus</i>	1%		
<i>Vaccinium oxycoccus</i>	1%		
<i>Equisetum palustre</i>	1%		
Bog (hummock)		Bog (lawn)	
<i>Sphagnum magellanicum</i>	85%	<i>Sphagnum fuscum</i>	95%
<i>Chamaedaphne calyculata</i>	45%	<i>Scheuchzeria palustris</i>	35%
<i>Andromeda polifolia</i>	25%	<i>Carex paupercula</i>	5%
<i>Sphagnum angustifolium</i>	15%	<i>Eriophorum vaginatum</i>	5%
<i>Eriophorum vaginatum</i>	5%	<i>Sphagnum magellanicum</i>	5%
<i>Betula nana</i>	1%	<i>Chamaedaphne calyculata</i>	3%
<i>Oxycoccus microcarpus</i>	1%	<i>Andromeda polifolia</i>	2%
<i>Drosera rotundifolia</i>	1%		
<i>Polytrichum strictum</i>	1%		

Microrelief features had a distinct vegetation cover. Hummocks were covered by dwarf shrubs, herbs and *Sphagnum* mosses (*Andromeda polifolia*, *Chamaedaphne calyculata*, *Sphagnum magellanicum*, *Sphagnum angustifolium*, *Pinus silvestris* and *Betula nana*). Lawns were covered with aerenchymatous plants, herbs and *Sphagnum* species (*Eriophorum vaginatum*, *Carex paupercula*, *Scheuchzeria palustris*, *Menyanthes trifoliata*, *Vaccinium oxycoccus*, *Sphagnum angustifolium*, *Sphagnum fuscum*, *Sphagnum subsecundum* and *Sphagnum magellanicum*); and hollows were only sparsely vegetated with aerenchymatous plants (*Sphagnum angustifolium*, *Sphagnum magellanicum*, and *Scheuchzeria palustris*) (Schneider et al., 2012).

3.6 Peatland utilization in the Komi Republic

Generally, peatlands in the Komi Republic are widely used for agricultural purposes. Several products (such as hay for domestic animals and vegetables and potatoes for human consumption) are cultivated in the peatlands. It is estimated that approximately 0.6-0.8 million tons of peat are harvested annually for energy generation (Alekseeva, 2000). The peatlands in Komi are also used for the collection of berries and medicinal plants. The main berries collected in the Komi Republic are cranberry (*Vaccinium oxycoccus*) and cloudberry (*Rubus chamaemorus*). Many peatlands in Komi are protected for scientific, recreational and water stabilizing

purposes as well as for the protection of rare plants (e.g., *S. rubellum* and *Calliergon reichardsonii*) and animals (e.g., *Grus grus*, *Cygnus Cygnus*, and *Haliaeetus albicilla*) (Alekseeva, 2000). The peatland where the current study was conducted was solely used for berry and mushroom collection by the local people.

4 Application of high-resolution spectral absorbance measurements for the determination of the dissolved organic carbon contents of surface and soil-pore waters in remote areas.

4.1 Abstract

Accurate quantification of dissolved organic carbon (DOC) in surface and soil-pore waters is crucial for understanding changes in water resources under the influence of climate and land use changes. Sampling and laboratory analysis of DOC contents at a sufficient frequency are especially difficult to achieve for natural DOC sources like the extensive boreal and arctic mires due to their remoteness. Therefore, the goals of this chapter are (1) to investigate the performance of a portable, high-resolution UV-visible light spectroscopic method for determining the DOC content of water samples and (2) to compare existing DOC measurement techniques. The study indicates that high-resolution spectroscopic measurements provide a simple, fast, robust and non-destructive method for measuring DOC content. These measurements are of short duration (< 1 minute), and the sample analysis is portable, rendering this method particularly advantageous for in-situ investigations at remote field locations. The study also demonstrates that if absorbance rates at specific wavelengths are used as proxies for DOC concentration, it is necessary to create site-specific calibration models that include more than one wavelength to achieve the optimal explanatory power and accuracy of the proxy-based DOC quantification. -It is suggested that for long-term DOC measurements, changes in watercolor and absorbance spectra should be periodically calibrated against DOC measurements using conventional laboratory methods based on high-temperature combustion or wet oxidation.

4.2 Introduction

Recent efforts have been made to qualitatively and quantitatively characterize dissolved organic matter (DOM), and several methods are available to determine the main component of DOM, i.e., the absolute dissolved organic carbon (DOC) concentrations. Typically, the DOC content is determined by measuring the oxidation of organic matter to CO₂, which is generally accomplished using high-temperature combustion or persulfate oxidation (Aiken et al. 2002, Cory et al. 2011). Currently, special cuvette tests can be used to determine DOC contents using the so-called expulsion method (e.g., LCK 385 and 386 test kits, Hach Lange GmbH, Germany). The expulsion method involves the heat oxidative digestion of organic carbon with sodium peroxydisulfate and a subsequent reaction between the produced CO₂ and lithium hydroxide, which leads to a colorimetric change. The colorimetric change is measured with a spectrophotometer and is interpolated into a DOC concentration.

However, because they require bulky instruments, laboratory space and additional consumables, none of the aforementioned methods can be directly used under field conditions. Such limitations make it particularly difficult to obtain frequent measurements in remote areas (e.g., Russian boreal mires), which generally lack information concerning DOM changes in their surface and soil pore waters. Moreover, these methods only provide information about absolute DOC values; the characterization of DOM quality (e.g., the distribution of molecular sizes and masses within the DOM), which is helpful to promote an improved understanding of DOM turnover dynamics and the environmental controls of these dynamics, cannot be accomplished without additional size fractionation (e.g., the use of tangential flow filtration, chromatographic analysis or characterization with a light-based proxy (absorbance or fluorescent emission)).

Because DOM has distinctive spectrophotometric properties and absorbs a wide range of wavelengths in the UV and visible radiation spectra, a variety of spectroscopic techniques have been proposed to provide information about the bulk content and qualitative characterization of DOM (e.g., McKnight et al., 1997; Weishaar et al., 2003; Baker et al., 2008; Tipping et al., 2009). However, the specific absorbance spectra of different DOM sources vary considerably. Thus, when using spectroscopic measurements as proxies for absolute DOC concentrations, it is

necessary to conduct a local calibration against one of the conventional absolute DOC content determination methods (such as high-temperature combustion or persulfate oxidation). In the absence of site-specific calibration, the absorbance-based determination of DOC concentration can be inaccurately performed due to varying absorbance strengths of the interference of other elements. For example, absorbance measurements at 254 nm can be influenced by dissolved nitrate and iron (Weishaar et al., 2003). Advantageously, measurements made with spectrophotometers generally require a small sample size, and are simple to perform. Due to recent technological developments, several advanced, “off-the-shelf” ultraviolet-visible light (UV-Vis) spectrometers are currently available to determine dissolved organic carbon levels under field conditions (e.g., ProPS-UV, Trios GmbH, Germany; CarboVis, WTW GmbH, Germany; and spectro::lyser, carbo::lyser and multi::lyser, s::can, Austria). The ability to operate an instrument in the field is particularly advantageous for environmental studies conducted in remote areas, which may lack laboratory space and equipment. Although these types of spectrometers are already widely used for effluent water-quality monitoring (Langergraber et al., 2004; Rieger et al., 2004), only a few studies within the geo-ecological sciences have used these probes (e.g., Waterloo et al., 2006; Koehler et al., 2009; Grayson & Holden, 2012; Jeong et al., 2012; Strohmeier et al., 2013).

Considering the importance of DOM in the carbon cycle, its influence on the cycling of other elements and its potential increase under the influence of climate change and other anthropogenic factors, it is particularly important to obtain accurate and rapid estimates of DOC in remote areas. Hence, this study has the five following objectives:

- 1) To evaluate the performance of a portable UV-Vis spectrometer in measuring DOC concentration under in surface and soil pore waters from a boreal mire complex remote field conditions.
- 2) To compare the DOC content derived using high-resolution absorption spectrophotometry with the content derived from other available DOC measurement methods, such as the wet heated persulfate oxidation method and the expulsion method.
- 3) To assay the application of high-resolution absorbance measurements for determining DOC concentration using a local calibration based on multiple

stepwise regression (MSR), partial least-squares (PLS) regression and principal-component regression (PCR).

- 4) To determine the wavelengths conferring an optimal explanatory power for different DOM size fractions that can be used as proxies to determine the DOC contents.
- 5) To identify the specific spectrophotometric absorption properties of DOM in surface and soil pore waters in different land cover types within a boreal mire complex that is typical for the extensive boreal lowland areas in Russia.

4.3 Materials and methods

4.3.1 Study site

The study was conducted on water samples collected from the Ust-Pojeg boreal mire complex (61°56'N, 50°13'E) in the Komi Republic (See Chapter 3 for additional site description details).

4.3.2 Sampling and filtration

Water samples were collected across the peatland from the surface and at different depths (0, 10, 30, and 60 cm, relative to the living moss surface) using perforated stainless-steel tubes ($\text{\O} 1/8''$) and from the surface of the adjacent Pojog River from July 2010 to October 2011. The DOM fraction was separated using pre-combusted glass-fiber filters ($0.7 \mu\text{m}$ GF/F, Whatman, UK) with a glass filtration set (Sartorius, Germany). To precondition the filtration system and avoid contamination from the filter prior to collecting samples, 30 ml of sample water was processed through the filter and then discarded. For further size fractionation, a tangential-flow filtration system was used to divide the overall bulk DOM fraction into two fractions: ≤ 1 kDa and ≤ 10 kDa, according to an established protocol of Schwalger & Spitzy (2009). For tangential flow filtration polyethersulfone cassette membranes (nominal molecular-size cut-offs of 1 kDa and 10 kDa, Omega, Centramate, PALL Corporation, USA) were used. The samples were then acidified with HCl to pH 2 and stored at 4 °C until laboratory analysis.

4.3.3 High-resolution spectroscopic measurements using a portable UV-Vis probe

A submersible, portable multi-parameter UV-Vis probe (spectro::lyser, scan Messtechnik GmbH, Austria) was used for the high-resolution spectroscopic measurements. The probe is a two-beam 256-photodiode UV-visible light (UV-Vis) spectrometer using a xenon lamp as a light source (Langergraber et al., 2003). The two-beam design provides long-term stability of the signal (Langergraber et al., 2003). One beam passes through the sample as a reference, while the other follows a parallel pathway, cancelling out light source fluctuations (Langergraber et al., 2003). All of the controller's electronics, including the data logger, are placed in four tubular

anodized aluminum housings. The length of the probe is approximately 0.6 m. The spectro::lyser measures absorbance across the UV-Vis range (200-750, at 2.5 nm intervals), which are saved in an internal datalogger. This spectrophotometer is able to measure different types of liquids, from ultra-pure water to concentrated wastewater (Langergraber et al., 2003). The measurement range of the probe depends on the optical path length, which can range from 2-100 mm. In this study, a probe with a path length of 5 mm was used, with the manufacturer's estimated range of 0-84 mg L⁻¹ DOC.

Using the manufacturer's default global calibration, it is possible to simultaneously estimate the concentrations of total organic carbon (TOC), DOC and nitrate and the turbidity of the sample. In the global calibration, the DOC concentrations are calculated using multi-wavelength algorithms of a turbidity-compensated absorbance fingerprint. The algorithms were created based on the UV-Vis spectra and reference DOC values (Langergraber et al., 2003). The turbidity-compensated fingerprint is obtained from the turbidity compensation algorithm which is calculated based on the relationship between the wavelength and scattering intensity as a function of the particle diameter, as described by Huber & Frost (1998) (as cited by Langergraber et al., 2003).

4.3.4 Assessment of a portable UV-Vis spectrophotometer's performance for DOC-content estimation

A local calibration was performed for a portable UV-Vis spectrophotometer (spectro::lyser; s::can Messtechnik GmbH, Austria) prior to initiating the main sampling campaign (Figure 4.1.a). First, 30 water samples were collected from different areas of the study site and analyzed with the spectro::lyser. Next, DOC concentration measurements for the same samples were conducted using the wet heated persulfate oxidation method ("wet oxidation") (Aurora Model 1030, O-I-Analytica, USA), and the results were integrated into the local calibration algorithm of the spectro::lyser. Then, to evaluate the performance of the local calibration, 204 samples were analyzed using both the wet oxidation and the spectrophotometric methods. This evaluation was conducted by regressing the DOC-concentration values obtained from the portable UV-Vis spectrophotometer against the values obtained from the wet oxidation technique.

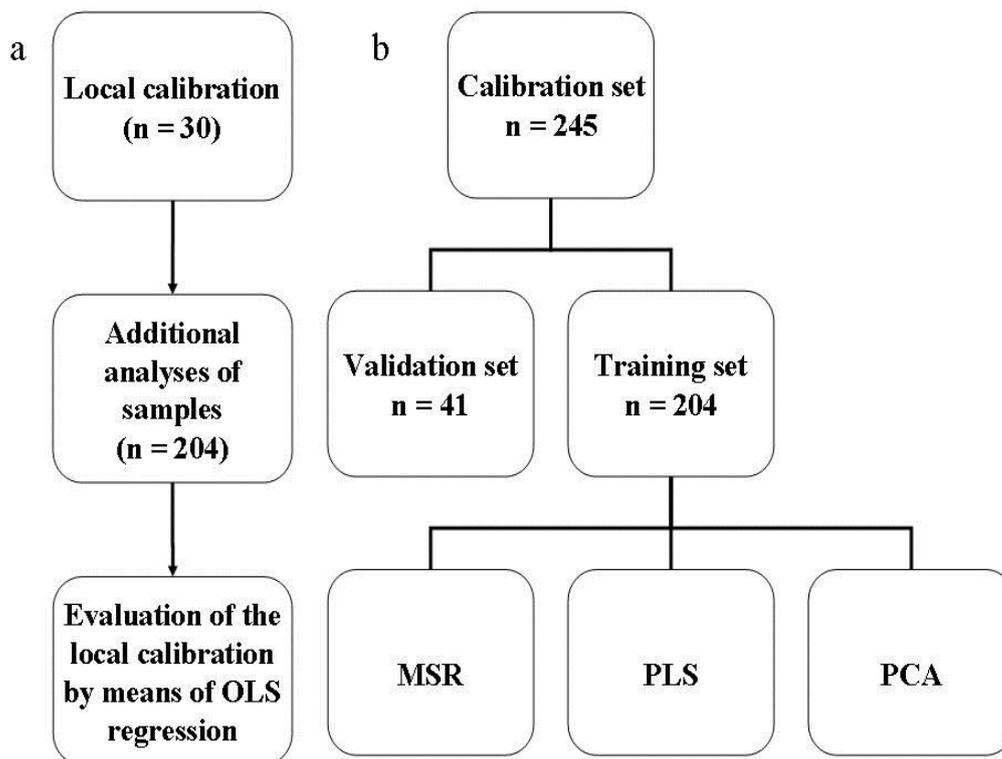


Figure 4.1 a. Local calibration procedure and b. The “inverse calibration” procedure to determine DOC content.

a. The samples were analyzed with the wet oxidation and spectroscopic methods ($n = 30$). Afterward, the values obtained from the wet oxidation method were included into the spectro:lyser’s algorithm for DOC estimation using absorbance values as proxies. The local calibration was evaluated using simultaneous measurements of samples with the wet oxidation and spectrophotometric methods.

b. The “inverse calibration” procedure to determine DOC content. The DOC content of 245 samples was measured using the wet oxidation and spectrophotometric methods. To model the DOC values, 204 samples were used in the multiple stepwise (MSR), partial least-squares (PLS) and principal-component regressions (PCR), while 41 samples were kept aside for validation.

In the wet oxidation method, potassium hydrogen phthalate (KHP, $\text{KHC}_8\text{H}_4\text{O}_4$) was used as a standard (5, 20, 40 mg L^{-1}), analyzed before and after each sample run to ensure that there was no analytical drift within and among sample runs. The standard deviations of triplicate KHP measurements were always lower than 0.4 mg L^{-1} , while the relative standard deviation was $< 3.6\%$, $n = 33$ (standard deviation and relative standard deviation for triplicate measurements (5 mg L^{-1} standard: $< 0.16 \text{ mg L}^{-1}$, $< 3.6\%$, $n = 11$; 20 mg L^{-1} standard: $< 0.23 \text{ mg L}^{-1}$, 1.2% , $n = 11$; 40 mg L^{-1} standard: $< 0.34 \text{ mg L}^{-1}$, 1.3% , $n = 11$).

To check the ability of the spectrophotometer to discriminate between the DOC content and the total organic carbon content, a subset of samples ($n = 51$) was analyzed for differences between the filtered (using 0.7 μm pore-size glass-fiber filters, GF/F, Whatman, UK) and the unfiltered samples. To evaluate the significance

of differences between filtered and unfiltered samples, a paired samples t-test was applied.

4.3.5 Determination of DOC concentration from absorbance values

To determine the DOC content from the absorbance fingerprint, an inverse calibration was performed with “real-life” samples ($n = 245$) (Figure 4.1.b). The term “inverse calibration” indicates that the sample’s concentration is modeled as a function of the absorbance spectrum (Miller and Miller, 2010), whereas in classical calibration, the wavelength-dependent absorbance measurements are a function of the concentration (Centner et al., 1998). The following statistical methods were used for the inverse calibration of the spectrophotometer measurements using the DOC values obtained from the wet-oxidation method as a predictand variable: multilinear ordinary least-squares (OLS) regression with variable selection (i.e., multiple stepwise regression-MSR), partial least-squares regression (PLS), and principal-component regression (PCR). These methods were selected due to their applicability to datasets containing collinear variables and a larger number of variables than observations.

For all of the regressions, only the absorbance values from 250 nm to 740 nm at 2.5 nm intervals were used as input data. Wavelengths shorter than 250 nm were excluded from the analyses because inorganic substances can lead to interference at the lower end of the UV-Vis range (Tipping et al., 1988). Additionally, the following two ratios for the absorbance measurements were added to the predictor variable list: Ratio 1 = A_{465}/A_{665} (E4/E6, humification index) and Ratio 2 = A_{255}/A_{365} (E2/E3, molecular size index). Both of these ratios are widely used for qualitative DOC characterization (De Haan, 1993; Peuravuori & Pihlaja 1997; Ågren et al., 2008).

Stepwise regression was conducted by combining forward selection and backward elimination. At each step, the best predictor variables were consecutively entered into the regression model only if they passed the 5 % significance criterion. Variable addition halted when the inclusion of additional variables failed to lead to the maximization and significant improvement of r^2 . Next, all of the variables included in the regression model were evaluated using the greater than 10 % significance criterion to determine whether any variables needed to be removed from the model (Dugard et al., 2010). The significance was tested with F statistics.

A different approach was used for the PCA and PCR regressions. These techniques reduce the number of dimensions in the data by computing latent linear variables (Varmuza & Filzmoser, 2009; Miller and Miller, 2010). However, the method by which these linear combinations are chosen differs. In PCR, the principal components are generated to describe the maximum variation in the predictors without considering the strength of the relationship between the predictor and predictand variables (Miller and Miller, 2010). In PLS, the variables exhibiting a high correlation with the response variables are given extra weight (Miller and Miller, 2010). The PCR and PCA analyses were conducted with the XLSTAT software package (Addinsoft, Paris, France), while the OLS and MSR analyses were performed with the SPSS 18.0 software package (IBM Corp., Chicago, USA).

An independent subset ($n = 41$) of systematically selected samples from each group and covering the complete range of measured values was separated from the calibration dataset for validation. Additionally, values obtained via the local calibration and default global calibration were compared with the results of the MSR, PCA and PLS.

To evaluate the interference of other chemical species with the DOC absorbance values, a subset of samples was analyzed to determine the iron ($n = 66$) and nitrate contents ($n = 42$). The iron content was measured with an atomic absorption spectrometer (1100B, Perkin-Elmer, USA), while the nitrate content was measured with a cadmium-reduction photometric method (Photometer KFK-3, Zagorsky Optical-Mechanical Plant, Russia). The Pearson correlation coefficient was used to evaluate the correlation between the residuals of DOC content, obtained by subtracting results of the wet oxidation method from the spectrophotometric method (local calibration) from the different calibration functions, and potentially interfering chemical species (SPSS 18.0, IBM Corp., Chicago, USA).

To illustrate the particular wavelength range at which the absorbance values significantly varied among sites, the DOC absorbance spectra were first normalized to the DOC content measured by wet oxidation and were then divided by the mean normalized (to DOC) absorbance spectra of the outflow site (during the summer). To select the most site- and fraction-specific wavelengths, stepwise multiple regressions were performed for different fractions (≤ 1 kDa: $n = 22$; ≤ 10 kDa: $n = 22$), sites (lagg: $n = 17$; bog: $n = 17$) and concentration ranges (low range: $15\text{-}25$ mg L⁻¹, $n = 35$; intermediate range: $26\text{-}36$ mg L⁻¹, $n = 35$; high range: $36\text{-}52$ mg L⁻¹, $n = 35$).

4.3.6 Comparison of DOC-measurement methods

Three methods were evaluated regarding their efficiency in determining a sample's DOC content. DOC contents were measured with high-resolution absorbance immediately following sample collection without acidification or filtration (spectro::lyser, s::can Messtechnik GmbH, Austria). Additionally, filtered and acidified samples were analyzed with a conventional laboratory technique - wet oxidation (Aurora Model 1030, O-I-Analytica, USA). Measurements with cuvette tests (LCK385 and LCK386 test kits, Hach Lange, Germany) using the TOC expulsion method were conducted immediately following sample collection, filtration and acidification. The expulsion method analyses were completed in a two-stage process. First, the dissolved inorganic carbon (DIC) was released from the sample with the help of a shaker. Next, a cuvette was placed into a thermostat (100 °C) for two hours, where it underwent heat oxidative digestion of organic carbon with sodium peroxydisulfate. The heat-oxidative digestion led to carbon dioxide production, which was transferred through a gas-permeable membrane into an indicator cuvette, where it reacted with lithium hydroxide. The indicator color changed based on the carbon dioxide inflow amount. The extent of the color change was measured with a spectrophotometer and converted into a DOC concentration. The wet oxidation method is accepted as highly accurate and is considered the "gold standard" for comparison in this study relative to the other methods. The differences between the methods were tested by a factorial ANOVA with the repeated-measures factorial design and followed by the Tukey HSD post-hoc test (if the sphericity assumption was fulfilled) or the Bonferroni test (if the sphericity assumption was violated). The sphericity assumption was tested by Mauchly's test. The results were considered to be significant at $p < 0.05$. Additionally, statistical comparisons based on RMSE and r^2 values of OLS regressions. All of the aforementioned statistical tests were conducted with the SPSS 18.0 software package (IBM Corp., Chicago, USA).

4.3.7 Evaluation of DOC stability after a storage period

To test whether storage affected the samples' spectroscopic features and changed their DOC content, repeated absorbance and absolute DOC-concentration measurements were made before and after four months of storage at 4 °C at several

wavelengths across the UV-Vis spectrum (250 nm, 280 nm, 330 nm, 632.5 nm, and 737.5 nm) with the portable multi-parameter UV-Vis probe (spectro::lyser, scan Messtechnik GmbH, Austria). A paired samples t-test analyses was used to evaluate the significance of the differences between the treatments.

4.4 Results

4.4.1 Assessment of the performance of a portable UV-Vis spectrophotometer

Based on OLS regression (Figure 4.2), the local calibration was consistent with the results obtained from the high-resolution absorbance measurements and the wet oxidation method ($r^2 = 0.99$, RMSE = 1.61 mg L⁻¹, $p < 0.001$, $n = 204$).

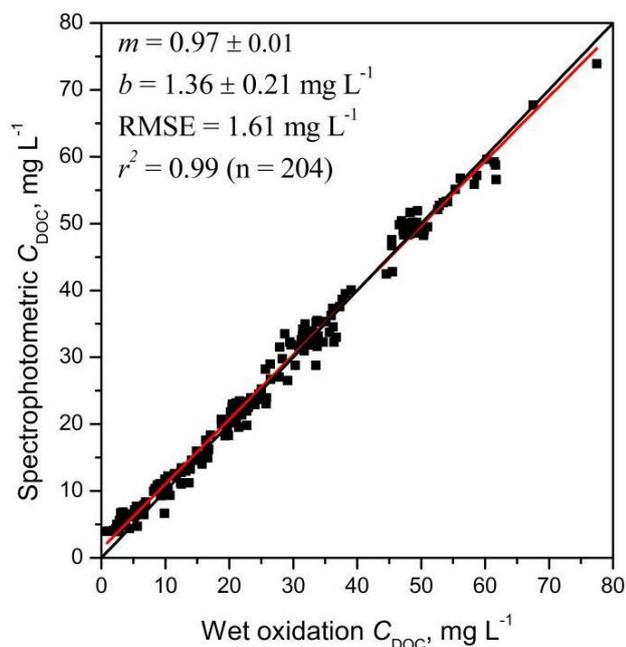


Figure 4.2 Evaluation of the local calibration. Linear regression ($y = mx + b$) of the DOC values measured with the wet oxidation (Aurora 1030) and spectrophotometric (spectro::lyser) techniques. The global calibration is compared in Table 4.1.

The spectrophotometer also satisfactorily discriminated the DOC content from the water samples without filtration. No significant difference in DOC content estimated using the spectro::lyser was detected between the filtered and unfiltered samples. The DOC content comprised $86 \pm 9 \%$ of TOC as measured by the portable spectrophotometer (TOC = 16-54 mg L⁻¹; particular organic carbon (POC) = 1-18 mg L⁻¹). The absolute mean difference in the DOC concentrations between the non-filtered and -filtered samples was $0.3 \pm 1.2 \text{ mg L}^{-1}$. In contrast to the DOC values, the absorbance values demonstrated significantly different values for filtered and unfiltered samples. This result indicates that the solely absorbance values produced in the spectro::lyser fingerprint without implementing manufacture's compensation algorithm may not be used to characterize DOM unless the samples are filtered.

Compared to the global calibration, the local calibration showed higher r^2 values and lower RMSE values for the produced models (Table 4.1). A paired samples t-test revealed a significant difference between the global and local calibration results. Global calibration ($m = 1.39 \text{ mg L}^{-1}$) also overestimated the DOC values compared with local calibration ($m = 0.97 \text{ mg L}^{-1}$). The DOC values from the PLS, PCR and MSR produced accurate DOC estimates based on the m value and models with a high explanatory power based on r^2 values. The PCR method produced the model with the highest r^2 and lowest RMSE values for the training set. However, for the validation set, the PCR results demonstrated the lowest r^2 and highest RMSE values, most likely as a result of over-parameterization. The MSR method resulted in the highest explanatory power for the validation set (RMSE = 2.43 mg L^{-1} , $r = 0.98$).

Table 4.1 Statistical test parameters of linear regressions ($y = mx + b$) of the values obtained from the partial least-squares (PLS), principal-component (PCR) and multiple stepwise (MSR) regressions as well as from the local and global calibrations regressed against DOC values measured with the wet oxidation (Aurora 1030) method.*

	Statistical parameters	PLS	PCR	MSR	Local calibration	Global calibration
Training set, n = 204	r^2	0.991	1.0	0.992	0.991	0.989
	RMSE(mg L ⁻¹)	1.65	0.36	1.55	1.61	2.53
	m	0.99 ± 0.01	1.0 ± 0.002	0.99 ± 0.01	0.97 ± 0.01	1.39 ± 0.01
	b (mg L ⁻¹)	0.25 ± 0.21	0.01 ± 0.05	0.22 ± 0.2	1.36 ± 0.21	-1.5 ± 0.33
Validation set, n = 41	r^2	0.981	0.706	0.986	0.983	0.982
	RMSE(mg L ⁻¹)	2.80	13.9	2.43	2.55	3.79
	m	0.95 ± 0.02	1.0 ± 0.1	0.95 ± 0.02	0.91 ± 0.02	1.29 ± 0.3
	b (mg L ⁻¹)	$-0.44. \pm 0.7$	3.78 ± 3.6	-0.29 ± 0.6	0.85 ± 0.6	-2.05 ± 0.9

*The number of parameters used for PLS and PCR were 197 (absorbance values of the 250-740 nm wavelengths at every 2.5 nm intervals). The MSR regression used absorbance values at selected wavelengths with the highest explanatory power (257.5, 380, 730 and 292.5 nm). The global calibration used the algorithm developed by the manufacturer based on a complete spectrum (200-740 nm in 2.5 increments), while the local calibration used the manufacturer's algorithm adjusted to the local site.

No influence of other chemical species on the absorbance values was detected. A preliminary screen revealed low concentrations of iron in the samples ($0.4 \pm 0.5 \text{ mg L}^{-1}$, max 2.2 mg L^{-1} , n = 66). The nitrate concentration was always less than 0.06 mg L^{-1} (n = 42). The Pearson correlation coefficient detected a slight and insignificant correlation between the residuals DOC and iron contents ($r = -0.17$). The correlation coefficient between nitrate and DOC residuals is not presented because the nitrate concentration in most of the samples was nearly zero.

4.4.2 Methods comparison

Figure 4.3 demonstrates the performance of the different methods for 27 randomly selected samples. Statistical test parameters comparing the regressions of the DOC values measured with wet oxidation against other methods reveal good agreement for all of the techniques (cuvette test: $r^2 = 0.96$, RMSE = 2.04 mg L⁻¹; spectrophotometric: $r^2 = 0.97$, RMSE = 1.71 mg L⁻¹). Based on the m values of the linear OLS regression cuvette tests overestimated the DOC concentration whereas results of the spectrophotometric method slightly underestimated DOC values.

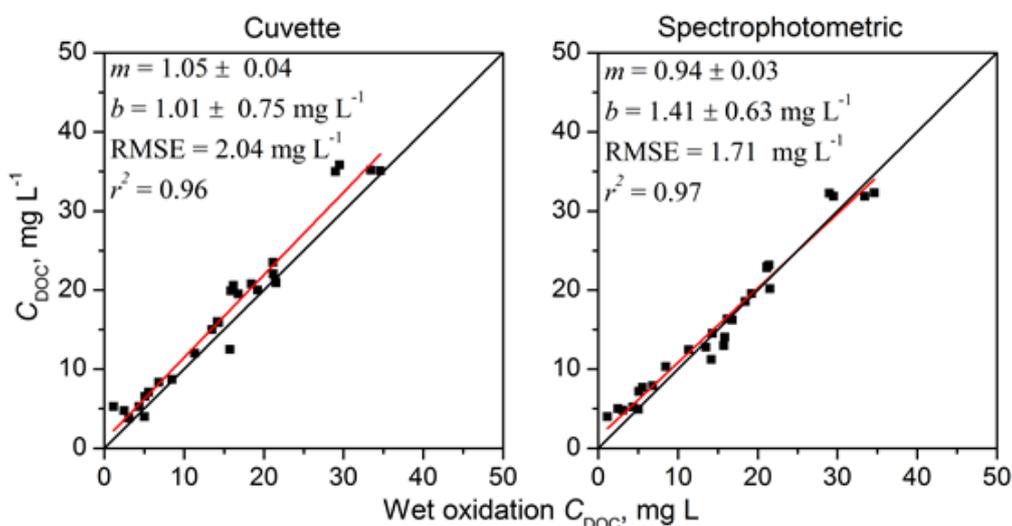


Figure 4.3 Performance of different methods compared to the wet oxidation method. DOC values ($n = 27$) obtained with different techniques (cuvette test, Hach Lange and spectrophotometric, spectro::lyser) were linearly regressed ($y = mx + b$) against values analyzed with the wet oxidation method (Aurora 1030).

The performance results of the cuvette test are disputable. When cuvette tests were used for an extended set of samples during the measurements, 25 % of the cuvette-test analyses were inaccurate and displayed negative values for the organic-rich samples, perhaps due to high ambient laboratory temperature conditions. After excluding the negative results, the remaining values were consistent with the wet-oxidation method ($b = 1.01 \pm 0.03$, $m = 0.72 \pm 0.76$, $r^2 = 0.93$, RMSE = 3.97 mg L⁻¹, $p < 0.001$, $n = 117$). This subset of the extended data exhibited lower r^2 and m values as well as higher RMSE values compared to the 27-sample comparison data set.

The factorial ANOVA with a repeated-measures factorial design demonstrated a significant difference among the methods. Mauchly's test showed that the assumption of sphericity was violated. Thus, the degrees of freedom were corrected using the Huynh-Feldt estimates of sphericity. The results demonstrated a significant

difference among the methods ($p < 0.001$). The Bonferroni pairwise comparison demonstrated that no significant difference was detected between the wet oxidation and spectrophotometric methods, whereas the cuvette test results differed significantly from the wet oxidation and spectrophotometric methods ($p < 0.05$).

4.4.3 Influence of storage on qualitative and quantitative DOC characteristics

The spectrophotometric measurements that were performed to assess the samples' ($n = 12$) stability after storage (4 months at < 4 °C) revealed small variations ($\Delta\text{DOC} = -0.97 \pm 1 \text{ mg L}^{-1}$, $\Delta A_{250} = -0.02 \pm 3.4 \text{ m}^{-1}$; $\Delta A_{280} = 0.6 \pm 2.6 \text{ m}^{-1}$; $\Delta A_{330} = 0.6 \pm 1.7 \text{ m}^{-1}$; $\Delta A_{632.5} = 0.6 \pm 1.2 \text{ m}^{-1}$; $\Delta A_{737.5} = 1.1 \pm 0.004 \text{ m}^{-1}$). The paired samples t-test analyses demonstrated that the differences were not significant at the 95 % confidence interval for the DOC and individual absorbance values with the exception of absorbance at 737.5 nm.

4.4.4 Comparison of multilinear calibration models

The results of the inverse calibration (Table 4.1) demonstrated that all of the models were consistent. However, for the validation set, the PCR method had relatively high RMSE and low r^2 values compared with the other methods. The MSR method produced lower RMSE and higher r^2 values not only compared to the PLS and PCA methods but also compared to the global calibration; further, the MSR results were relatively similar to the local calibration results. The MSR regression included only a limited number of wavelengths and resulted in the following best-fit equation:

$$C_{\text{DOC}} = (4.95 + 0.3 \text{ m } A_{257.5} - 1.1 \text{ m } A_{380} + 1.4 \text{ m } A_{730} + 0.2 \text{ m } A_{292.5}) \text{ mg L}^{-1} \quad (1)$$

Detailed results of the MSR regression for the different fractions, sites and concentrations are presented in Table 4.2. The MSR indicated that, in most cases, the highest r^2 and lowest mean square error (RMSE) of the prediction were achieved when more than one wavelength was included in the model. The inclusion of wavelengths between 600-740 nm also increased the accuracy. This improvement increase was attributed to a semi-partial correlation of the included predictor variables, which add their “unique” contributions to r^2 .

Table 4.2 Statistical test parameters of the multiple stepwise regression (MSR) applied to the spectrophotometric absorbance values as predictor variables against DOC values measured with the wet oxidation (Aurora 1030) technique as predictand variable.*

Fraction	N	Wavelength used in the model, nm	r^2	RMSE, mg L ⁻¹	F _{change}
All fractions, n = 204	1	257.5	0.99	1.85	16943.77
	2	257.5, 380	0.99	1.63	60.36
	3	257.5, 380, 730	0.99	1.60	9.06
	4	257.5, 380, 730, 292.5	0.99	1.56	7.70
	5	257.5, 380, 730, 292.5, Ratio 2	0.99	1.55	5.38
DOC (≤0.7 μm), n = 158	1	295	0.98	1.89	9787.354
	2	295, 322.5	0.99	1.73	32.23
	3	295, 322.5, 250	0.99	1.67	11.27
	4	295, 322.5, 250, 275	0.99	1.56	24.69
	5	295, 322.5, 250, 275, 720	0.99	1.47	18.56
	6	295, 322.5, 250, 275, 720, 737.5	0.99	1.44	7.44
	7	295, 322.5, 250, 275, 720, 737.5, 632.5	0.99	1.43	4.71
≤1 kDa, n=22	1	Ratio 2	0.60	0.92	30.41
≤10 kDa, n = 22	1	250	0.93	1.31	282.84
	2	250, 632.5	0.97	0.89	24.05
	3	250, 632.5, 642.5	0.98	0.75	8.99
	4	250, 632.5, 642.5, 672.5	0.99	0.58	12.63
	5	250, 632.5, 642.5, 672.5, 677.5	0.99	0.52	5.74
	6	250, 632.5, 642.5, 672.5, 677.5, 565	0.99	0.42	9.06
	7	250, 632.5, 642.5, 672.5, 677.5, 565, 655	0.99	0.36	6.98
	8	250, 632.5, 642.5, 672.5, 677.5, 565, 655, 695	0.99	0.30	6.30
Lagg, n = 17	1	250	0.62	1.36	24.32
	2	250, 645	0.77	1.10	8.89
Bog, n = 17	1	305	0.73	1.38	40.58
Low range: 15-25 mg L ⁻¹ , n = 35	1	275	0.82	1.27	151.41
	2	275, 357.5	0.85	1.19	5.53
	3	275, 357.5, 495	0.87	1.13	4.77
	4	275, 357.5, 495, 497.5	0.89	1.07	4.49
Middle range: 26-36 mg L ⁻¹ , n = 35	1	295	0.44	2.13	26.01
	2	295, Ratio 2	0.54	1.97	6.71
High range: 36-52 mg L ⁻¹ , n = 35	1	250	0.80	1.72	133.95
	2	250, Ratio 2	0.88	1.34	22.19

*The absorbance values from 250 nm to 740 nm at 2.5 nm intervals, Ratio 1 (A_{465}/A_{665}), and Ratio 2 (A_{255}/A_{365}) were used as input data. MSR was implemented separately for the different fractions, sites and concentrations. All F statistics are significant, stepwise regression stopped when further addition of absorbance values at any wavelength did not add a significant contribution to the model. F_{change} indicates the difference made by including new predictors to the model.

The number of possible models decreased when the samples were separated by site type (e.g., lagg or bog) and within limited concentration ranges (e.g., intermediate and high range). A relatively high number of suitable models were obtained for the groups with the low concentration range. For all of the sub-groups, the highest contribution to r^2 was attributed to the absorbance values in the UV range.

As indicated in Table 4.2, several of the models included an additional molecular size index (Ratio 2: A_{255}/A_{365}).

The absorbance characteristics differed among the sites (Figure 4.4). Specifically, the absorbance values varied significantly among the sites at the 360-420 nm range. At wavelengths above 420 nm, the variations in the absorbance intensities increased.

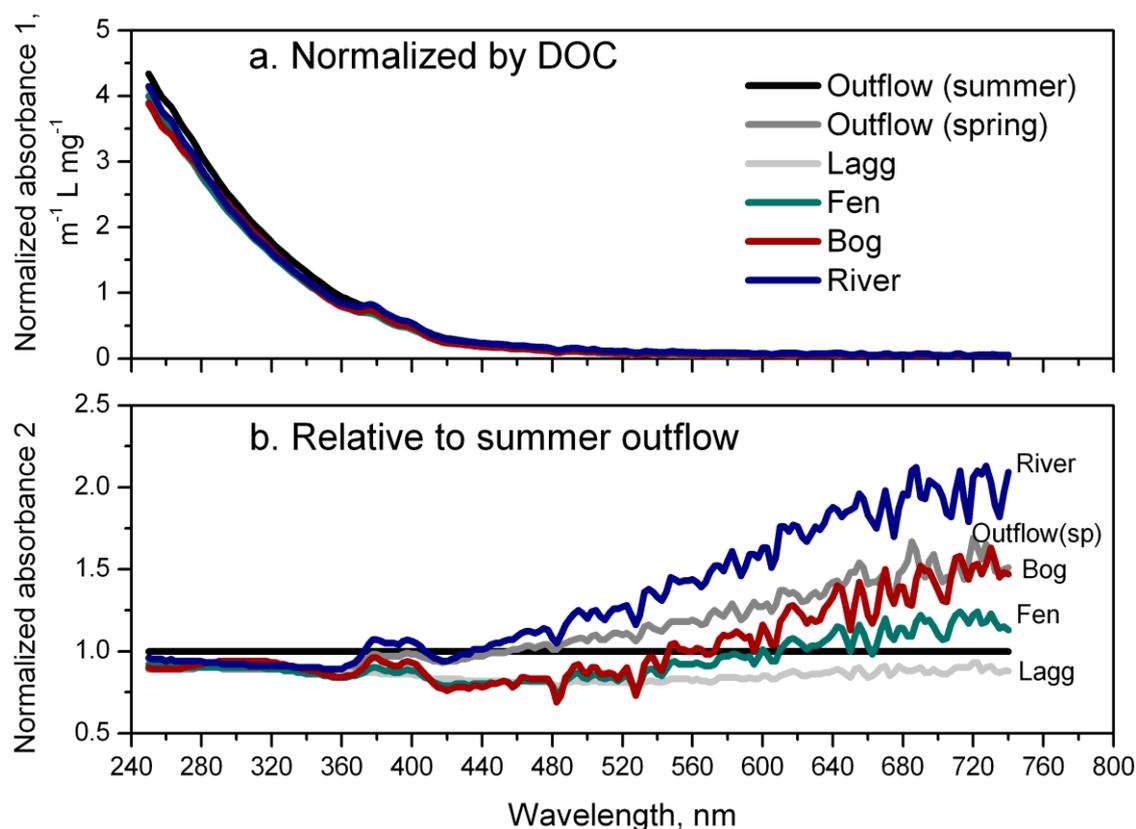


Figure 4.4 Normalized absorbance ratios of DOC. All of the calculations are conducted for the sites' mean absorbance values (lagg, $n = 16$, fen, $n = 16$; bog, $n = 16$, outflow summer period, $n = 2$; outflow spring, $n = 3$; and river, $n = 4$). From the lagg, fen and bog samples were collected during the summer-fall (June-September) baseflow period, while the river samples were collected during the snowmelt (April-May).

a. Normalized absorbance values with the DOC-content for all sites.

b. Normalized absorbance values with the DOC content divided by the corresponding normalized absorbance values of the DOC of the mean outflow (summer values).

4.5 Discussion

4.5.1 Local calibration and DOC discrimination capability of the spectro::lyser

Portable UV-Vis spectrophotometers have been used in a limited number of geoecological studies (Waterloo et al., 2006; Koehler et al., 2009; Grayson & Holden, 2012; Jeong et al., 2012; Strohmeier et al., 2013). However, not all of these studies performed a local calibration utilizing the subset UV-visible spectrum to determine DOC content. For example, Waterloo et al. (2006) only used single wavelengths as proxies when estimating DOC (during the first study period, the absorbance was 350 nm, and the second period utilized absorbance at 255 nm), and the absorbance values at these wavelengths were calibrated based on a regression against the DOC concentrations measured using a TOC analyzer (Shimadzu, Japan). However, the use of a single wavelength can lead to low-accuracy results, and Wallage & Holden (2010) previously demonstrated that some samples may demonstrate identical absorbance values at the 400 nm wavelength but differ in their absolute DOC concentrations by 50 %. Tipping et al. (2009) suggested that methods relying on absorbance at two wavelengths offer a much-improved DOC-concentration estimate compared with the use of only a single wavelength. Similarly, in the current study, the accuracy of the models was improved by including an increased number of wavelengths. Thus, to predict DOC content, it is helpful to use absorption characteristics over a range of several or more wavelengths.

Koehler et al. (2009) measured DOC concentrations continuously in a stream draining an Atlantic bog using the spectro::lyser probe, and samples collected using a 24-bottle auto-sampler were further analyzed using the heat-combustion method (TOC-V cpH, Shimadzu Scientific Instruments, USA). The results from the heat combustion method were then used to correct the spectro::lyser measurements for linear offset (Koehler et al., 2009). The DOC concentrations in the latter study ranged from 2.7 to 11.5 mg L⁻¹, and the r^2 value of a regression between DOC concentration measurements of the two different methods was 0.58 during a storm period and 0.3 during a dry period. Koehler et al. (2009) did not perform a local calibration, and the DOC concentration range that they covered was narrower than that presented here. Grayson & Holden (2012) did not estimate DOC values with the global calibration of

the spectro::lyser because the relationship between the absorbance at specific wavelengths and DOC has been found to considerably vary among sites. Instead, this study focused on changes of different absorbance values over times as a proxy for indicating temporal DOM dynamics. In another recent study, Jeong et al. (2012) used the carbo::lyser probe and corrected the TOC and DOC values obtained using a global calibration based on complementary laboratory measurements with the heat combustion technique (TOC 5000a, Shimadzu, Japan). Recently, Strohmeier et al. (2013) conducted a local, customized calibration with regular cross-checks against the heat combustion method (TOC-V_{CPN} Analyzer, Shimadzu, Japan); the DOC values used in their calibration ranged from 2.6 to 33.8 mg L⁻¹. The present study describes the performance of the local calibration and a wider range of DOC values (1-78 mg L⁻¹) and includes the separation of the study site into portions, such as lagg, fen, bog, river, and runoff points. Moreover, in addition to the bulk DOC fraction ($\leq 0.7 \mu\text{m}$), the following DOC fractions were tested: $\leq 1 \text{ kDa}$ (1-7 mg L⁻¹) and $\leq 10 \text{ kDa}$ (3-21 mg L⁻¹).

In the current study, it was possible to obtain accurate DOC estimates with the portable UV-Vis spectrophotometer by pre-calibrating the system with 30 samples. It may be possible to achieve even better results by increasing the number of samples used during the pre-calibration phase. However, in many cases, it may not be possible to obtain enough samples prior to the main sampling campaign. Therefore, the local calibration step can be performed for a sub-set of representative samples during the sampling campaign, and previously collected absorbance fingerprint results can be uploaded into a new calibration algorithm. The performance of a local calibration between spectrophotometric measurements and DOC concentration analyses with any conventional laboratory method (e.g., heat combustion or wet oxidation) should be performed during the same day. If these guidelines are not followed, the spectrophotometric futures of DOM may change during storage, and thus a newly obtained local calibration algorithm would not produce robust results. The recalculation of calibrated results is automatically completed by the spectro::lyser. To obtain an efficient local calibration and to minimize errors, it is important to include samples from a variety of sites, preferably in equal proportions.

This study identified no significant differences in the DOC contents of filtered and unfiltered samples, indicating that the spectro::lyser is a suitable tool to determine

DOC content in a nondestructive and time-efficient manner even in the presence of particulate organic matter. However, it should be noted that all of the natural samples collected contained a DOC content of approximately 90 % of the total organic carbon. Therefore, if the spectrophotometer is used at sites with high POC loads, the DOC fraction differentiation may be disturbed. Jeong et al. (2012) demonstrated that DOC concentrations under high-flow conditions were overestimated by a portable spectrophotometer (carbo::lyser, s::can, Austria) due to inaccurate turbidity compensation. Therefore, it has previously been suggested that additional correction equations should be established to accommodate the wide range of flow conditions that may occur at a specific study site (Jeong et al., 2012). Thus, it should avoid the application of unfiltered samples for DOM content determination.

4.5.2 Methods comparison

Generally, different measurement techniques are expected to give slightly differing results for the same sample, and the DOC concentrations measured are expected to be over- or underestimated based on the selected method. Because commonly used DOC measurement methods estimate the DOC content relative to standards that are easy to oxidize (e.g., potassium hydrogen phthalate or glucose), the DOC content can be underestimated; its complex mixture includes many refractory organic compounds that are more difficult to oxidize and consequently may have unequal oxidation potentials (Aiken et al. 2002). For example, in the case of caffeine measurements, high-temperature systems overestimated the concentration, while the concentration was underestimated using Pt-persulfate systems (Aiken et al. 2002). Therefore, unless they are inter-calibrated, measurements taken with different instruments should be avoided in long-term studies because variations in the instrument's performance could be misinterpreted as a change in the environmental conditions.

Overall, the cuvette tests performed at a relatively satisfactory level. However, as previously mentioned, some of the carbon-rich samples generated negative values, which can be explained by the unusually high room temperatures during the laboratory analyses in Syktyvkar, Russia (up to 35 °C). According to the manufacturer, this measurement requires either room-temperature (+15 - +25 °C) or refrigerated samples (+2 - +8 °C) depending on the type of test kit. Furthermore,

consideration should be given to the differences in detection limits before selecting the proper cuvette tests for the desired measurements. For example, the LCK 385 kit measures within a range of 3-30 mg L⁻¹, while the LCK 386 kit's range is 30-300 mg L⁻¹. Therefore, it is desirable to have an advanced estimate of the expected DOC concentration. Moreover, the cuvette test requires a special disposal procedure after use. Table 4.3 details a further comparison of these different methods for operation in remote field conditions.

Table 4.3 Comparison of the methods conventional methods: heat combustion (Shimadzu TOC-L) and wet oxidation (Aurora 1030); cuvette test (Hach Lange) and spectrophotometric (spectro::lyser).

Parameters	Wet oxidation, heat combustion	Cuvette tests	Spectrophotometric measurements
Premeasurement calibration	√	√	-
Local site specific calibration	-	-	√
Operation in the field	-	-	√
Filtration for DOC separation	√	√	-
Additional consumables (e.g., acids)	√	√	-
Special disposal requirements	-	√	-
Time per 1 sample measurement	3-5 min.	125 min.*	< 1 min.

“√” stands in case the parameter is required by the method, while “-” stands if the parameter is not required by the method. *125 min., including 120 min. for thermostat incubation prior to the measurements, cooling and measurement with the spectrophotometer (Hach Lange, Germany).

The high-resolution absorption measurements demonstrated a number of advantages of using this robust, small-sized, on-line spectrophotometer over the conventional single- or dual-wavelength spectrophotometers. A UV-Vis probe can be used for both in-situ real-time measurements at a field site and in the offline mode in the laboratory, and the method does not require filtration to determine the DOC content. The high-frequency absorbance measurements made under field conditions enable the use of this method for detecting rapid temporal fluctuations in DOC content and quality at a study site, which can be used to quickly detect changes in land-use management practices, such as peatland drainage and the conversion of forest to arable land. Moreover, in-situ measurements reduce the number of sampling errors (e.g., contamination from the bottles), transport logistics, storage time and dilution. Furthermore, this method does not require frequent maintenance and can be used in a challenging environment (e.g., industrial wastewater systems or high-flow events, such as snowmelt or floods). The spectrometer is equipped with an auto-cleaning system that uses pressurized air to prevent bio-fouling. Although cleaning with compressed air significantly reduces the maintenance requirements, care should be taken at sites with high sediment loads. Thus, it is advisable to frequently monitor

the condition of the sensors and to complete additional manual cleaning if the mirrors are disturbed by fouling. Furthermore, increased power consumption because of cleaning with compressed air should be considered.

Moreover, the spectrophotometer's ability to operate using a battery or solar power supply render it possible to work in remote locations, although frequent charging is required for high-frequency measurement campaigns. The data logger on the spectrophotometer can store one month of data taken at 30-minute time intervals (Langergraber et al., 2003). The spectro::lyser exhibits long-term stability; after 10 months of near-continuous deployment, blank measurements using distilled water indicated minimal instrument drift ($400 \text{ nm} < 0.7 \text{ Abs m}^{-1}$) (Grayson & Holden, 2012). Moreover, when determining absolute DOC contents, several absorbance coefficients provide a qualitative description of the DOC's aromaticity content, molecular size and humification degree for filtered samples, which can be advantageous when tracing biochemical changes (Peuravuori & Pihlaja 1997; Worrall et al. 2002; Berggren et al., 2007; Spencer et al. 2007; Helms et al. 2008; Ågren et al. 2008; Baker et al. 2008).

Additionally, the method of transportation should be considered if measurements are to be conducted overseas, given the heavy mass ($> 30 \text{ kg}$) of the equipment for the wet oxidation and heat combustion methods. Although the spectrophotometer for the cuvette tests is relatively light, the restrictions for flight can be an obstacle for the test chemicals because they require special transportation due to safety concerns. Following the analyses, the cuvette tests require special disposal of the glass cuvettes and the chemicals used. In contrast, the high-resolution absorbance probe does not require any additional security clearance, is portable, and does not require additional chemicals. Thus, notwithstanding certain limitations (such as limited battery capacity), this probe provides an opportunity to monitor dynamics of water-quality changes in logistically challenging areas.

4.5.3 Different multilinear calibrations

For an inverse calibration, the MSR, PCR and PLC regressions were chosen because they can be used with datasets that have collinear variables and a larger number of predictor variables than observations (Varmuza & Filzmoser 2009; Miller

and Miller, 2010). It is important to note that the absorbance values for neighboring wavelengths are often highly correlated (Varmuza & Filzmoser 2009). However, these correlated variables are considered “parallel” measurements in chemometrics, offering the advantage of noise reduction. Thus, there is no incentive to eliminate correlated variables (Varmuza & Filzmoser 2009).

The current study shows that although the MSR regression included a limited number of variables into the model for the validation set, it produced a model with the highest explanatory power and the lowest RMSE value when applied to an independent validation dataset. MSR was also preferable over PLS and PCR because the regression models produced by PCR and PCA included all of the variables and were thus difficult to interpret. Generally, interpretation is feasible if no more than approximately a dozen variables are used in a model (Varmuza & Filzmoser 2009). Furthermore, due to its possible overparameterization, the PCR model failed to produce accurate estimates for the validation set in contrast to the training set.

4.5.4 Multiple stepwise regression results for different sub-sets

As previously mentioned, the spectro::lyser produces a fingerprint report with a wide range of wavelengths; this detailed output enables researchers to select the most suitable wavelength for the qualitative and quantitative characterization of DOC. As indicated in Table 4.2, the MSR models included many closely located wavelengths that were also commonly used previously as proxies for DOC concentrations. The wavelengths that have previously been used as proxies include 254 nm (Baker et al. 2008; Tipping et al. 2009), 272 nm (Baker et al. 2008), 320 nm (Pastor et al. 2003), 340 nm (Tipping et al. 1988; Baker & Spencer 2004; Baker et al. 2008; Tipping et al. 2009; Grayson & Holden 2012), 365 nm (Baker et al. 2008), 400 nm (Worrall et al. 2002; Wallage & Holden 2010; Grayson & Holden 2012) and 410 nm (Baker et al. 2008).

As indicated in Figure 4.4, the highest absorbance values per mg L^{-1} were recorded at wavelengths below 400 nm. According to the review by Korshin et al. (1997), most of the chromophores that absorb light below 400 nm are aromatic groups with various degrees and types of substitution, including mono- and polysubstituted phenols and diverse aromatic acids. These chromophores are primarily associated with the humic fraction of the DOM (Korshin et al., 1997). The increased variation of

absorbance intensities greater than 450 nm may be caused by turbidity differences (i.e., the particle-size differences among samples) because the wavelengths at which the absorbance is affected by turbidity are located within the visible range between 450 and 650 nm (Jeong et al., 2012).

For all of the models apart from the ≤ 1 kDa fraction, the primary contributors to r^2 were the UV-range wavelengths. The absorption of UV light is caused by π -electron changes in energy levels and reflects aromatic, carbonylic and carboxylic electron systems and their conjugates (Abbt-Braun & Frimmel, 1999). The natural waters of terrestrial reserves, such as peatlands, have high aromatic carbon levels; therefore, DOC concentrations strongly correlate with absorbance values in the UV range.

The MSR regressions for the different sites, fractions and concentrations demonstrated that the highest r^2 and best accuracy were achieved when more than one wavelength was included in the model. Similarly, in the study of Simonsson et al. (2005), DOC concentrations resulting from a regression model using multiple wavelengths produced more accurate results compared to the results obtained using only absorbance values at a single wavelength (280 nm). Moreover, longer wavelengths can also be useful for improving measurement accuracy (Table 4.2). For example, the accuracy of this model increased when wavelengths from 600-740 nm were included. It appears appropriate to use several absorbance values from different intervals (e.g., A_{2xx} , A_{3xx} , A_{4xx} and A_{6xx} or $7xx$) when performing these regressions.

In the current study a preliminary screening for iron and nitrate contents in the samples revealed low concentrations, which are not assumed to significantly interfere with DOM absorption. In other water samples with high iron and nitrate contents, possible interference from these species should be considered.

The relationship between DOC concentration and absorbance varied at different sites. A decreased number of acceptable models was observed after separating the samples according to the sites (e.g., lagg or bog) or different concentration intervals (e.g., intermediate and high ranges). The relatively high number of models for the “low range group” can be explained because this group included samples collected from different sites during the snowmelt period, thus incorporating samples that presented a mixture of DOC from different sources that became hydrologically connected during the snowmelt period. Similar findings were obtained by Baker et al. (2008), who observed that their entire mixed catchment

exhibited the strongest relationship between the absorbance coefficients and DOC concentration at 340 nm; however, DOM from the peat subcatchment had the most significant relationship at 272 nm. Thus, even within a single catchment, it may be necessary to distinguish sub-sites to create specific regressions that produce more accurate results. It may also be sub-optimal to use the same wavelengths to determine the organic carbon content during different seasons because the specific absorbance values of different DOC sources may vary considerably over time. Therefore, it is necessary to create seasonal site-specific calibration curves. For long-term spectrophotometric estimates of DOC concentrations, it should be necessary to periodically calibrate the changes in water color against the measured DOC concentrations using a wet oxidation or heat combustion method.

4.6 Conclusions

The UV-Vis submersible probe facilitates the rapid, robust and continuous measurement of DOC contents under field conditions. Additionally, the fingerprint results of filtered samples enable researchers to trace biogeochemical changes through the ratios of absorbance at specific wavelengths, which provide information about the DOM composition. This study also demonstrates that studies that use absorbance values as a proxy for DOC-content determination should include more than one wavelength in their absorbance-concentration models. Moreover, in addition to the widely used wavelengths in the range of 254-400 nm, the inclusion of absorbance values at the wavelengths of 600 nm and 740 nm can significantly increase the accuracy of DOC estimates. Application of the high-resolution absorbance method may be beneficial for many water research-related disciplines, potentially providing the biogeochemical research community with a new opportunity to expand its understanding of DOM fluctuations at different sites and in different seasons.

5 Biogeochemical gradients and dissolved organic carbon variability in a complex peatland landscape in Northwest Russia

5.1 Abstract

The investigation of hydrochemical gradients and dissolved organic matter (DOM) variability is important in mire ecology and biogeochemistry to better understand the factors and processes that control the production, transformation, decomposition and export of DOM. Thus, this study aims to characterize the hydrochemical gradients that affect the surface and pore water concentrations of DOM and major ions in response to vegetation and water table changes in a typical mire complex in northwest Russia (July-October, 2010). Furthermore, this study evaluates the importance of ecohydrological transitional zones, i.e., zones where the influences of upland forest landscape units and mire landscape units overlap. Based on the local surface water chemistry gradients, the area was divided into the following sites: lagg (pH: 5.6, C_{Ca} : 6.5-7.3 mg L⁻¹), fen (pH: 5.3, C_{Ca} : 2.9-3.6 mg L⁻¹), and bog (pH: 4.4, C_{Ca} : 0.2-0.3 mg L⁻¹) zones. The highest dissolved organic carbon (DOC) concentrations (42-54 mg L⁻¹) were detected in the lagg zone located at the edges of the mire complex and representing a transition zone between the forest and mire soils, and the lowest concentrations were observed at the bog site (20-28 mg L⁻¹). The fen site exhibited DOC concentrations between those found in the lagg and bog zones (28-38 mg L⁻¹). The water-chemical results showed that the lagg, bog, and fen zones represent distinct hydrological and biogeochemical units within a single mire complex. The diverging pH values and DOC, calcium, magnesium, and silica concentrations indicated that the lagg site was the primary contributor to the investigated outflow stream. The transitional lagg zones between the mire and surrounding mineral soils should be investigated in more detail because these previously largely neglected landscape units appear to have a strong effect on the biogeochemical properties of the water discharged from boreal mire-forest landscapes into the limnic systems.

5.2 Introduction

Spatial variations in water chemistry have been described for different ombrogenous bog and minerogenous fen peatlands, including small-scale variability in pH and major ion concentration due to various vegetation patterns (e.g., Glaser et al., 1990; Bubier, 1995; Boeye and Verheyen, 1994; Walbridge, 1994; Vitt et al., 1995; Bragazza & Gerdol, 1999a,b; Tahvanainen et al., 2002). Tall vegetation was described to occur more frequently in peatlands with more alkaline surface waters, whereas low shrubs and bryophyte species were more frequent with more acid water conditions (Walbridge, 1994). In addition, vascular plant communities appeared to respond mainly to changes in the nutrient content, and bryophytes appeared to respond to changes in the pH/alkalinity level (Vitt and Chee, 1990).

In contrast, a limited number of studies on the spatial and temporal variability of the dissolved organic matter (DOM) content in surface and soil pore waters across mires have been conducted (e.g., Moore, 1987; Marin et al., 1990; Dalva & Moore, 1991; Fraser et al., 2001; Waddington & Roulet, 2000), especially in remote areas of the boreal region of Russia (Pokrovsky et al., 2005, 2006; Shvartsev et al., 2012). Missing information on the lateral fluxes of DOM can cause significant errors in peatland carbon budget estimates (e.g., Dawson et al., 2002a; Roulet et al., 2007). Hydrochemical gradients can also differ considerably among regions (Tahvanainen et al., 2002; Bragazza et al., 2005; Howie & van Meerveld, 2013). For example, although the pH values in the mires of northern Sweden are similar to those in the UK and North America, the electrolyte ranges are lower in Sweden as a result of siliceous, poorly weathering bedrock (Tahvanainen et al., 2002). Furthermore, Wolf (2009), at the same study site used in the current study, detected that the CH₄ flux (up to 1614.2 mg m⁻² d⁻¹) exceeded the fluxes measured in other studies in boreal zones, e.g., Canada. Thus, due to differences in the geology, vegetation, and climate among regions, it is difficult to extrapolate the results from well-studied regions such as the UK and North America to underrepresented boreal regions in Russia.

In peatland-rich areas such as West Siberia, climate change is estimated to increase the mean dissolved organic carbon (DOC) content in streams from 16 to 21-24 mg L⁻¹ (an increase of approximately 29-46 %) by 2100 (Frey & Smith, 2005). However, most of these predictions do not consider the individual contributions to

this DOC source by the different landscape subunits (e.g., bog, fen and lagg) that typically compose the large mire complexes of boreal Russia.

A better understanding of the different DOM sources would also be useful for a better prediction of the solubility and transport of metals and organic pollutants, which are closely coupled to the DOM dynamics due to the high cation binding capacity of DOM (Helmer et al., 1990; Kalbitz & Wennrich, 1998). DOM also regulates the photochemistry of natural waters (Karlsson et al., 2009), the acidification of fluvial systems (Oliver et al., 1983), and the availability of nutrients to limnic ecosystems (Carpenter et al., 2005).

Indicators such as the pH, concentrations of calcium, sodium, magnesium, aluminum, manganese, and silicon, and Ca:Mg ratio can be used to separate chemical gradients across minerotrophic-ombrotrophic mire complexes and to detect the limits of minerogenous water inflows. These water-chemical indicators also often correlate with the distributions of plant species in mires (e.g., Wells, 1996; Glaser et al., 1990; Bragazza & Gerdol, 1999; Bragazza et al., 2005; Tahvanainen et al., 2002; 2004; Howie & Tromp-van Meerveld, 2011; Howie & van Meerveld, 2012, 2013). In this study, water-chemical indicators were used not only to characterize the chemical gradients across the mire but also to trace the source of water that was discharged at the mire complex outflow point.

In peatlands, the importance of small-scale patterning has already been emphasized for vertical fluxes, such as CH₄ and CO₂ land-atmosphere fluxes (Baird et al., 2009; Wolf, 2009; Forbrich et al., 2011; Schneider et al., 2012). Additionally, heterogeneously patterned boreal peatlands vary in the DOM content among different sites. For instance, Wolf (2009), who detected a great variability in CH₄ fluxes among microsites and between ombrogenous and minerogenous sites, also demonstrated that DOM concentrations are higher at the minerogenous sites. However, a limited number of samples were collected in that study.

Most studies have focused on bog-fen gradients and forested areas separately without integrating marginal and transitional lagg zones. Lagg zones are located in topographic depressions and collect runoff from ombrotrophic bogs and adjacent upland areas with mineral soils (Howie & Tromp-van Meerveld, 2011). Because of their location in boundary areas, lagg zones exhibit transitional chemical properties that are influenced by surface and interflow waters from both ombrotrophic bog areas and adjacent mineral soil areas. Lagg zones also act as hydrological buffer zones for

bogs, reducing the influence of mineral areas on the bog biogeochemistry and thus favoring the development of ombrotrophic conditions (Bragazza et al., 2005; Howie & Tromp-van Meerveld, 2011).

Currently, only few studies have reported the chemistry of lagg zones and considered the function of transitional lagg zones in regulating lateral export fluxes in mire complexes (e.g., Smit et al., 1999; Howie & Tromp-van Meerveld, 2011, 2012, 2013). Howie & Tromp-van Meerveld (2011) discussed the importance of lagg zones for raised bog restoration, and Smit et al. (1999) focused on the hydrological aspects of lagg zones. The lagg zone is hypothesized to differ from the fen and bog zones with respect to the DOM content due to differences in the vegetation cover, water table, and water sources, and within the mire complex the lagg zone can be the main pathway for lateral mass transfer across and out of the mire.

This study had the following objectives:

- 1) To determine the spatial and temporal dynamics of DOM in a boreal mire complex in northwest Russia.
- 2) To compare DOM concentrations found in Northwest Russia with those found in other northern peatlands.
- 3) To characterize the hydrochemical gradients and compare them with respect to the vegetation and DOM changes.
- 4) To identify the primary hydrological flowpaths in the mire complex during the baseflow period.
- 5) To evaluate the importance of transitional upland-mire zones as the main hydrological pathways under baseflow conditions.

5.3 Materials and Methods

5.3.1 Study site

The study was conducted during the 2010 summer-fall season at the Ust-Pojeg forest-mire complex (61°56'N, 50°13'E) in the Komi Republic, which is located in the northwestern region of Russia (see Chapter 3 for further details).

5.3.2 Sampling and field measurements

Water samples were collected along a transect across the mire complex to characterize the spatial distribution of DOM. The transect started at the edge of the mire complex in the lagg zone, ran straight for 1.2 km in the northeastern direction, and ended in an area of the mire complex that was characterized as a bog zone (Figure 3.3). Within the lagg, treeless fen, treeless bog, river and outflow zones representative sampling points were selected for frequent sampling.



Figure 5.1 Photos of water sampling sites. From July 2010 to October 2010, duplicate samples were collected weekly from various depths (10, 30, and 60 cm below the surface). At the outflow, flumes were installed for discharge measurements. The main vegetation species in the lagg zone included *Menyanthes trifoliata*, *Sphagnum magellanicum*, *Pinus sylvestris*, *Betula pendula*, and *Alnus incana*. The fen zone was predominantly vegetated with *Scheuchzeria palustris* and *Sphagnum fuscum*, and the bog zone was vegetated with *Sphagnum magellanicum*, *Chamaedaphne calyculata*, *Sphagnum fuscum* and *Scheuchzeria palustris*.

From June of 2010 to October of 2010, duplicate samples were collected weekly from these representative points at various depths (10, 30, and 60 cm below the surface) using perforated stainless steel tubes ($\text{\O} 1/8''$) at the lagg, fen and bog sites. Surface water was collected from the mire outflow point near the Pojeg River

(Figure 5.1). In the present study, water samples from a 10-cm depth below the moss surface are considered representative of the surface water at the mire sites. Except for the outflow point and the depth of 10 cm in the bog, all of the sites and depths were sampled over the entire study period. From the 10-cm depth at the bog, samples were not collected on July 7, 2010, July 12, 2010, August 17, 2010, and August 24, 2010 because of a low water table. At the outflow point, measurements were conducted for two weeks in the summer (July 7, 2010 and July 26, 2010), but water was not collected during the fall because the water outflow from the mire toward the river was not detected due to the summer drought.

Upstream from the study site, river water samples were collected to compare their water-chemical properties with those of the mire samples and to assess the influence of the region's mixed forest-mire landscape on the hydrochemistry of the river. Precipitation samples were collected in open flasks at the lagg zone below the canopy and in the open peatland during the vegetation senescence period (September 1, 2010 and September 8, 2010). The water temperature and pH measurements were conducted directly at the study site (EcoSense® pH10A Handheld pH/Temperature Meter, Yellow Springs, USA).

5.3.3 Chemical analysis

Water samples for the DOC analyses were collected in acid-washed glass bottles. Before sample collection, the bottles were rinsed multiple times using sample water. To separate bulk DOC from particulate organic matter, the samples were filtered within 24 hours of collection through pre-combusted glass-fiber filters with a pore size of 0.7 μm (GF/F, Whatman, UK). To avoid contamination from the filters, the first 30 mL of the sample water was discarded after filtration. Then, the samples were acidified with HCl to pH 2 and stored at 4 °C until laboratory analysis. The DOC content was determined by a wet-heated persulfate oxidation method (Aurora Model 1030, O-I-Analytica, USA). The standards (potassium hydrogen phthalate, KHP, $\text{KHC}_8\text{H}_4\text{O}_4$: 5, 20 and 40 mg L^{-1}) were analyzed before and after every 60 samples to ensure that there was no analytical drift during or between sample runs. Three injections from each sample were analyzed. The reproducibility of the DOC analysis in terms of standard deviation based on triplicate injections was always better than 0.5 mg L^{-1} and was 0.2 mg L^{-1} on average. The overall average accuracy (test

result-assigned value) of the KHP standard measurements was within a range of -1.2-1.2 mg L⁻¹.

The concentration of nitrite (NO₂⁻) was analyzed with the photometric cuvette test (LCK 341, Hach Lange, Germany). The concentrations of nitrate (NO₃⁻), ammonium (NH₄⁺), phosphate (PO₄³⁻), and sulfate (SO₄²⁻) were analyzed using the photometric method (Photometer KFK-3, Zagorsky Optical- Mechanical Plant, Russia; the analyses were performed by the certified Ecoanalyt Laboratory of the Institute of Biology, Komi). Dissolved nitrogen (DN) analyses were performed using a thermal catalytic oxidation at 720 °C chemiluminescence method (TNM-L, Shimadzu, Japan). Samples for the other major ion analyses were collected in plastic bottles, filtered through 0.45-µm nominal-cut-off-size polycarbonate filter paper and stored frozen. The water samples were analyzed for the Na, K, Mg, Ca, Fe, Zn, and Mn contents with an atomic absorption spectrometer ('AAS'; 1100B, Perkin-Elmer, USA). Photometric cuvette tests (LCW 028, Hach Lange, Germany) based on the molybdenum blue method were used to determine the silica (SiO₂) content.

5.3.4 Data analyses

To evaluate the effects of seasonal vegetation development on the water chemistry, the sampling season was divided into two phases, including the active vegetation growth phase (VAG: July 7, 12, 19, and 26, 2010) and the vegetation senescence phase (SEN: September 19, 22, and 26, 2010 and October 3, 2010). Similar to the study performed by Howie & van Meerveld (2012, 2013), to minimize the concentrating effects of evapotranspiration, the results collected in August were not included in the statistical analyses because it was the driest month. However, all of the data obtained in the transitional period (August) between the VAG and SEN phases are presented in the appendix section (Table 5.4).

Differences between the sites, depths, and seasons were tested by univariate analyses of variance followed by Tukey's HSD post-hoc tests. The results are reported for significance levels of $p < 0.05$. Pearson's correlation analysis was used to evaluate the relationships between the DOC contents and the concentrations of Fe, Mg, Ca, Mn, Zn, and K, respectively. Based on the pore water chemical characteristics at 10 cm depth of the different sample sites, agglomerative hierarchical clustering according to Ward's method was used to separate ecohydrological sub-

units across the mire, identify closely related flow paths, and detect the main unit contributing to the discharge from the mire complex (Ward, 1963). To separate groups, agglomerative hierarchical clustering was initiated with a single group and used to merge the closest pair of clusters based on their similarity (the square of the Euclidean, E^2). With the exception of agglomerative hierarchical clustering, for which the XLSTAT statistical package (Addinsoft, Paris, France) was used, the SPSS 18.0 statistical package (IBM Corp., Chicago, IL, USA) was applied for the statistical analyses.

5.4 Results

5.4.1 pH and temperature

The pH values at the lagg, fen, bog, and outflow zones were relatively constant throughout the seasons and at different depths, presenting mean values of 5.6, 5.3, 4.4, and 5.3, respectively (Table 5.1). The average water temperatures (over 10-, 30-, and 60-cm depths within the mire sites and from the surface water) at the time of sampling over the VAG and SEN periods are presented in Table 5.1. During the VAG period, the temperature was highest in the treeless zone (bog: 20.3 °C) and lowest in the site shaded by trees (lagg: 17.7 °C). In contrast, during the SEN period, the opposite trend was observed: the lagg site had the highest temperature (7 °C), whereas the bog site had the lowest temperature (4.1 °C).

Table 5.1 Temperature and pH values at the different sampling locations. *

Site	Season	Outflow(SD)	Lagg (SD)	Fen (SD)	Bog (SD)
pH	VAG and SEN	5.3. ± 0.4	5.6 ± 0.1	5.3 ± 0.1	4.4 ± 0.3
T_{water} , °C	VAG	n/a	17.7 ± 0.2	19.1 ± 0.1	20.3 ± 0.9
T_{water} , °C	SEN	n/a	7.0 ± 3.4	5.5 ± 0.1	4.1 ± 0.01

*pH values are averages of the soil pore water samples from the different sampling depths (10 cm, 30 cm, and 60 cm) measured during the VAG and SEN periods (Jul 19, Sept 26 and Oct 3 and 10). The average water temperature (T_{water}) measurements (over a 0-60 cm depth at the mire sites and from the surface of the outflow sampling point) were conducted during the VAG (Jul 12 and 18) and SEN (Oct 3 and 9) periods.

5.4.2 Dynamics of dissolved organic carbon

During the summer and fall periods, the pore water from different parts of the mire complex exhibited significantly different DOC concentrations (Figure 5.2). The highest DOC concentrations (42-54 mg L⁻¹) were detected in the lagg zone, whereas the lowest concentrations were observed at the bog site (20-28 mg L⁻¹). The fen zone exhibited DOC concentrations that were intermediate between those of the lagg and bog zones (28-38 mg L⁻¹). The DOC concentrations were relatively constant over the depth of all investigated mire soils during the sampling periods, with no significant differences detected. Between seasons, a significant difference was only observed in the lagg zone at a depth of 10 cm. During the SEN period, the concentrations in the lagg zone at the depth of 10 cm were increased compared with those in the VAG period.

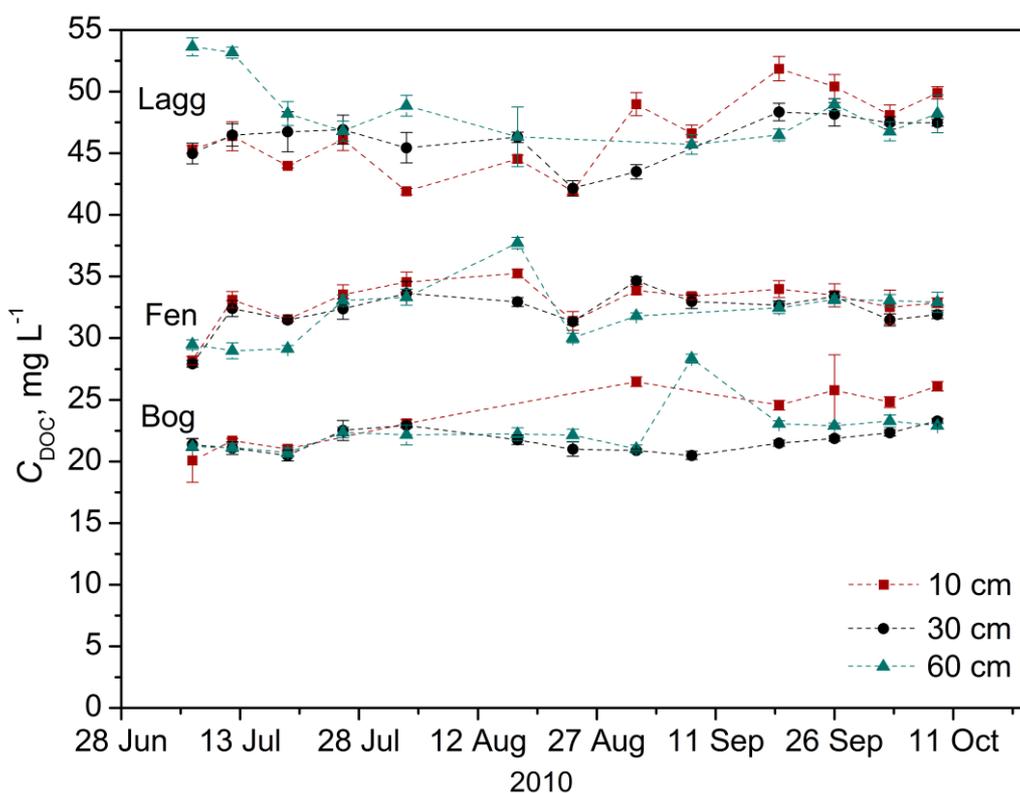


Figure 5.2 Temporal variability of dissolved organic carbon (DOC) concentrations at three sample depths in the mire soils of the lagg, fen, and bog sites. The error bars represent the standard deviation of the duplicate field measurements.

The DOC content in the precipitation sampled at the soil surface varied among the sites; in the treeless bog and fen sites, the DOC concentrations were low ($1.4\text{-}2.9\text{ mg L}^{-1}$), whereas in the lagg zone, the concentrations were higher as a result of the precipitation passing through the tree and shrub canopy ($8.7\text{-}9.3\text{ mg L}^{-1}$).

During the summer, the river DOC concentration was $8.2 \pm 0.2\text{ mg L}^{-1}$ (22 July) and decreased to $4.5 \pm 0.2\text{ mg L}^{-1}$ during the fall (September 19). The DOC content of the outflow water samples remained relatively constant at $48\text{-}52\text{ mg L}^{-1}$. Discharge at the outflow location was observed until the beginning of August. Afterward, due to the strong drought, outflow from the peatland was not observed.

5.4.3 Macro and Microelements

The present study showed clear gradients in the soil pore water concentrations of the micro- and macroelements across the catchment. The highest PO_4^{3-} content in the pore water was detected in the bog zone, whereas the highest SO_4^{2-} , NO_2^- and DN concentrations were observed in the pore water of the lagg site (Table 5.2). No NH_4^+ and NO_3^- were detected in the pore waters of all sites. The measurement of the NO_2^-

content during the SEN period demonstrated that in contrast to the VAG phase, the nitrite concentration in the lagg site at a depth of 10 cm ($0.09 \pm 0.01 \text{ mg L}^{-1}$) was higher than the concentration at a depth of 60 cm ($0.07 \pm 0.01 \text{ mg L}^{-1}$) during the SEN season. The NO_2^- concentrations at the bog and fen sites did not differ significantly between seasons (VAG: fen $0.03 \pm 0.003 \text{ mg L}^{-1}$, bog $0.02 \pm 0.006 \text{ mg L}^{-1}$, outflow $0.06 \pm 0.04 \text{ mg L}^{-1}$; SEN: fen $0.04 \pm 0.02 \text{ mg L}^{-1}$, bog $0.03 \pm 0.01 \text{ mg L}^{-1}$). During the VAG season, the PO_4^{3-} , SO_4^{2-} , and DN concentrations exhibited minor fluctuations with depth (Table 5.2).

Table 5.2 PO_4^{3-} , SO_4^{2-} , and DN concentrations with depth at the mire site.

Site	Depth	PO_4^{3-} conc. (mg L^{-1})	SO_4^{2-} conc. (mg L^{-1})	NO_2^- conc. (mg L^{-1})	DN conc. (mg L^{-1})
Outflow	-	0.101	1.18	0.067	n/a
	10 cm	0.081	1.49	0.053	0.8
Lagg	30 cm	0.073	1.55	0.059	0.9
	60 cm	0.084	1.39	0.067	1.0
	10 cm	n/d	1.11	0.032*	0.9
Fen	30 cm	0.044*	1.0	0.04*	0.8
	60 cm	0.037*	1.05	0.04*	0.8
	10 cm	0.204	n/a	n/a	n/a
Bog	30 cm	0.127	0.28	0.027*	0.4
	60 cm	0.079	0.24	0.032	0.5

*indicates that the presented value is under the analytical measurement range. Measurement dates:

PO_4^{3-} : 8 August 2010; NO_2^- , DN and SO_4^{2-} : 26 July. n/a-not available.

The depth and seasonal variations in the concentrations of Ca, Mg, Fe, Na, Mn, and K during the VAG and SEN periods are presented in Table 5.3. The results obtained in August are presented in Table 5.4 (Appendix). Except for C_K , all elemental concentrations were highest in the lagg zone and lowest in the bog zone. According to the ANOVA statistical analyses of all site measurements, sampling periods, and various depths, the concentrations of Ca, Mg, Fe, Na, and Mn were significantly different among the sites. At the lagg site, the Ca and Fe concentrations differed significantly among the sites and increased with depth. The C_K did not differ among the sites but decreased and varied significantly with depth at the bog and fen sites. During the SEN period, the C_K exhibited a significant upward trend at the fen and bog sites. Seasonal changes in the C_{Ca} and C_{Mn} were also detected. During the SEN period, the C_{Ca} decreased at the lagg site at a depth of 60 cm. The value of C_{Mn} decreased at the lagg (10 cm) and fen (10 and 60 cm) sites. The C_{Na} and C_{Zn} concentrations were not significantly different among sites, depths, or seasons. The mean C_{Zn} across the field sites was $0.03 \pm 0.02 \text{ mg L}^{-1}$.

Table 5.3 Seasonal variability of the mean concentrations (C) of chemical species measured in the pore waters at different sites in the mire complex. From all sites and depths except the outflow* and bog* sites at a 10-cm depth, water samples were collected during the following periods of vegetation active growth (VAG: 7, 12, 19, and 26 Jul 2010) and vegetation senescence (SEN: 19, 22, and 26 Sep 2010 and 3 Oct 2010).

Chemical element	Site/Depth	Vegetation active growth season			Senescence		
		10cm (SD)	30 cm (SD)	60 cm (SD)	10 cm (SD)	30 cm (SD)	60 cm (SD)
C_{Ca}^1	Lagg	7.0 (0.3) ²	7.7 (0.1)	7.9 (0.4) ^{2,3}	7.0 (0.4)	7.6 (0.2)	6.9 (0.2) ³
	Fen	3.1 (0.1)	3.5 (0.5)	3.8 (0.2)	3.2 (0.5)	3.8 (0.3)	3.8 (0.2)
	Bog	0.3 (0.01)	0.3 (0.04)	0.5 (0.01)	0.2 (0.1)	0.3 (0.1)	0.4 (0.1)
	Outflow	4.8 (0.4)					
C_{Mg}^1	Lagg	1.5 (0.06)	1.6 (0.03)	1.7 (0.07)	1.6 (0.02)	1.7 (0.02)	1.7 (0.07)
	Fen	0.9 (0.04) ²	0.9 (0.1)	1.1 (0.07) ²	0.9 (0.1) ²	1.1 (0.08)	1.2 (0.03) ²
	Bog	0.1 (0.01)	0.1 (0.02)	0.1 (0.05)	0.1 (0.02)	0.1 (0.03)	0.1 (0.03)
	Outflow	1.3 (0.1)					
C_{Fe}^1	Lagg	0.5 (0.08) ²	0.5 (0.03) ²	1.8 (0.6) ²	0.4 (0.1) ²	0.5 (0.03) ²	1.9 (0.1) ²
	Fen	0.5 (0.08)	0.7 (0.06)	0.6 (0.10)	0.3 (0.08) ²	0.7 (0.01) ²	0.5 (0.05) ²
	Bog	0.06 (0.01)	0.08 (0.03)	0.1 (0.03)	0.06 (0.01)	0.08 (0.07)	0.2 (0.07)
	Outflow	1.06 (0.4)					
C_K	Lagg	0.1 (0.06)	0.2 (0.1)	0.2 (0.1)	0.2 (0.1)	0.2 (0.1)	0.6 (0.55)
	Fen	0.6 (0.3) ^{2,3}	0.3 (0.2) ²	0.3 (0.3) ²	1.7 (0.5) ^{2,3}	0.6 (0.4) ²	0.1 (0.09) ²
	Bog	0.4 (0.1) ³	0.3 (0.1)	0.1 (0.1)	2.9 (0.8) ^{2,3}	0.4 (0.2) ²	0.3 (0.1) ²
	Outflow	0.3 (0.1)					
C_{Mn}^1	Lagg	0.04 (0.005) ³	0.05 (0.01) ²	0.02 (0.01) ²	0.01 (0.01) ^{2,3}	0.04 (0.01) ²	0.03 (0.01)
	Fen	0.08 (0.01) ³	0.07 (0.006)	0.07 (0.006) ³	n/d	0.05 (0.01) ²	0.03 (0.02) ^{2,3}
	Bog	n/d	n/d	n/d	n/d	n/d	n/d
	Outflow	0.03 (0.01)					
C_{Na}^1	Lagg	1.2 (0.2)	1.2 (0.2)	1.3 (0.1)	0.9 (0.2)	0.7 (0.4)	0.8 (0.3)
	Fen	1.3 (0.2)	1.0 (0.1)	1.1 (0.2)	1.5 (0.5)	1.1 (0.1)	0.9 (0.3)
	Bog	0.7 (0.3)	0.6 (0.2)	0.6 (0.1)	0.6 (0.2)	0.4 (0.1)	0.4 (0.1)
	Outflow	1.3 (0.4)					

*The bog measurements for 10-cm depths were conducted during VAG (7 and 12 Jul 2010), and water samples were not collected during the second half of VAG (19 and 26 Jul 2010) due to a low water table. At the discharge point, measurements were conducted over a two-week VAG period (7 and 26 Jul 2010), but no water was collected during the SEN period because no water outflow from the mire toward the river was detected after the extreme drought in the summer. ANOVA analyses were conducted separately for the sites, depths, and seasons. Significant differences were detected if $p < 0.05$ (1 indicates that a significant difference was detected between sites, 2 denotes a significance difference between different depths, and 3 denotes a significance difference between seasons).

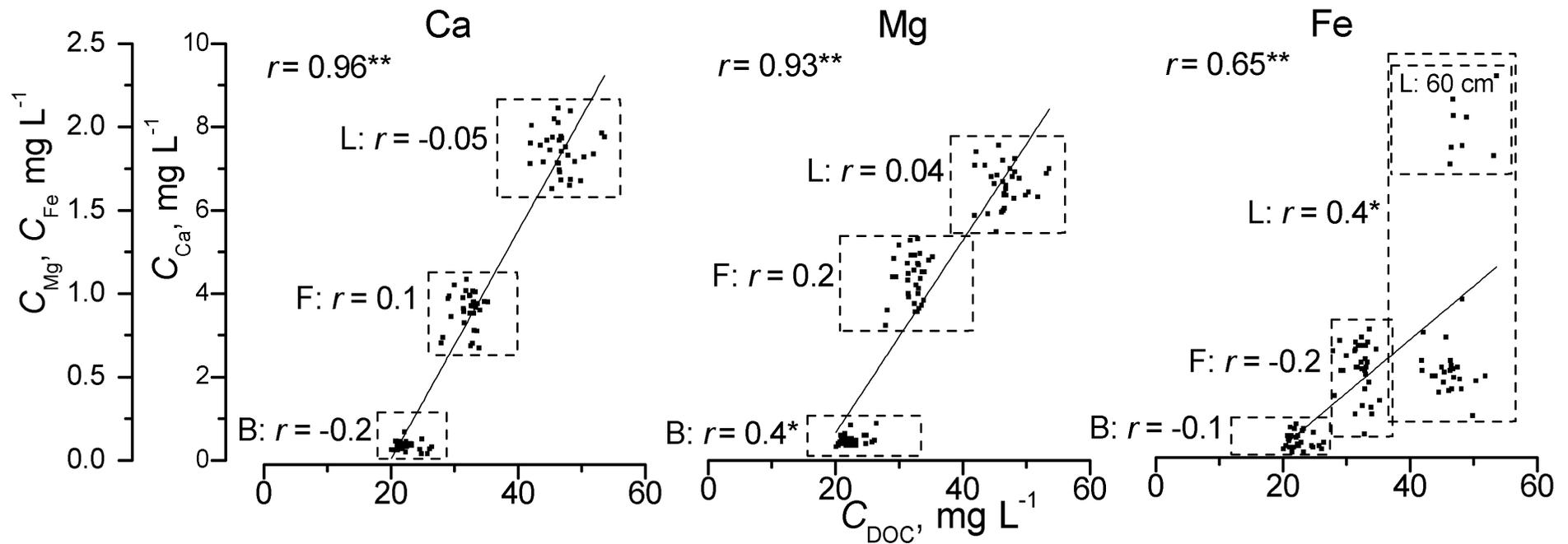


Figure 5.3 All concentrations of dissolved Ca, Mg and Fe plotted against C_{DOC} for the lagg (L), fen (F) and bog (B) sites during the summer and fall sampling periods. Pearson correlation coefficients were calculated separately for the overall study site values ($n = 95$) and separately for the values of each group (lagg $n = 32$, fen $n = 33$, bog $n = 30$).

The Pearson correlation coefficient for a sample size of $n = 95$ indicated a strong positive correlation between the C_{DOC} values and the C_{Ca} ($r = 0.96$), C_{Fe} ($r = 0.65$), and C_{Mg} ($r = 0.93$) values (Figure 5.3), whereas within each group (lagg, fen, and bog zones), a strong correlation between the C_{DOC} and the C_{Mg} , C_{Ca} , or C_{Fe} could not be observed. At a depth of 60 cm in the lagg zone, a distinctive difference in C_{Fe} was observed, and an additional separate Pearson correlation analysis was performed for this depth, which demonstrated a positive correlation with $r = 0.37$ ($n = 8$). A weak positive relationship was detected between the overall C_{DOC} and C_{Mn} ($r = 0.3$). The overall DOC concentration did not correlate with the C_{Zn} ($r = 0.004$) and was weakly negatively correlated with the C_{K} ($r = -0.15$). Furthermore, within each group (lagg, fen, and bog zones), a strong correlation between the C_{DOC} and the C_{Mg} , C_{Ca} , or C_{Fe} could not be observed.

Figure 5.4 shows that the Ca:Mg ratio was significantly different between the lagg and fen sites. However, because of the large variation of the values at the bog site, this site could not be differentiated from the fen and lagg sites with respect to the Ca:Mg ratio (Figure 5.4). The Ca:Mg ratio decreased and exhibited greater variability during the SEN period than during the VAG period.

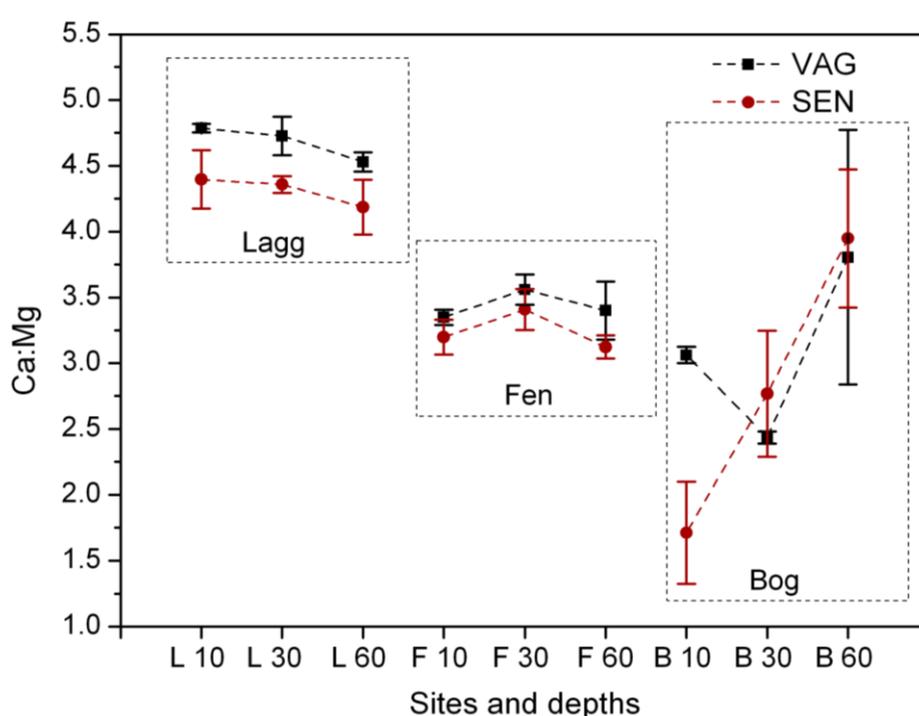


Figure 5.4 Comparison of the Ca:Mg ratios in the pore waters for different depths in the lagg, fen, and bog zones during the vegetation active growth period (VAG; 7, 12, 19, and 26 Jul 2010) and during the vegetation senescence period (SEN; 19, 22, and 26 Sep 2010 and 3 Oct 2010). The error bars represent the standard deviation of the values obtained during the 4-week measurement period. On the x-axis, L, F, and B represent the lagg, fen, and bog sites, respectively, and 10, 30, and 60 correspond to the respective depths in cm.

At the mire, the silica content increased during VAG season at the 10-cm depth from 3.8 to 4.4 mg L⁻¹ in the lagg zone, from 0.9 to 1.5 mg L⁻¹ in the fen zone, and from 0.9 to 1.5 mg L⁻¹ in the bog site (Figure 5.5). In contrast to the 10-cm depth, higher concentrations were observed at the 60-cm depth, which showed relatively constant ranges in the lagg (9.4-10.4 mg L⁻¹) and fen (1.5-2.6 mg L⁻¹) zones but a wider variation in the bog zone (1.3-3.02 mg L⁻¹). At the 30-cm depth, the observed silica concentrations were in the intermediate range between those of the 10-cm and 60-cm depths. The silica content at the outflow point was similar to the silica content in the lagg zone and increased during July from 3.8 to 6.8 mg L⁻¹ (Figure 5.5). The bog and fen sites exhibited no visible trends over the sampling period and relatively similar ranges of SiO₂ concentrations. The increase in the outflow water concentration was coincidental with the reduced flows. The concentration at the fen site was more similar to that at the bog site than to that at the lagg zone.

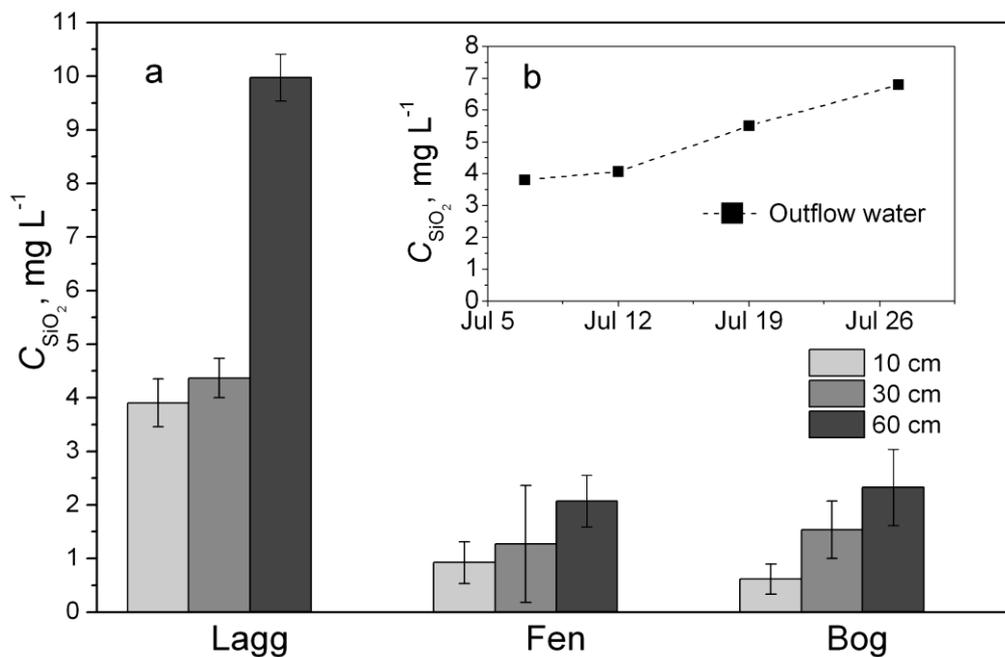


Figure 5.5 a. Silica contents in the surface and soil pore water at different depths in the lagg, fen, bog sampling sites. The error bars represent the standard deviation across the mean of four successive sampling weeks (sampling period: 7, 12, 19, and 26 Jul 2010). b. Silica content in the outflow water. The mean standard deviation of the analytical duplicate measurements is 0.08 mg L⁻¹.

Agglomerative hierarchical clustering was conducted on the water chemistry data from the seasonal 10-cm pore and discharge samples collected during the VAG season (Appendix, Table 5.6). This study demonstrated that the main flow path was over the lagg zone, which was marginally influenced by the bog and fen chemistry.

Thus, the outflow water was most closely related to the lagg zone, and both sites were placed in the same group, whereas the bog and fen sites were placed in a separate group (Figure 5.6).

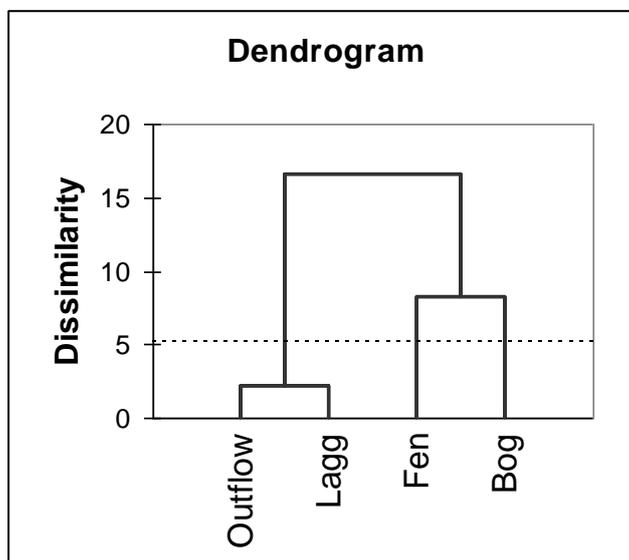


Figure 5.6 Dendrogram based on the agglomerative hierarchical clustering method. The agglomerative hierarchical clustering was performed based on a set of mean water chemical properties over the VAG period (n=11) as indicated in Table 5.5 (Appendix). The diagram shows that the water-chemical properties of discharge waters are similar to the ones of the waters at 10 cm depth in the lagg zone. Dissimilarity was calculated based on the Euclidean distance. The dotted line represents the automatic truncation, leading to the separation of groups (XLSTAT, Addinsoft, France).

5.5 Discussion

5.5.1 Dissolved Organic Carbon (DOC)

The concentration of DOC in the mire pore water was 20-54 mg L⁻¹ at Ust-Pojeg, a finding consistent with the range for northern peatlands (20-60 mg L⁻¹) (Blodau 2002). The concentration in the fen zone (28-38 mg L⁻¹) was comparable with the seasonal average (20-40 mg L⁻¹) for pore water in fen zones reported by Moore et al. (2003) in a Canadian peatland. Shvartsev et al. (2012) observed a higher DOC range in a wetland of western Siberia (25-165 mg L⁻¹), where the greatest DOC concentrations were observed in the regions with the most stagnant conditions. However, in that study, the authors did not indicate the method and filter size that were used to separate and analyze the DOC fraction, and thus the data may not be directly comparable. Furthermore, in contrast to the study of Ulanowski & Ulanowski & Branfireun (2013), who studied a heterogeneous peatland in Canada and found that a bog site had a higher DOC concentration than a fen site, the current study found that the fen exhibited a higher DOC concentration than the bog. This finding highlights the fact that extrapolating results of peatland studies in one region to other areas may generate an erroneous understanding of local landscape functioning.

In contrast to the study performed by Fraser et al. (2001), who detected decreases in the DOC concentrations in a Canadian bog up to a depth of 75 cm over the summer, such seasonal decreases were not observed for the bog site in the current study. However, during the fall, increased concentrations were observed at a depth of 10 cm compared to those of deeper layers (Figure 5.2). This result may be attributed to the cumulative effect of increased DOM intake and decomposition rate of particulate organic carbon in the aerobic layer because of fallen leaves during fall. Investigations of the active vegetation growth period are particularly interesting, as the ecosystem productivity (Pinney, 2000) and consumption are greatest during these warm months. As demonstrated by Fenner et al. (2004), during the active growth season, *Sphagnum* spp. transform a portion of their recent photosynthates into the dissolved fraction within time scales of hours (e.g., a carbon labeling experiment showed that after 4 h, up to 4 % of the total DOC in peat leachate was produced from ¹³C₂ pulse labeling). During the active growth season, there are two main sources of DOM. The first source is derived from the leachates and exudates of fresh vegetation

decomposition, and the second source is derived from the peat itself. However, Palmer et al. (2001) performed ^{14}C analyses and showed that the pore water DOC in peat was significantly younger than peat organic carbon, which could indicate that the main DOC fraction is derived from fresh vegetation. Thus, most of the DOC may have been derived from fresh vegetation during the observation period of this study. Furthermore, the seasonal increase in the DOC at a depth of 10 cm in the lagg zone (Figure 5.2) during the SEN period, which was likely caused by fallen leaves acting as an additional carbon source, indicated the importance of fresh plant tissue in DOC production (Hongve, 1999; Blodau et al., 2004). Carbon addition from trees during the SEN period was caused by litter from deciduous plants because coniferous litter and peat release DOC more evenly throughout the year compared to deciduous litter (Hongve, 1999).

The higher carbon content in the precipitation at the lagg site compared to that of the other sites can be attributed to stemflow and rainfall passage through the canopy. The rainfall DOC concentrations in the treeless bog, fen ($1.4\text{-}2.9\text{ mg L}^{-1}$), and lagg ($8.7\text{-}9.3\text{ mg L}^{-1}$) zones were comparable to those observed at a swamp in Canada, in which Dalva & Moore (1991) recorded both DOC concentrations of 2.0 mg L^{-1} in the above-canopy precipitation and increased DOC concentration levels after passage through tree canopies as throughfall ($9.1\text{-}14.6\text{ mg L}^{-1}$) and stemflow ($23.1\text{-}30.1\text{ mg L}^{-1}$). Koprivnjak & Moore (1992) reported DOC concentrations of $1\text{-}2\text{ mg L}^{-1}$ in the above-canopy precipitation, as well as much higher values in stemflow and tree throughfall ($50\text{-}150\text{ mg L}^{-1}$).

Factors that control the rates of production and export of DOM are still poorly understood for peatlands (Holden 2005). In the current study, one of the main environmental controls of the observed variations in the DOC concentrations among sites (Figure 5.2) was most likely the site-specific vegetation, which served as the main source of DOC. The main vegetation species in the lagg zone were *Menyanthes trifoliata*, *Betula pendula*, and *Alnus incana*. The fen zone was covered predominantly with *Scheuchzeria palustris* and *Sphagnum fuscum*, while the vegetation cover at the bog site was predominantly *Sphagnum* spp. Litter from *Sphagnum* spp. has low bioavailability because it has low nutrient content and is characterized by polyphenols, which strongly inhibit microbial decomposition (Verhoeven & Toth, 1995; Bragazza et al., 2006). The decomposition of deciduous vascular plant species' litter was observed to be two times faster than that of bryophytic litter (Hobbie et al.,

2000), which can cause increased DOC production. In contrast to the *Sphagnum* litter, which has low bioavailability, the DOC that is leached from *Sphagnum* spp. is highly labile and disappears faster than the DOC leached from vascular plants (Wickland et al., 2007). Therefore, the higher decomposition rate of plant organic matter and the slower decomposition of the leached DOC at the lagg and fen zones can cause higher DOC concentrations than those of the bog zone.

An additional important factor that controls DOM production is the temperature. If the temperature continues to rise due to climate change, alterations in plant production may occur (Weltzin et al., 2003; Wiedermann et al., 2007), which may modify the quantity of DOM produced in the mire. However, the response would depend on the type of plant and the ecosystem. Furthermore, temperature increases will lead to a number of other process alterations such as changes in the bacterial activity, energy balance, and water table etc., which may influence DOM production. Another factor that affects DOM production is the nutrient content. At the bog site, the lower nutrient content (Tables 5.2 and 5.3) may be a limiting factor in the transformation of particulate organic carbon (POC) to DOC and can cause decreased DOC concentrations. The lagg zone received the highest nutrient supply from the surrounding mineral soils, which may increase microbial decomposition of POC and higher DOC production in the lagg zone compared to the ombrotrophic site.

Furthermore, the height of the water table plays an important role by creating oxic or anoxic conditions. A high water table may lead to anaerobic decomposition, which is slower than aerobic decomposition. Consequently, DOC in different states of decomposition accumulated in the fen and lagg zones. In contrast, the bog zone had a thicker aerobic layer because of the lower water table, which led to faster DOC mineralization through oxidation and CO₂ emission into the atmosphere (Schneider et al., 2012). However, several studies have reported conflicting results on the influence of the water table on the DOC content. For instance, Tipping et al. (1999) found that low water tables increased peat-derived DOC production, while Blodau et al. (2004) found that the water table did not significantly affect DOC production. The predicted changes in temperature and rainfall patterns due to climate change will likely affect both the amount and the characteristics of the organic carbon transported downstream from boreal catchments (Köhler et al., 2008).

Temperature, pH, and UV radiation differences among different mire sites can lead to variations in the DOC content. For example, differences in the pH between

sites can influence DOC solubility, and a pH increase of 0.5 units in pore water can cause a 50-60 % increase in the DOC content (Tipping & Woof, 1990; Clark et al., 2005). The pH in the lagg zone was higher (5.6) than the pH of the bog (4.4), which should increase the DOC solubility in the lagg zone. Temperature directly affects the rates of many physical, chemical, and biological processes (Limpens et al., 2008). Temperature increases of approximately 5 °C may cause the decomposition rate to double in high-latitude soils (Hobbie et al., 2000). In the current study, the summer water temperatures at the open bog and fen sites were higher than the temperatures at the lagg site. Therefore, during the hot summer season, both DOC decomposition and POC to DOC transformation rate at the bog and fen sites may be higher than that of the lagg site. Moreover, organic matter degradation in peatlands is affected by UV light. Treeless bogs and fens are more exposed to UV radiation and sunlight during the summer, which can lead to additional mineralization. Furthermore, because of its slightly elevated location, the bog site continuously discharges exported DOC toward the fen and lagg zones, which lowers the amount of carbon in the bogs and gives additional carbon inputs to the fen and lagg sites. In summary, differences in the DOC concentrations among sites were caused by multiple physical and chemical parameters across the lagg-fen-bog transect, and one single factor cannot explain the observed differences.

The DOC (48-52 mg L⁻¹) concentrations in the outflow draining the mire complex were higher than the upper values of the total organic carbon concentration (20-40 mg L⁻¹) in the streams from a snow-free boreal mire (Köhler et al., 2008). The high temperature during the summer reduced the flow rate of water from the bog and fen sites toward the lagg site, which halted the delivery of DOC to the adjacent river. The reduced supply of DOC was also observed on a larger scale, as indicated by the lowered DOC concentrations in river samples located upstream from the study site, which were influenced by a mixed forest-mire landscape. River concentrations decreased from 8.2 to 4.5 mg L⁻¹ due to the drought, leading to a stronger relative contribution of deeper groundwater sources to the river water. The decreased export of DOM from the mire to the river during the dry summer may decrease the net aquatic primary production downstream and other biogeochemical processes, such as the transport of organic pollutants, colloid chemistry, and acidity regulation.

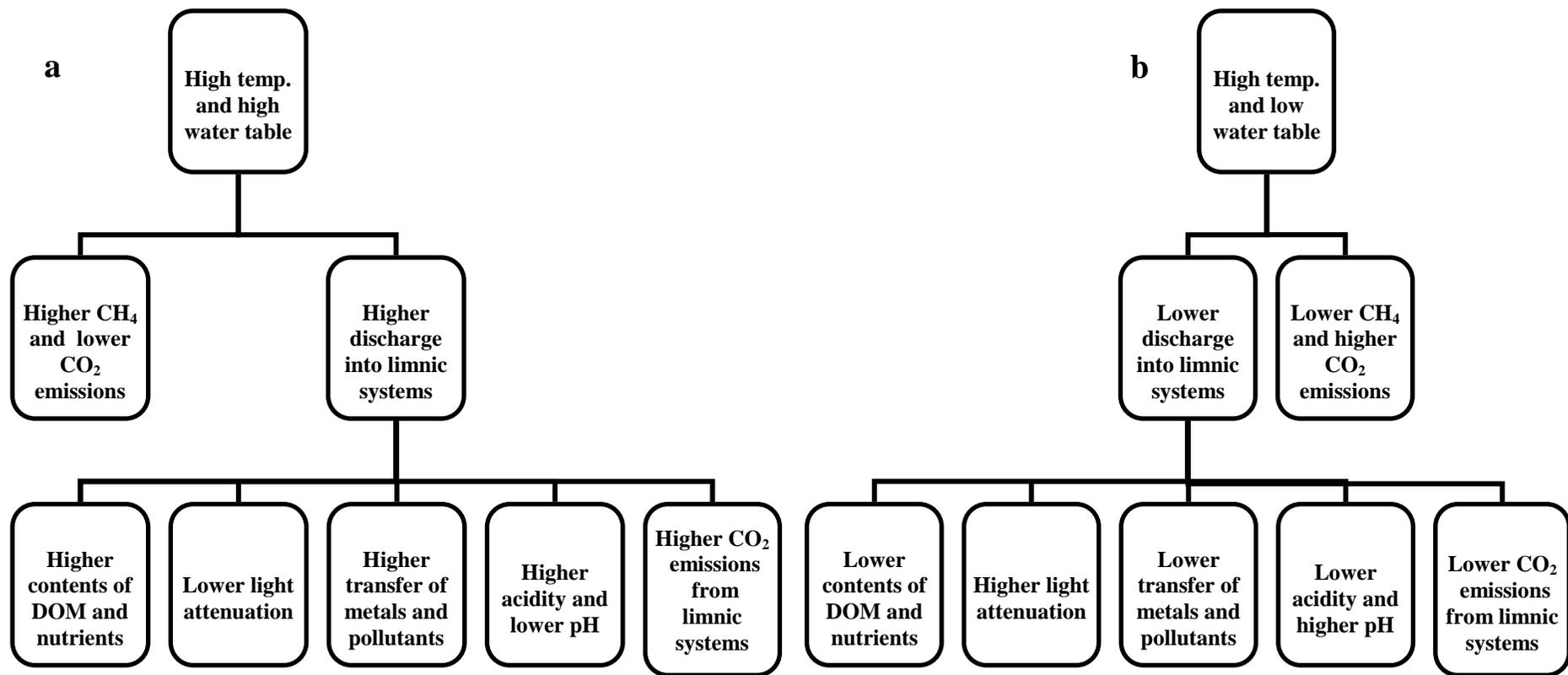


Figure 5.7 A conceptual model of possible peatland effects on fluvial system and atmosphere under climate change conditions. Comparing a. high and b. low water table scenarios. The model assumes no changes in vegetation cover.

A schematic representation of the possible responses to climate change under increased temperature and water level changes is presented in Figure 5.7. As presented in the conceptual model, changes in the temperature or water table may lead to multiple changes in the ecosystem. The DOC retained in the mire complex because of the low discharge is can be transferred to the atmosphere in the form of CO₂ and CH₄ emissions due to microbial activity. Pastor et al. (2003) demonstrated an exponential increase in the CO₂ and CH₄ emissions that coincided with the increased retention of DOC from boreal peatlands because of decreased discharge. Therefore, if the current temperature increase continues, more DOC will be retained within the mire and will not be transferred into the aquatic system, which would increase greenhouse gas emissions in the atmosphere from the terrestrial system. In particular, lagg zones can act as strong CH₄ producers, similar to the wet forested zones (Fiedler et al., 2005; Christiansen et al., 2010; Grunwald et al., 2012).

However, all of these potential responses may be short-term changes. For example, further DOC decomposition could be limited by nutrient availability. Moreover, under the protracted influence of global warming, the ecosystem could undergo alterations in species composition. Fenner et al. (2009) detected increased vascular plant coverage at the expense of *Sphagnum* coverage in a weakly minerotrophic peatland exposed to elevated CO₂ levels. Hence, if CO₂ levels in the air increase and cause changes in the species composition of the peatland, the release of DOC from the mire could potentially change.

5.5.2 Water-chemical gradients: pH, macroelements, and microelements

Determination of the ion content and pH during both measurement periods was conducted on a weekly basis. However, because of the small weekly variations in the values, sampling could also have been conducted bi-weekly or monthly during the baseflow periods in summer and fall. Frequent sampling is only required in the case of strong rain events or substantially changing additional water inflows. Similarly, Howie & Van Meerveld (2012) showed that a one-time sample collection may be adequate for bog sites but not for minerogenic sites. Thus, it has been suggested that the one-time sample collection may broadly approximate the changes over the hydroperiod and that sampling should be conducted during the key hydrological phases of the year, (i.e., winter (ground unfrozen conditions), spring and late summer

(Howie & Van Meerveld, 2012). This type of sampling will provide a better overview of the pore water hydrochemistry variability in response to changes in evapotranspiration and precipitation.

A strong link among the water chemistry, hydrology, and vegetation was observed across the lagg-fen-bog gradient at the study site. Tall shrubs and trees were present in the lagg zones, while moss communities were dominant at the fen and bog sites. Similar observations were made by Walbridge (1994), who found that tall communities occurred more frequently in peatlands with more alkaline surface waters (pH 4.6-5.0) while low shrub and bryophyte species were more frequent with more acid water conditions (pH 4.0-4.4). Vitt and Chee (1990) found that the vascular plant communities appeared to respond mainly to changes in the nutrient content and that bryophytes responded to changes in the pH/alkalinity level.

The lagg zone exhibited the highest pH values. This result is comparable to those of other studies (e.g., Bragazza et al., 2005; Howie & van Meerveld, 2012). The bog site exhibited the lowest pH because of the extensive coverage by *Sphagnum* spp., which excretes organic acids, and the high physiological cation-exchange capacity of *Sphagnum* peat, which removes cations from the pore water (Charman, 2002; Rydin & Jeglum, 2006). The pH values were relatively constant and did not vary between seasons; therefore, the pH may be a stable parameter for all mire sites. Similar observations were made by Howie & Van Meerveld (2012).

The gradient in surface water chemistry at the study site (lagg: pH 5.6, C_{Ca} 6.5-7.3 mg L⁻¹; fen: pH 5.3, C_{Ca} 2.9-3.6 mg L⁻¹, and bog: pH 4.4, C_{Ca} 0.2-0.3 mg L⁻¹) was comparable to the ranges reported for other bogs and fens, such as for bogs in North America. Glaser et al. (1981) reported a pH of 3.8-4.1 and a C_{Ca} of 0.5-2.1 mg L⁻¹ for a raised bog and obtained a pH of 4.0-5.1 and a C_{Ca} of 2.2-4.4 mg L⁻¹ for an extremely poor fen. Generally, the pH ranges between 3.5 and 4.2 for bogs and between 5 and 7 for intermediate to moderately rich fens (Sjors & Gunnarsson, 2002; Rydin & Jeglum, 2006). Based on this classification, the fen site can be included in the moderately rich category.

The measurements of the deeper pore waters were comparable to those found by Bendell-Young (2003), who studied 15 peatlands at depths of 50 cm in Ontario. In this location, the mineral-poor mire exhibited the following chemical parameters: pH, 5.8-6.2; C_{Ca} , 2.5-4.8 mg L⁻¹; C_{Mg} , 0.8-1.4 mg L⁻¹; C_{Si} , 0.3-1.3 mg L⁻¹; C_{Mn} , 0.03-0.05 mg L⁻¹; and C_{Fe} , 0.3-0.8 mg L⁻¹. These values are comparable to those obtained at a

depth of 60 cm at the fen site in the present study, and the following mean values were measured over the four sampling weeks: pH 5.5, C_{Ca} $3.1 \pm 0.2 \text{ mg L}^{-1}$, C_{Mg} $1.1 \pm 0.07 \text{ mg L}^{-1}$, C_{Si} $0.9 \pm 0.2 \text{ mg L}^{-1}$, C_{Mn} $0.07 \pm 0.01 \text{ mg L}^{-1}$, and C_{Fe} $0.6 \pm 0.1 \text{ mg L}^{-1}$. However, the DOC concentrations obtained in the study performed by Bendell-Young (2003) were much lower than those obtained in the present study. Compared to previous investigations in Russian boreal wetlands (Inisheva & Inishev, 2001; Shvartsev et al., 2012), the current study yielded relatively lower mean ion contents. The observed differences in the concentrations were largely due to differences in the geology of the upland areas surrounding the studied mires. Inisheva & Inishev (2001) conducted a study in an area containing carbonate rocks and iron ores and reported mean Ca and Fe concentrations as high as 15.6 and 7.8 mg L^{-1} , respectively, in the soil pore waters in mires. These differences highlight the importance of further water chemistry studies in the boreal regions of Russia, which are underrepresented in the literature.

The lagg zone exhibited the highest contents of most nutrients and minerals other than K. The major cation and anion content was generally higher at the marginal sites of the mire complex because of the adjacent and underlying mineral soil (e.g., Bragazza & Gerdol, 1999; Tahvanainen et al., 2002; Howie & van Meerveld, 2012). The low K concentration was most likely due to a stronger uptake by vascular plants in the lagg zone. A similar trend has been described by Waughman (1980). The high concentrations of Fe at a depth of 60 cm at the lagg site were most likely due to the higher delivery of Fe by the mineral soil at the layer compared to the organic soil (Figure 5.3). Because bog sites are only fed by atmospheric deposition, the lowest nutrient and mineral concentrations were detected at the bog site, where the acidity is mainly regulated by the presence of organic acids. Additionally, *Sphagnum* spp. have a high physiological cation exchange capacity and remove cations from the pore water (Charman, 2002; Rydin & Jeglum, 2006). The lagg zone can potentially act as a biogeochemical hotspot because of the high DOM and ion content. In this context, a hotspot is defined as an area exhibiting “*disproportionately high reaction rates relative to the surrounding matrix*” (McClain et al., 2003).

Although there were strong positive correlations between the DOC concentrations and the Ca, Fe, and Mg concentrations in all of the samples ($n = 95$), positive correlations were not present within each ecohydrological subunit group (lagg, fen,

and bog samples) (Figure 5.3). The weak relationships within the groups may be explained by pseudo-correlation. Higher DOC concentrations, such as those observed in the lagg, could be due to more productive vegetation, whereas a high ion concentration could be due to different hydrological water sources. Thus, there may be no direct relation between the DOC content and ion content, even though a strong correlation may be observed over the large-scale gradient but not within the groups.

5.5.3 Flow-path tracing

This study demonstrates that the pH, C_{Ca} , C_{Mg} , and C_{SiO_2} values and agglomerative hierarchical clustering can be used as potential tracers of lateral mass transfer across catchments, which is particularly important for catchments without distinct flow paths. Because silica is a product of the geochemical weathering of minerals, the silica content can be used to investigate the degree of minerogenous water influence (Bendell-Young, 2003). Similarities between the silica content at the discharge point and at the lagg zone may indicate that the lagg zones are the main contributor to the discharge. The observed increase in the outflow water concentration was coincidental with reduced flows, which was indicative of increased contributions from deeper soil pore waters. The low silica content at the fen site also indicated that the fen site was only slightly affected by mineral inflow water during the summer, and demonstrated the effect of the extremely hot summer on the water flow. Due to the observed decrease in the water table, minerogenous interflow or groundwater did not reach the fen site. Determining the variation in the silica content across the mire is an important endeavor because information on silica transport within wetlands is limited and represents a major gap in the understanding of climate change, as carbon sequestration is coupled to the silica cycle (Sommer et al., 2006; Struyf & Conley, 2009).

In contrast, the Ca:Mg ratio could not be used to distinguish the three sites because of the high variation of the ratio at the bog site. In a study performed by Wells (1996), a Ca:Mg ratio of 2.5 was suggested as the boundary between ombrotrophic and minerotrophic peatlands. In the current study, it was not possible to separate ombrotrophic from minerotrophic peatlands based on this value. The ratio also decreased and exhibited greater variability during the SEN period, which was most likely caused by dilution due to precipitation. The high variation at the bog site

was most likely caused by very low concentrations of Ca and Mg, as small fluctuations cause large variations in ratio calculations. Therefore, the Ca:Mg ratio could not be successfully implemented for flow path tracing. Similarly, a recent study by Howie & Van Meerveld (2012) showed that the Ca:Mg ratio was not a useful indicator of the mineral soil water limit. The Ca:Mg ratio may also vary because of the annual precipitation (Waughman, 1980). Thus, the Ca:Mg ratio only can be used for mineral soil water limit delimitation if a representative number of bog water and rainwater sites in the region of interest have been measured (Shotyk, 1996).

5.6 Conclusions

The current study showed that the DOC content within the boreal mire complex ranged from 20-54 mg L⁻¹, which is within the range of the values described for other northern peatlands. The diverging hydrochemistry and DOC content indicated high heterogeneity between different ecohydrological subunits within one mire complex. The lowest DOC content was observed within the bog (20-28 mg L⁻¹); intermediate concentrations were detected in the fen zone (28-38 mg L⁻¹); the transitional lagg zone, which has been poorly characterized in the literature, demonstrated the highest DOC content (42-54 mg L⁻¹). The DOC gradient was most likely governed primarily by the vegetation differences. Additionally, other physical and chemical parameters, such as differences in the pH, UV exposure, and nutrient contents, could have caused diverging DOM concentrations. Thus, for regional assessment and upscaling, at least three (lagg, fen, and bog) areas should be spatially distinguished to appropriately assess both the dynamics of DOM in surface and pore waters of mire soils and the biogeochemical processes that rely on them, such as CO₂ and CH₄ production and emission.

Furthermore, the current study shows that the lagg zone may act as a hotspot within the mire in terms of the hydrochemistry. Due to the high nutrient and DOC content, the lagg zone can potentially act as a major CO₂ and CH₄ emitter. The diverging pH, C_{DOC}, C_{Ca}, C_{Mg}, and C_{SiO₂}, together with the agglomerative hierarchical clustering results, indicate that the lagg site is the primary contributor to the outflow streams. Thus, the lagg zone is the mire zone that determines the quantity and quality of the organic matter that is exported from boreal mire-forest landscapes to the limnic systems (lakes and rivers). These interface zones should be delimited and more thoroughly studied to better assess the DOC export and the CO₂ and CH₄ emission rates from boreal forest-mire landscapes on both the regional and continental scales.

5.7 Appendix

Table 5.4 Chemical concentrations measured in pore waters at different sites during the transitional period between VAG and SEN sampling periods.

Chem. elem .	Date	Lagg			Fen			Bog		
		10 cm	30 cm	60 cm	10 cm	30 cm	60 cm	10 cm	30 cm	60 cm
C_{Ca} , mg L ⁻¹	3-Aug	7.12	7.75	-	3.29	3.76	4.03	0.66	0.36	0.40
	17-Aug	7.68	8.45	8.10	3.80	4.05	-	-	0.39	1.04
	24-Aug	7.61	8.03	-	3.64	3.90	4.20	-	0.37	0.67
	1-Sep	6.94	7.56	7.59	2.69	3.81	4.06	0.32	0.46	0.36
	8-Sep	6.91	-	8.19	2.94	3.79	3.56	-	0.24	1.54
C_{Mg} , mg L ⁻¹	3-Aug	1.47	1.71	-	1.02	1.13	1.24	0.18	0.12	0.10
	17-Aug	1.70	1.80	1.67	1.22	1.33	1.37	-	0.13	0.19
	24-Aug	1.77	1.85	-	1.08	1.18	1.29	-	0.12	0.12
	1-Sep	1.52	1.77	1.75	0.96	1.20	1.32	0.22	0.15	0.10
	8-Sep	1.51	-	1.89	0.97	1.00	0.98	-	0.09	0.45
C_{Fe} , mg L ⁻¹	3-Aug	0.58	0.51	-	0.49	0.77	0.57	0.09	0.09	0.12
	17-Aug	0.39	0.52	1.76	0.34	0.52	0.61	-	0.06	0.14
	24-Aug	0.52	0.75	-	0.26	0.64	0.61	-	0.10	0.20
	1-Sep	0.28	0.49	0.83	0.30	0.65	0.54	0.09	0.11	0.11
	8-Sep	0.41	-	0.72	0.36	0.59	0.63	-	0.07	0.28
C_K , mg L ⁻¹	3-Aug	0.21	0.16	-	0.50	0.22	0.26	4.71	0.15	0.22
	17-Aug	0.52	0.77	0.51	0.56	0.55	0.51	-	0.16	0.39
	24-Aug	0.09	0.07	-	0.25	0.17	0.13	-	0.21	0.14
	1-Sep	0.15	0.17	1.83	1.66	0.35	0.07	1.07	0.13	0.09
	8-Sep	0.69	-	0.21	-	0.45	0.47	-	0.27	0.41
C_{Mn} , mg L ⁻¹	3-Aug	0.02	0.02	-	0.05	0.07	0.05	0.01	0.02	0.03
	17-Aug	0.04	0.04	0.02	0.05	0.06	0.08	-	0.03	0.03
	24-Aug	0.05	0.03	-	0.02	0.09	0.07	-	0.02	0.02
	1-Sep	0.02	0.04	0.01	0.04	0.07	0.04	0.03	0.03	0.03
	8-Sep	0.04	-	0.02	0.05	0.08	0.07	-	0.02	0.01
C_{Na} , mg L ⁻¹	3-Aug	1.11	1.17	-	1.35	0.92	0.88	4.39	0.48	0.53
	17-Aug	1.18	1.63	1.49	1.69	1.72	1.57	-	0.72	0.97
	24-Aug	0.83	1.14	-	1.32	1.33	1.14	-	0.50	0.54
	1-Sep	1.28	0.92	1.38	1.36	1.24	1.00	1.14	0.59	0.51
	8-Sep	0.81	-	0.77	1.40	1.27	1.15	-	0.42	0.76
C_{Zn} , mg L ⁻¹	3-Aug	0.03	0.02	0.13	-	0.01	0.01	0.31	0.02	0.02
	17-Aug	0.04	0.05	0.05	0.04	0.04	0.06	-	0.03	0.04
	24-Aug	0.03	0.03	-	0.03	0.04	0.03	-	0.02	0.03
	1-Sep	0.05	0.02	0.05	0.04	0.02	0.01	0.06	0.01	0.02
	8-Sep	0.02	-	0.01	0.08	0.03	0.03	-	0.01	0.01

*Samples at the bog site at a depth of 10 cm were not collected on August 17th and 24th due to the low water table. All other missing values were not presented because the samples were lost during transportation.

Table 5.5 Mean seasonal values of chemical species concentrations used for the agglomerative hierarchical clustering analyses measured in pore waters at different sites during VAG season.

Species	Outflow	Lagg	Fen	Bog
C_{DOC} , mg L ⁻¹	46.2	45.5	31.6	20.9
C_{SiO_2} , mg L ⁻¹	5.03	3.9	0.92	0.5
C_{Fe} , mg L ⁻¹	1.1	0.5	0.5	0.1
C_{Ca} , mg L ⁻¹	4.8	7.0	3.1	0.3
C_{Mg} , mg L ⁻¹	1.3	1.5	0.9	0.1
C_{Na} , mg L ⁻¹	1.3	1.2	1.3	0.7
C_{Mn} , mg L ⁻¹	0.03	0.04	0.08	n/d
C_{K} , mg L ⁻¹	0.3	0.1	0.6	0.4
C_{Zn} , mg L ⁻¹	0.03	0.04	0.08	0.06

6 Dissolved organic carbon fluxes during the spring snowmelt and the subsequent baseflow period in a mire-forest landscape in the Komi Republic, Northwest Russia

6.1 Abstract

The spring snowmelt period is the major hydrological event in the annual water cycle of the boreal regions that strongly influences the carbon flux between the terrestrial and aquatic systems. Typically, most of the carbon exported via lateral fluxes from the boreal mire catchments is in the form of dissolved organic carbon (DOC). However, the contributions of different ecohydrological subunits within the mire complexes, to the water and carbon export of the catchments are not well understood. An increased understanding of the different contributions of the ecohydrological subunits to the discharge can help to better predict the potential regional loss of DOC based on the land cover type. Thus, the aim of this study was to identify the flow paths of runoff water during the snowmelt period and to provide a conceptual understanding of the spatial and temporal dynamics of the surface water chemistry along a lagg-fen-bog gradient after the snowmelt period in a mire complex (61°56'N, 50°13'E) in Northwest Russia. Both hydrochemical and absorbance measurements were used to trace flow paths and to characterize dissolved organic matter (DOM) in the inflow, peat pore, and outflow waters during this period. During the first stages of the snowmelt, the “old carbon,” which represents carbon that had been accumulated during the previous year before the freeze-up, was flushed out to the adjacent river. Afterwards, the fen and the surface layer of the lagg were the main contributors to the carbon export flux because they were better connected hydrologically to the outflow streams. During the spring snowmelt period, a significant amount ($\sim 1.7 \text{ g C m}^{-2}$) of DOC was transferred by the $\sim 74 \text{ mm}$ of runoff from the catchment into the river. The DOC surface water concentration increased during the subsequent summer and fall seasons, ranging from 19 to 74 mg L^{-1} across the mire, with an average of $45 \pm 14 \text{ mg L}^{-1}$, which presumably sets up the carbon flux of the following year's spring melt period. The combination of high-frequency absorption and hydrochemistry measurements conducted in this study provides a better understanding of the transport processes that occur within peatlands and helps to identify the sources of the DOC in their streamflow discharge.

6.2 Introduction

The lateral carbon losses from the terrestrial to fluvial and lacustrine systems are typically dominated by dissolved organic carbon (DOC), and most temperate and boreal catchments export between 1 and 13 g C m⁻² yr⁻¹ (Hope et al. 1994; Laudon et al. 2004; Ågren et al. 2007; Nilsson et al. 2008; Jager et al., 2009). Thus, carbon export in the form of DOC can represent a significant part of the annual net carbon uptake. Nilsson et al. (2008) measured losses via lateral fluxes of up to 37 % of the annual net CO₂-C uptake of a boreal oligotrophic minerogenic mire, whereas Fraser et al. (2001) estimated the DOC export from a peatland area as approximately 12 % of the magnitude of the residual carbon sink. In the study by Dinsmore et al. (2011), DOC represented 24 % of the net ecosystem exchange uptake. These high numbers emphasize the importance of integrating lateral carbon fluxes into carbon budget estimates. Apart from redistributing parts of the carbon budget between terrestrial and limnic systems (lakes and rivers), the lateral fluxes of dissolved organic matter (DOM) also affect the transport and toxicity of heavy metals and organic pollutants (McKnight et al. 1992; Pokrovsky et al. 2006), the photochemistry (Karlsson et al., 2009; Williamson & Zagarese, 1994), the acidification of limnic systems (Oliver et al., 1983), and the nutrient availability in limnic ecosystems (Carpenter et al., 2005).

Knowledge of the factors that control the transport of organic carbon within peatlands and the hydrological processes that deliver organic carbon to fluvial and lacustrine systems is still lacking (Holden 2005; Limpens et al. 2008), especially for the extensive lowland mire complexes which are found in large areas of boreal Russia. Tracing lateral carbon fluxes can be particularly challenging in the northern peatlands due to the diffuse surface water flows and outflows (Waddington & Roulet, 1997), which require complex measurements. Tracing DOM production and export across the mire is complicated because of the high degree of spatial heterogeneity the peatland landscapes (Bridgham, 1998).

Generally, hydrology is considered the main factor controlling lateral organic carbon fluxes (Boyer et al. 1997; Holden 2005; Dawson et al. 2008), and most of the carbon export fluxes occur during short periods of high flow (e.g., Schiff et al. 1998; Clark et al. 2007). The fate and export of DOC in boreal catchments with significant peatland areas are also considered to depend on climatically controlled changes (e.g., temperature change, frost duration, snowpack change), discharge, and DOC export of

preceding years (Pastor et al. 2003; Laudon et al. 2004; Nilsson et al. 2008; Ågren et al. 2010b; Haei et al. 2010). Frost leads to the addition of DOC to soil pore waters through the possible physical disruption of the soil (Kalbitz et al., 2000), the lysis of the cells of soil microorganisms (Morley et al., 1983; Giesler et al., 2007), and the increased fine root mortality (Giesler et al., 2007; Tierney et al., 2001). However, the frost-related DOC release can be limited. In an experimental study by Hentschel et al. (2008), severe soil frost increased the release of DOC from the O horizons, but the effect was only detected in the first freeze-thaw cycle.

In the boreal region, the DOC content of streams varies temporally and spatially (Köhler et al. 2008). It has been estimated that approximately 35-70 % of the annual runoff and DOC export from boreal landscapes occurs during the spring snowmelt period (Laudon et al. 2004; Dyson et al. 2011). Thus, as the major hydrological event in the annual water cycle of boreal regions, the spring snowmelt plays an important role in the distribution of carbon and nutrients between terrestrial and aquatic systems (e.g., Oczkowski et al. 2006, Nilsson et al. 2008; Dinsmore et al. 2011; Dyson et al. 2011). Therefore, snowmelt can be considered to be a hot moment for the DOC fluxes in northern ecosystems. A hot moment is defined as “*a short period of time that exhibits disproportionately high reaction rates relative to longer intervening time periods*” (McClain et al., 2003).

Currently, most studies on these topics have been conducted in Canada, Fenno-Scandinavia, and the UK. On the other hand, DOM is a poorly characterized component of the carbon cycle in the boreal regions of Russia, which are home to a major portion of the world's carbon-rich peatlands. It has been demonstrated previously that interpolation from the well-investigated boreal regions, such as Canada, can lead to the misestimation of carbon stocks in Russia (Zubrzycki et al., 2012). Similarly, it can be suggested that DOM production and export vary between sites and regions because of the different geology, vegetation and topography. Furthermore, few studies that present frequent sampling over space and time, and thus, published peatland geochemical results must be considered critically (Ulanowski & Branfireun, 2013). Therefore, different land classes should be sampled across the heterogeneous peatlands; alternatively, in northern peatlands the abundance and distribution of natural elements can be underrepresented (Ulanowski & Branfireun, 2013).

Despite many studies showing that most dissolved carbon losses from peatlands occur during high-flow periods, fewer studies have monitored the changes in the properties and chemical composition of the discharged water (Hood et al. 2006; Ågren et al. 2008). Such an investigation could indicate the parts of a forest-mire complex catchment that become hydrologically connected to the outflow stream(s) at different stages of the annual hydrograph with different types of carbon that are exported to the aquatic systems (Hood et al., 2006). Thus, to trace the flow paths and monitor the changes in the outflow water, it is important to select a conservative tracer capable of distinguishing between the separate ecohydrological subunits within the mire complexes (such as bogs, fens, and lagsgs-transition zones between mires and the adjacent mineral soils) and between different seasons.

Various hydrochemical parameters can be used to trace the flow paths of lateral fluxes (Dinsmore et al., 2011). For example, pH, calcium (Ca), sodium (Na), magnesium (Mg), manganese (Mn), and silicon (Si) are widely used to delineate minerotrophic-ombrotrophic gradients and to explain the distribution of plant species across mire landscapes (Vitt et al., 1995; Sjors & Gunnarsson, 2002; Tahvanainen, 2004). These tracers can potentially be used to trace flow paths and to separate different ecohydrological subunits within mire complexes. It is also possible to track the qualitative changes of DOM using various absorbance ratios based on spectrophotometry, which can provide information on the aromatic content, the molecular weight, and the extent of humification of the DOM (e.g., Peuravuori & Pihlaja 1997; Worrall et al. 2002; Weishaar et al. 2003; Berggren et al. 2007; Spencer et al. 2007; Ågren et al. 2008; Baker et al. 2008; Inamdar et al. 2012). Ågren et al. (2008) demonstrated that the chemical composition of exported DOC depends on the catchment type; for example, peatlands export DOM with a higher aromaticity than non-peatland ecosystems. Berggren et al. (2007) used the A_{254}/A_{365} absorbance ratio to demonstrate that bacterial growth is higher in streams from forest soils than in streams from mires because of the higher proportion of low-molecular size carbon present in the stream from forest soils. Using similar methods, Wilson & Xenopoulos (2008) suggested that wetlands are often associated with humic and structurally more complex DOM. It has also been shown that DOM exported from mires has a high aromatic content and structural complexity (Ågren et al. 2008), but the relative contributions from different parts of the mire are rarely examined. Using $SUVA_{254}$ and A_{250}/A_{365} ratios, Olefeldt et al. (2012) demonstrated that the DOC aromatic

content and average molecular weight are positively related to increases in the catchment peatland coverage and to decreases in the minerogenous groundwater impact.

To evaluate the contribution to the discharge of different ecohydrological subunits of a mire complex, it can be hypothesized that during the snowmelt period, different parts of the forest-mire complex exhibit different melting times. Mire sites should start to melt earlier than the forested sites, because trees shade the ground of the latter. It is expected that after snowmelt, the DOC concentrations should gradually increase as a result of increasing organic matter production by the vegetation, particulate organic matter decomposition by soil microorganisms and the water evapotranspiration over the summer.

Thus, to enhance the understanding of the carbon dynamics of the lowland mire-forest landscapes that are typical for large areas of boreal Russia, this study was conducted with the following objectives:

- (1) To quantify the DOC concentrations and fluxes in a northwestern Russian boreal mire-forest-river landscape during the snowmelt period;
- (2) To apply an integrated approach combining both hydrochemical and physical measures for detecting the major hydrological pathways for the transport and redistribution of dissolved organic carbon across the boreal mire; and
- (3) To characterize the spatial variability of the quantitative and qualitative DOM properties during the snowmelt peak flow period in comparison to the subsequent summer/fall baseflow period.

6.3 Materials and Methods

6.3.1 Study site

During 2011, water samples were collected from the near-pristine Ust-Pojeg mire complex (61°56'N, 50°13'E) and the nearby Pojeg River, into which the mire complex drains, in the Komi Republic, Russia (see chapter 3 for further study site description).

6.3.2 Environmental conditions during sampling period

The seasonal weather changes during the sampling period at the study site are presented in Figure 6.1.

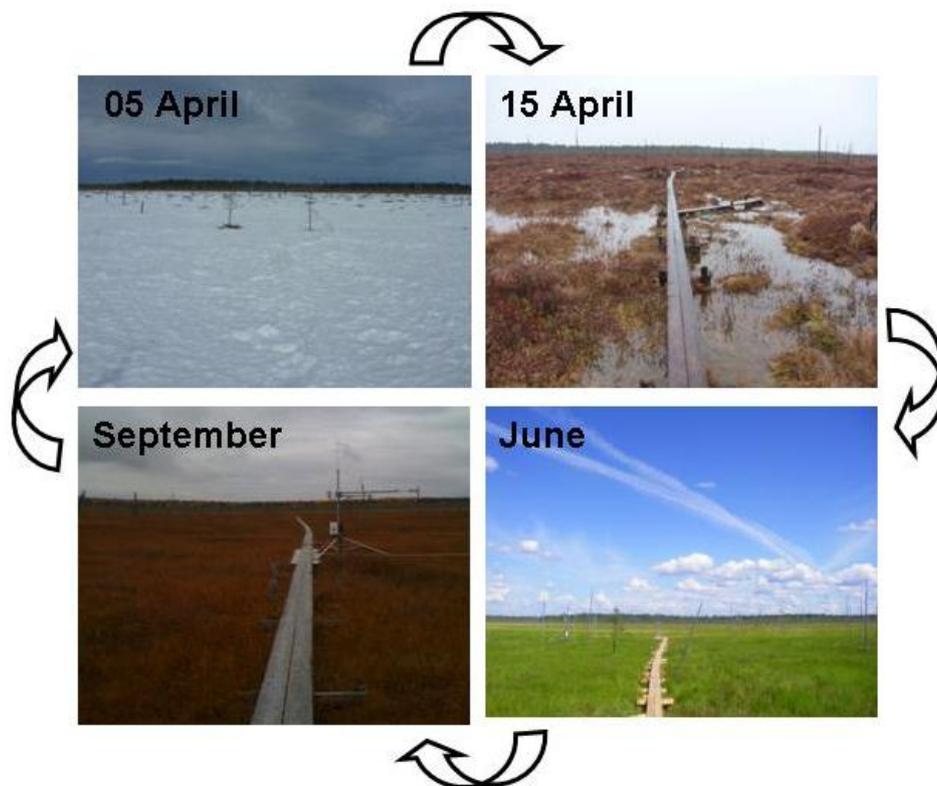


Figure 6.1 Seasonal changes at the study site. Permanent snow cover begins at the end of October and continues until the beginning of April. The vegetation active growth season lasts from the end of May until the end of August. In September the vegetation starts to senescence (see chapter 3 for further climatic data).

Before snowmelt, the average snow height was 63 cm in the open peatland zones, 67 cm in the forested peatland zones, and 55 cm in the forest zone (March 4-18). Snowmelt was triggered by increased temperatures in April at all sites; however, the exposed, treeless peatland areas were more prone to rapid snowmelt than the

forested areas. The snowmelt dynamics are presented in Figure 6.2 and 6.3. During the first phase of snowmelt (April 6-9), the snow height decreased significantly from 23 ± 5 to 0 cm in the treeless peatland zones, from 32 ± 10 cm to 20 ± 8 cm in the forested peatland zones, and from 32 ± 1 cm to 20 ± 7 cm in the forested peatland zone. Complete melting was observed by April 12-13 in the bog area, April 18 in the forested peatland, and April 22 in the forest zone.



Figure 6.2 The snowmelt dynamics with panoramic views (360°) of the treeless peatland during the first weeks of snowmelt. The time series shows the fast melting in the open terrain (Note that the horizon line appears distorted due to merging of the photographs. Photographs: Benjamin Runkle; edited Hannes Haupt).

During most of the snowmelt period, the soils were frozen and covered with ice. The frozen ground inhibited percolation and interflow. Therefore, the major flows during the snowmelt period occurred superficially, and the lagg zone was the main flow channel for the water discharging from the mire complex and parts of the surrounding upland forests. The ground in the treeless bog thawed on April 27, whereas the treeless fen site did not thaw until May 2. The ground in the lagg area was still frozen at the 10 cm depth on May 9.

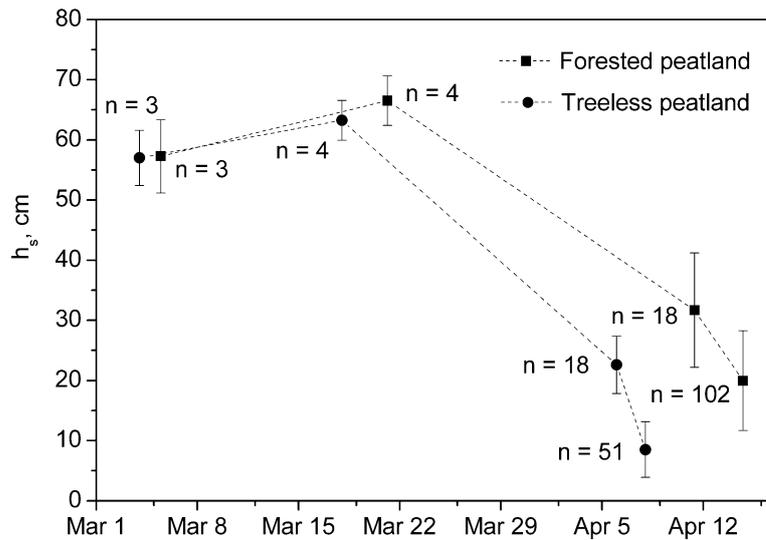


Figure 6.3 The snow height at the forested and treeless peatland zones, where n indicates the number of measurements. The error bars represent the standard deviations based on replicate measurements.

The water table changes are presented in Figure 6.4. An increase in the snowmelt water table was observed throughout the complex. Water table heights peaked during the second week of April (fen: 13-15 cm; bog: 18-23 cm).

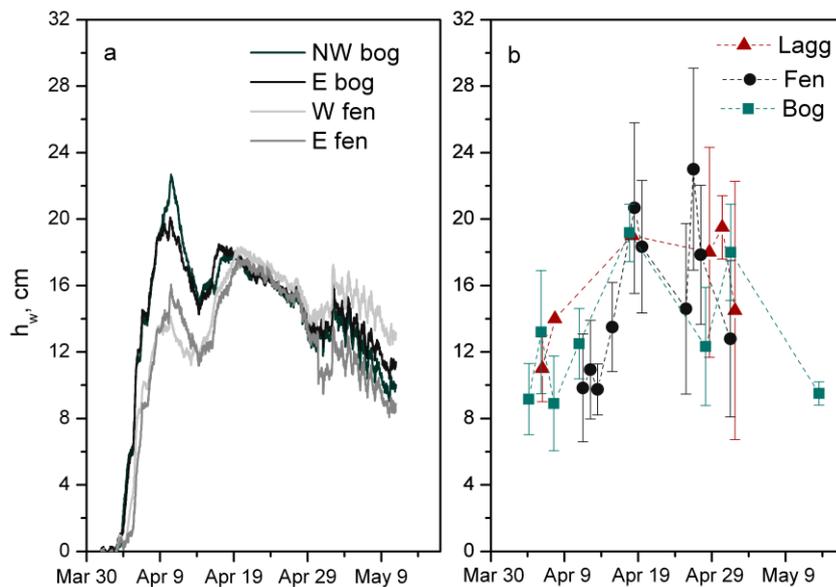


Figure 6.4 The surface water table heights relative to the soil surface across the peatland. a. The water table height measured from the permanently installed pressure sensors and b. the manually measured water table height above the surface. The errors bars represent the standard deviations based on replicate measurements. Data source: Haupt (2012).

On April 14, the water table decreased to 15 cm in the bog site and 12 cm in the fen site, followed by a later increase on April 19 to 18 cm. After April, the water table heights started to decline. Daily water table height fluctuations were particularly prevalent during the later weeks of the snowmelt period.

During the snowmelt period a meteorological station was installed directly at the study site. The data recorded by precipitation and air temperature sensors (52202 Rain Gauge, Young, USA and HMP45A, Vaisala, Finland, respectively) during snowmelt are presented in Figure 6.5. Temperature data were additionally obtained from the weather station at Syktyvkar (Figure 6.5).

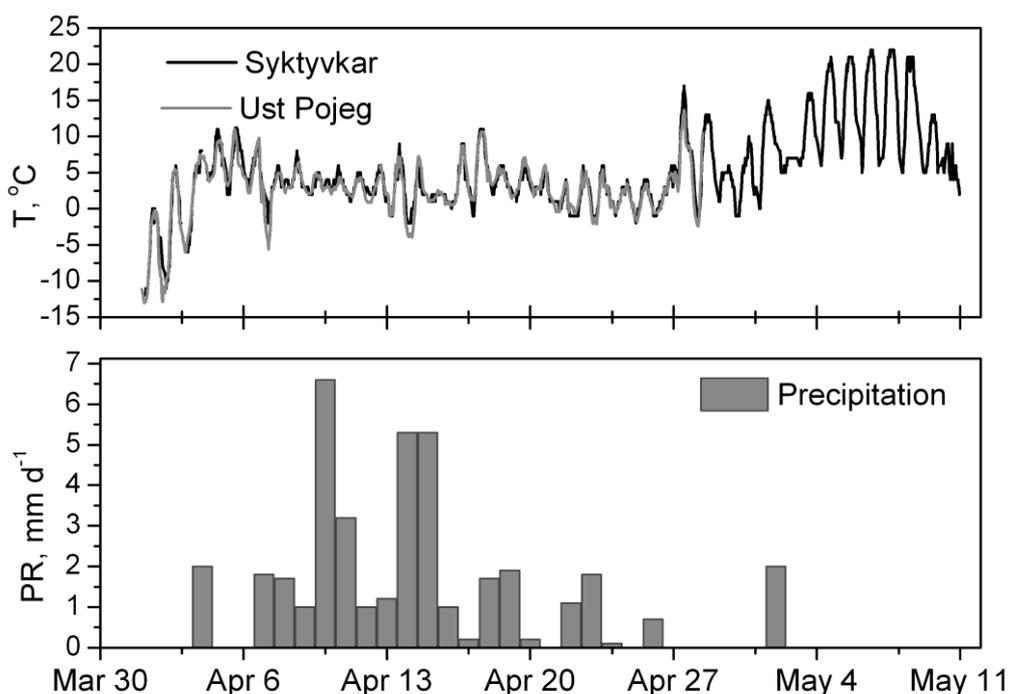


Figure 6.5 The prevailing meteorological conditions during the sampling campaign in the spring of 2011. The air temperature (T) was measured at the weather station in Syktyvkar and directly at the study site (until 27 April).

In March, the temperature ranged from -10 °C to +1 °C. In the beginning of April, the daily mean temperatures increased to +6 °C; frost and temperatures below freezing (0 °C) were common during the nights. In May, the mean temperature increased to +10 °C with daytime temperatures of up to 20 °C and temperatures above freezing at night. Occasional rainfall after the first week changed to nearly continuous light precipitation during the second and third weeks with a daily maximum of 7 mm. The frequency and amount of precipitation decreased by the end of April.

6.3.3 Sampling

Sampling started during the spring snowmelt and continued until fall (April 1-October 28). Snow samples were collected prior to the start of snowmelt at various depths (0-50 cm) and were analyzed for DOC content. Starting from the snowmelt

until fall, water samples were taken from the surface of the mire (22 points at 50-m maximum intervals) and at the outflow point (Figure 6.6).

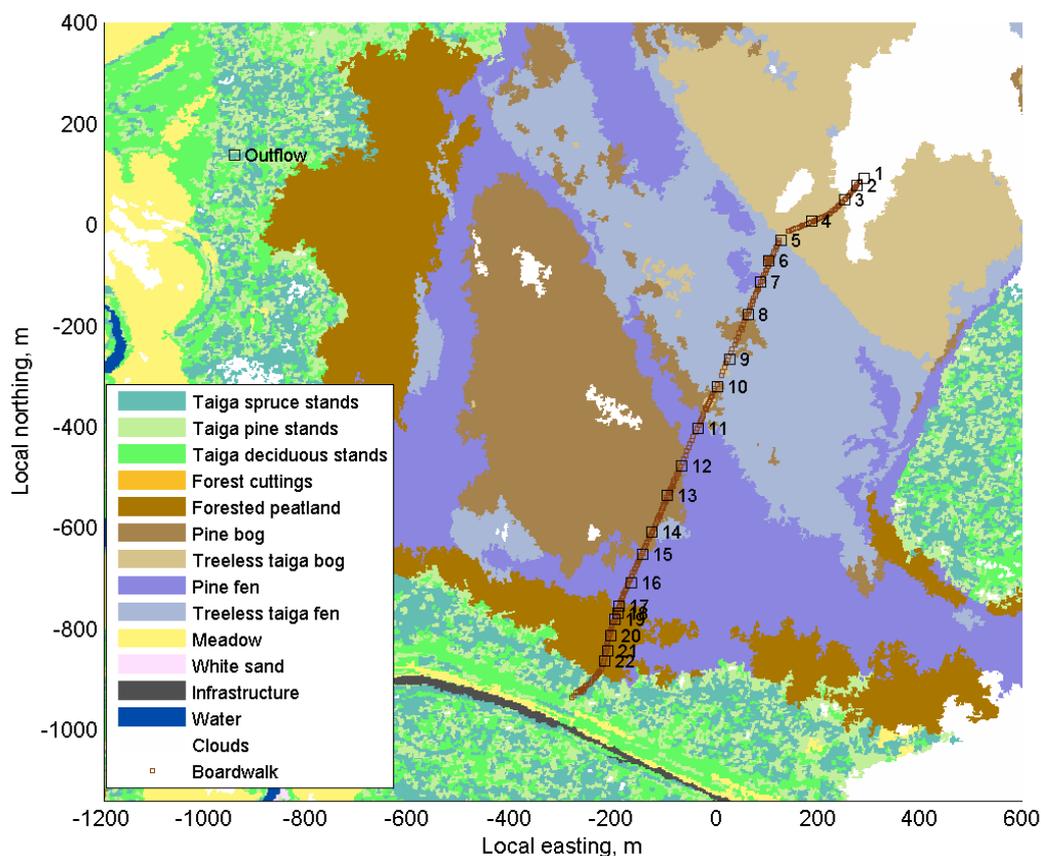


Figure 6.6 Map of the study site location showing sampling locations along the transect (~1.2 km) spanning the Ust-Pojeg forest-mire complex (61°56'N, 50°13'E) in the Komi Republic, Russia. Map source: Susiluoto & Virtanen *et al.* (unpublished data). The forested peatland land class represents the lagg zone.

The surface and pore water samples for DOC analyses were collected in acid-washed glass bottles, whereas the samples for ion content measurements were stored in polyethylene bottles that had been pre-rinsed with distilled water. The sampling frequency was determined based on the runoff intensity as follows: the samples were collected every day during the peak of the spring snowmelt period and every third day on the receding limb of the spring snowmelt peak flow period. After the snowmelt period, additional surface and soil pore water samples were collected from various soil depths (0, 10, 30, and 60 cm relative to the soil surface) via perforated stainless steel tubes (\varnothing 1/8"). After May 9 during the stable base-flow period until the beginning of October 2011 weekly or biweekly sampling was conducted along the transect. During the snowmelt period and at the end of the fall sampling period (Sept 27 and 29), samples were also taken from the Pojega River. The sampling site at the Pojega River was located upstream from the mire described in this study. Thus, the

water collected at this site was used as a general indicator of the effect of the region's forest-mire mixed landscape on the river's hydrochemistry.

6.3.4 Qualitative and quantitative analyses of dissolved organic carbon

During the snowmelt, daily total organic carbon (TOC) and DOC concentration measurements of water samples were conducted directly at the site using a portable submersible ultraviolet-visible (UV-Vis) spectrophotometer (spectro::lyser, scan Messtechnik GmbH, Austria), which uses high-resolution absorbance measurements over the wavelength range of 200-742.5 nm at 2.5-nm intervals as a proxy for DOC content. Because the DOC composition of natural waters varies by site, a local calibration was performed rather than using the default settings of the spectro::lyser (global calibration) to enhance the accuracy of the measurements (see chapter 4 for details).

To evaluate the local calibration and to correct for drift, samples ($n = 157$) were analyzed using the wet persulfate oxidation method (hereafter, wet oxidation) (Aurora Model 1030, O-I-Analytica, USA). Wet oxidation analyses of the DOC fraction were performed on water samples filtered through glass fiber filters with a 0.7- μm nominal cutoff size (GF/F, Whatman, UK). Potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$: 5, 20, 40 mg L^{-1}) was used as a standard and was analyzed prior to and after the analyses to ensure that no analytical drift had occurred within or between the sample runs. Based on ordinary least squares (OLS) regression, the local calibration showed good agreement between the results obtained from the high-resolution absorption measurements and those obtained using the wet oxidation method ($r^2 = 0.99$, root-mean-square error = 1.7 mg L^{-1} , $n = 157$). Based on the OLS regression, the DOC values were corrected using the following regression:

$$C_{\text{DOC}} = 1.01 C_{\text{DOC}_{\text{spectrolyser}}} - 0.66 \quad (6.1)$$

To evaluate the qualitative characteristics of the DOC, the absorbance ratios A_{254}/DOC (also known as UV absorbance at 254 nm, SUVA_{254} , which is reported in units of $\text{L mg C}^{-1} \text{m}^{-1}$), A_{254}/A_{365} , and A_{465}/A_{665} were used to evaluate the aromaticity, molecular size, as well as the differentiation in humic and fulvic acids, respectively. The percentage of aromaticity was estimated using the following empirical model (Weishaar et al., 2003):

$$\text{Aromaticity (\%)} = 6.52 \text{SUVA}_{254} + 3.63 \quad (6.2)$$

To interpret the A_{465}/A_{665} values, the gradation developed by Thurman (1985) was used: values between 2 and 5 characterize mature humic acids, while values from 8 to 10 correspond to mature fulvic acids.

The water samples were analyzed for Na, potassium (K), Mg, Ca, iron (Fe), and zinc (Zn) concentrations using atomic absorption spectrometry (AAS) (1100B, Fa. Perkin-Elmer, USA). Sulfate (SO_4^{2-}), nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}) were analyzed using photometry (Photometer KFK-3, Zagorsky Optical- Mechanical Plant, Russia), whereas the chloride (Cl^-) content was detected using an HgNO_3^- photometric titration method (Biohit Biotrate, Finland). Cuvette tests (LCW 028, Hach Lange, Germany) were used to determine the silica (SiO_2) contents. During the snowmelt period, the water samples from the discharge point were analyzed for the trace elements copper (Cu), Mn, and arsenic (As) using inductively coupled plasma atomic emission spectrometry (ICP-AES, Spectro Ciros CCD, Germany), as well as for mercury (Hg) and lead (Pb) using the AAS-cold vapor technique and the AAS-flameless-electrothermal technique, respectively (RA-915+ Hg analyzer, Lumex, Russia and AA-6800G, Shimadzu, Japan, respectively).

Additionally, water and snow heights were measured manually during transect walks across the peatland site. Continuous measurements of the water table depth were measured by temperature-compensated pressure transducers (Mini-Diver, Schlumberger, USA). Continuous measurements of the snow height in the open peatland were made using the SR50A-L Sonic Ranging Sensor (Campbell Scientific, UK). Air temperature and relative humidity at 2 m were recorded using an HMP45 (Vaisala, Finland) with radiation shield. Precipitation was measured using a Tipping Bucket Rain Gauge 52203 (R. M. Young, USA). Finally, the temperature and pH of the water samples were measured directly in the field (EcoSense® pH10A Handheld pH/Temperature Meter, Yellow Springs, USA).

6.3.5 Lateral carbon export measurements

The daily lateral outflow, Q_i , was determined from a stage-discharge relationship based on measurements taken every 5 min by a pressure sensor (46-X, Keller GmbH, Germany) calibrated with velocity-profile and salt-dilution measurements (for further details, see Haupt 2012). The following equation was used for the lateral organic carbon export, C_{out} :

$$C_{out} = \int_{t=0}^{t_{end}} Q DOC dt \approx \sum_{i=11 April}^{9 May} Q_i DOC_i \quad (6.3)$$

The methods used for the runoff quantification and catchment area delimitation are presented in Haupt, (2012).

6.3.6 Data analysis

To detect differences in chemical characteristics among the peatland zones, a one-way analysis of variance (ANOVA) followed by the Tukey honest significant difference (HSD) post-hoc test were performed. Pearson's correlation analysis was used to evaluate the relationship between the discharge rate and the carbon concentration in the discharge water. ANOVA, Pearson correlation, and descriptive statistics were performed using the SPSS 18.0 package (IBM Corp., Chicago, USA). All analyses were evaluated at the 5 % level of significance.

To trace the flow paths, agglomerative hierarchical clustering was implemented using chemical water properties to group sites into clusters based on Ward's method (Ward, 1963). Agglomerative hierarchical clustering locates each object within a separate cluster and later merges the closest pair of clusters based on the nearest distance measure based on similarity (the square of the Euclidean, E^2) (Miller & Miller 2010). The distances between the clusters are again compared, and the two nearest clusters are combined until the defined number of groups is reached (Miller & Miller 2010). For agglomerative hierarchical clustering analyses, the XLSTAT statistical package (Addinsoft, France) was used.

6.4 Results

6.4.1 Spatio-temporal variability in organic carbon concentrations

The organic carbon in the mire's surface and soil pore waters, in the outflow water, and in the river water occurred predominantly in the dissolved form. According to the portable spectrophotometric method, more than 90 % of the TOC occurred in dissolved forms in all zones (i.e., lagg, 96 ± 4 %; fen, 93 ± 7 %; bog, 93 ± 9 %; and outflow, 97 ± 2 %).

The DOC concentrations in the surface waters throughout the forest-mire complex increased during the snowmelt period. Before snowmelt began, the DOC content was low (0.8 ± 0.3 mg L⁻¹, n = 12) in the snow water samples. Two stages of snowmelt and runoff into the streams were observed at the outflow point; the first originated from the peatlands and the second originated from the forest. The temporal changes in DOC concentration at the different sample sites within the investigation area are presented in Figure 6.7.

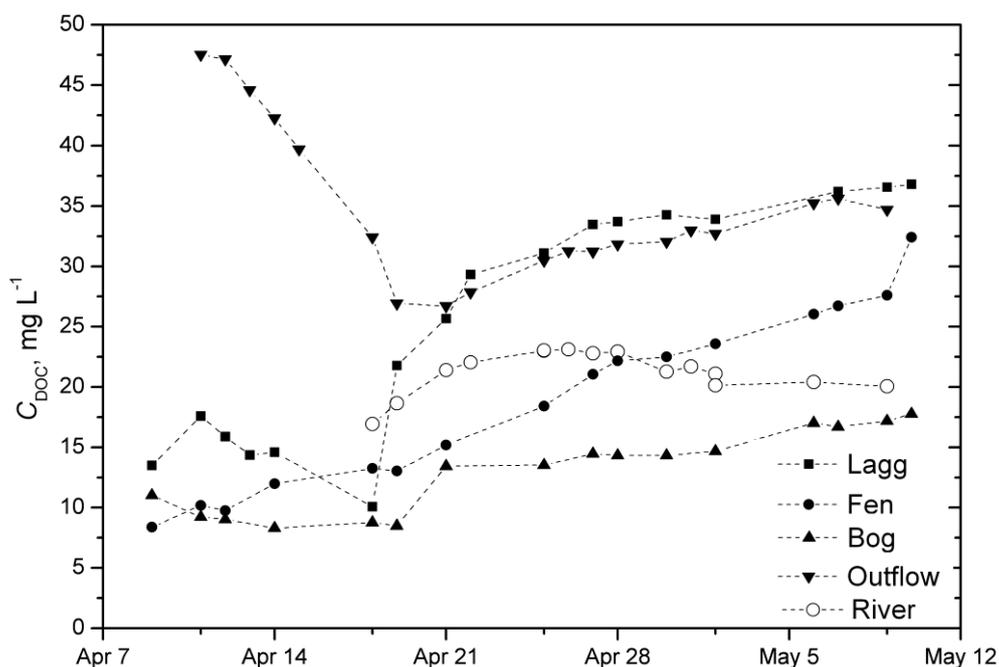


Figure 6.7 Time series of dissolved organic carbon (DOC) concentrations at the outflow, river and in the surface waters of different mire zones during the snowmelt period. DOC values represent the average of two measurements per sample. For the presentation of the DOC dynamics at the different ecohydrological sites, duplicate samples from the following points were selected: N 2 (bog) N 6 (fen), N 20 (lagg). Measurements were conducted using a portable submersible UV-Vis spectrophotometer (spectro::lyser, s::can). The average standard deviation for the field duplicate measurements was 0.06 ± 0.11 mg L⁻¹, and the standard deviation was always less than 0.9 mg L⁻¹.

At the beginning of the snowmelt period, parts of the surface organic matter were flushed away by meltwater, whereas the deeper soil layers remained frozen. During this time, the surface water DOC concentrations fluctuated within the range of 8-15 mg L⁻¹ (April 7) across the entire mire complex. After April 18, the concentrations diverged between the sites; the DOC concentration reached 30 mg L⁻¹ in the surface water in the lagg zone (April 25) but was only 15 mg L⁻¹ at the bog site (April 25). When the snow across the region began to melt, it partly carried the near-surface organic matter to the river, and the DOC concentration in the river reached approximately 26 mg L⁻¹ (Figure 6.7). The concentration of DOC in the river water was significantly higher during spring (16-26 mg L⁻¹) than fall (7.2 ± 0.1; sampling date: 10 October 2011).

The water discharged from the mire complex during the first flush via the outflow creek into the Pojæg River exhibited a high DOC concentration of approximately 45 mg L⁻¹ (April 11) in the outflow creek; however, after seven days, the DOC concentration decreased to 31 mg L⁻¹ during high flow rates and then slightly increased again during lower discharge periods. After April 25, the DOC concentration in the outflow stabilized in the range of 30-35 mg L⁻¹ (Figure 6.7). The DOC concentration in the outflow was strongly and negatively correlated with the discharge rates in the outflow ($r = -0.9$) (Figure 6.8). Overall, during the spring snowmelt period (April 1 to May 9), 1.7 ± 0.3 g C m⁻² of DOC was discharged, and 74 ± 15 mm of runoff was measured from the 2.58 km² catchment area to the nearby regional Pojæg River (Haupt, 2012).

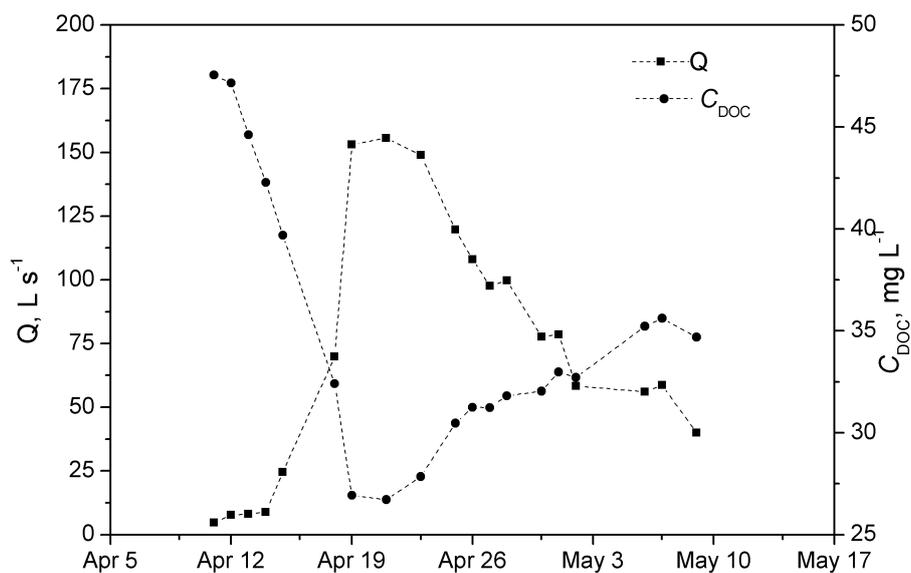


Figure 6.8 The relations between the discharge rates and organic carbon concentration in the runoff water. Further details concerning the Q measurements can be found in Haupt (2012).

At the end of the snowmelt period, in addition to the soil surface, pore measurements at the different sub-surface depths (May 7) demonstrated wide variability (Figure 6.9). Within the treeless bog site, the transect soil pore water measurements showed that the concentrations of DOC at different soil depths did not vary significantly. At the other sites, the concentration increased from the surface to a depth of 60 cm. The soil pore and surface water measurements on May 9 did not vary significantly compared with the measurements conducted on May 7 (see Appendix Table 6.6 for values measured on May 9). The surface water DOC concentrations were higher at the transitional lagg site than at the bog or fen sites. The ground remained frozen in the transitional zone on May 9; therefore, it was not possible to measure the DOC content at various soil depths.

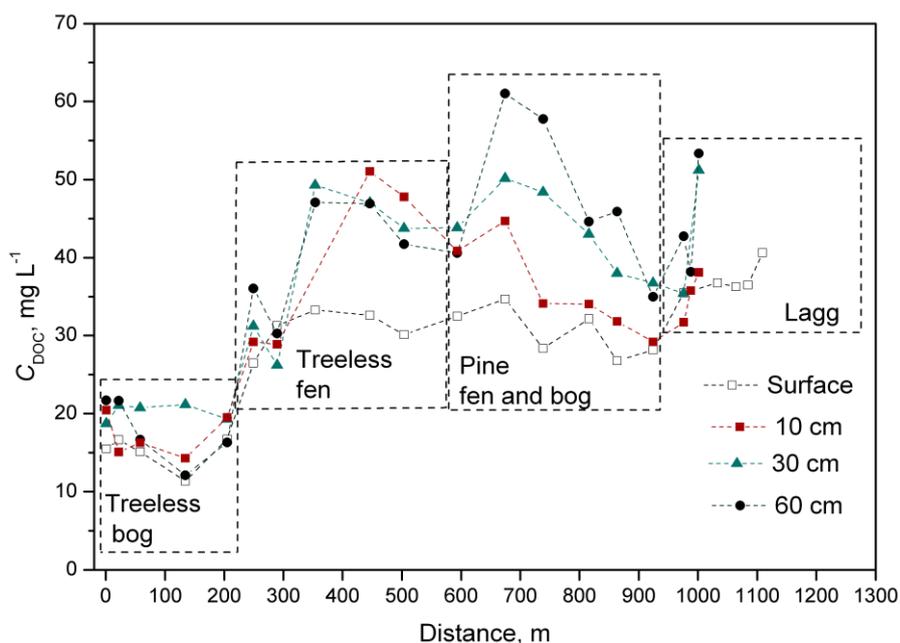


Figure 6.9 Concentrations of dissolved organic carbon (DOC) in the soil pore-waters at different depths along the transect after the snowmelt period (May 7, 2011). The average standard deviation of the duplicate measurements was $0.1 \pm 0.5 \text{ mg L}^{-1}$, and the standard deviation was always less than 3.3 mg L^{-1} . Spatial variability may indicate uneven DOC flushing with snowmelt water due to the different thawing dynamics. Deeper measurements in the lagg zone were not possible because these layers remained frozen.

After the snowmelt period, the DOC concentrations increased during the spring and became relatively stable during the summer and fall, and the difference in concentrations between the sites remained consistent throughout the seasons (Figure 6.10). The lowest surface water concentrations were observed at the bog site. The surface water DOC concentrations increased toward the lagg zone, while the surface DOC concentrations at the fen site were intermediate between that of the bog and lagg

zones. A water sample collection across the transect during October revealed that the concentrations of DOC across the mire ranged from 19 to 74 mg L⁻¹ with an average of 45 ± 14 mg L⁻¹ (data not shown). The highest concentration was detected within the pine fen zone (74 mg L⁻¹), and the lowest concentration was detected in the treeless bog (19 mg L⁻¹).

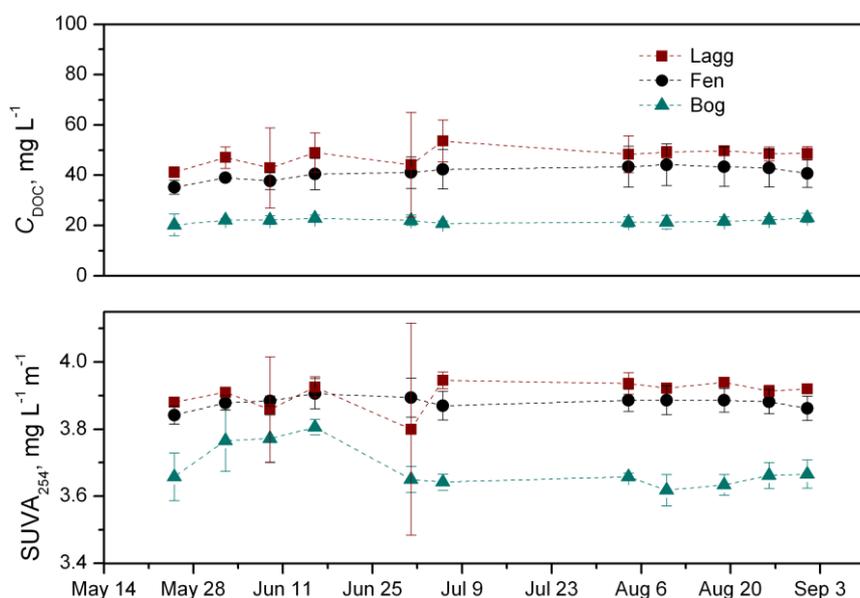


Figure 6.10 The C_{DOC} and $SUVA_{254}$ time series after snowmelt from May to September 2011 at the lagg (forested peatland), fen (treeless taiga fen), and bog (treeless taiga bog) sites. The mean standard deviation for the DOC duplicate field measurements was 0.08 ± 0.2 mg L⁻¹, and the standard deviation was always less than 1.2 mg L⁻¹. The error bars for $SUVA_{254}$ represent the standard deviations based on replicate field measurements. In the appendix, Table 6.4-6.5 presents the C_{DOC} and $SUVA_{254}$ time series for the pine bog and pine fen sites.

6.4.2 Variability in the quality indicators of dissolved organic matter

During the snowmelt period, variability in organic matter spectrophotometric characteristics was also observed. For example, Figure 6.11 (a) demonstrates that structural characteristics of organic matter that was discharged into the river from the outflow point varied over time, while Figure 6.11 (b) demonstrates that the low molecular size organic carbon proportion differs across the mire. In particular, during the first weeks of snowmelt, a high variation in the proportions of humic and fulvic acids was detected. In contrast to the first weeks, more mature humic acids were discharged during the subsequent weeks of the snowmelt period.

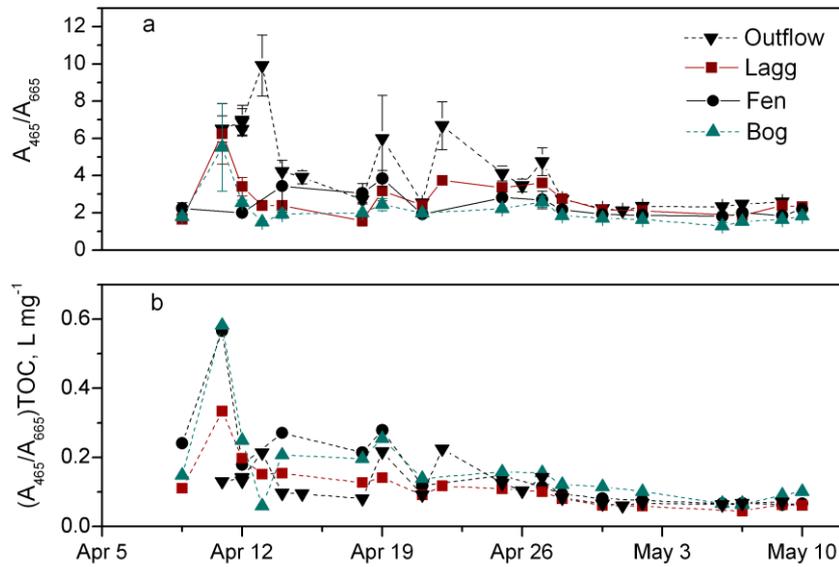


Figure 6.11 The humification index: A_{465}/A_{665} (a) and the A_{465}/A_{665} index normalized by total organic carbon (TOC) content (b). The different ecohydrological zones are presented by representative points within each sub-unit: N 2 (treeless bog) N 6 (treeless fen), N 20 (lagg).

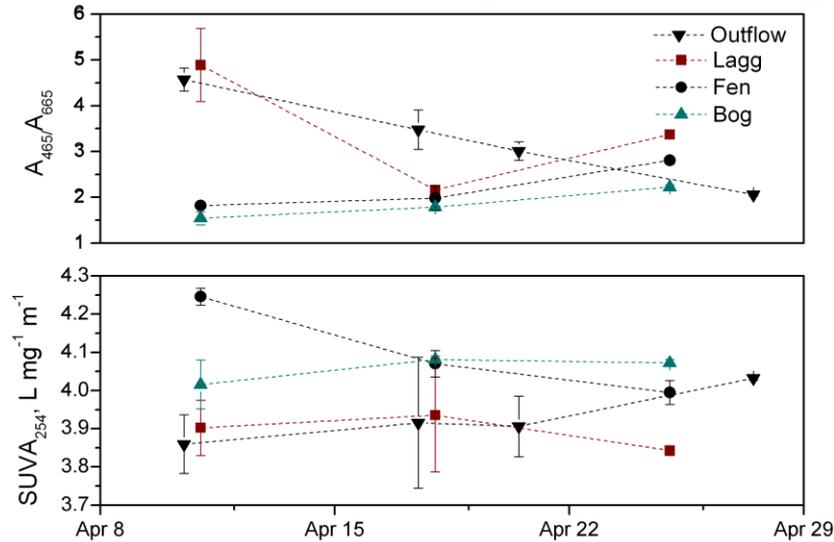


Figure 6.12 The aromaticity index : $SUVA_{254}$ and humification index: A_{465}/A_{665} indexes for the snowmelt period. The DOC samples were filtered through a 0.7- μm glass fiber filter. The different ecohydrological zones are presented by representative points located across the sampling transect: N 2 (treeless bog), N 6 (treeless fen), N 20 (lagg). The standard deviation is calculated based on duplicate field measurements.

Figure 6.12 demonstrates the variation in the aromaticity (in the $SUVA_{254}$ index) as well as in the humification degree (A_{465}/A_{665} index) of the filtered DOM samples. During the first week of snowmelt, the outflow and the lagg zone demonstrated higher amounts of low-molecular-size organic carbon and lower aromaticity compared with that of the bog and fen sites. In the middle of the snowmelt period, the aromatic carbon contents at the outflow increased while A_{465}/A_{665} decreased. The observed decrease in A_{465}/A_{665} and increase in aromaticity indicate that molecules with higher molecular size and aromatic carbon contents were

discharged into the river. In contrast to the outflow, at the fen and bog aromatic carbon contents decreased over the snowmelt period, while the humification index A_{465}/A_{665} values increased, indicating an increasing proportion of fulvic acids. The lagg zone did not demonstrate a significant variation in aromatic carbon, while the A_{465}/A_{665} values decreased during subsequent days.

At the end of the snowmelt period (May 7), differences were detected between the humification indexes A_{465}/A_{665} (Figure 6.13). The highest A_{465}/A_{665} value was observed at the fen site and the lowest was observed at the bog site. The mean values of the aromaticity indexes and molecular size indexes A_{254}/A_{365} differed between sites and depths; however, no statistically significant differences were observed, except for the molecular size indexes for the surface waters at the bog and fen sites (Figure 6.13).

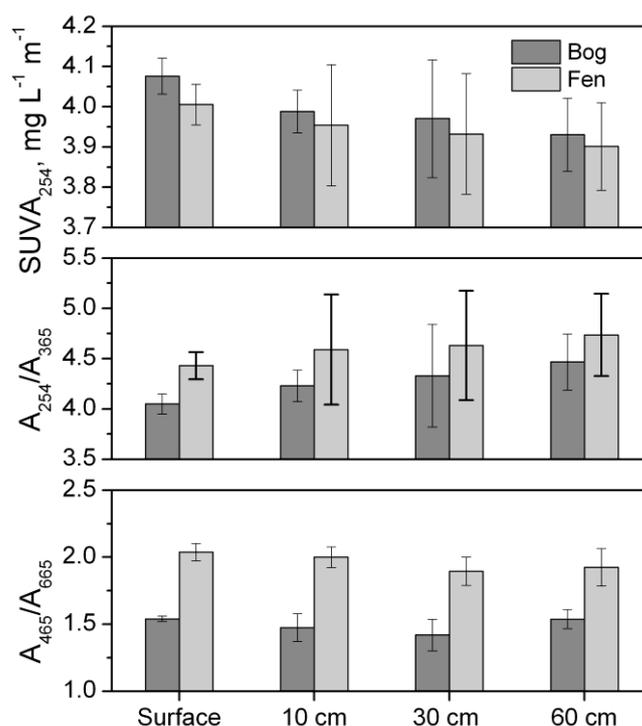


Figure 6.13 The aromaticity index (A_{254}/C_{DOC}), molecular size index (A_{254}/A_{365}), and humification index (A_{465}/A_{665}) for the treeless bog and treeless fen zones (sampling date: May 7). The DOC samples were filtered through a 0.7- μm glass fiber filter. The standard deviation is calculated based on triplicate field measurements. The different ecohydrological zones are presented by representative points within every sub-unit: N 1, 2, 3 (treeless bog) N 6, 7, 9 (treeless fen), N 20 (lagg).

Higher SUVA_{254} and lower A_{465}/A_{665} values indicate the relative enrichment of aromatic carbon and higher-molecular-size organic compounds in the treeless bog compared with the treeless fen at the end of the snowmelt period. A_{465}/A_{665} values less

than five demonstrate the presence of mature humic acids at the treeless bog and treeless fen sites.

During the fall (October 1), the index values were in the following ranges: A_{465}/A_{665} : 3.7-9.7; and aromaticity: 3.6-3.8 $L\ mg\ C^{-1}\ m^{-1}$ (27-29 % of aromatic carbon) (Figure 6.14). The highest aromatic carbon content was detected in the lagg zone, while the lowest was found in the bog (29.2 %, 28.6 %, and 27.7 % for the lagg, fen, and bog, respectively). Higher A_{465}/A_{665} values indicated the presence of a higher proportion of immature fulvic acids at the lagg zone.

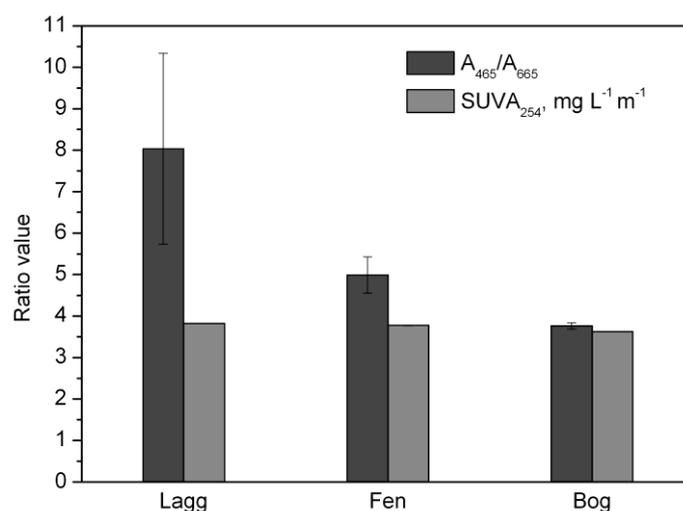


Figure 6.14 Humification index (A_{465}/A_{665}) and aromaticity index (A_{254}/C_{DOC}) for the treeless bog, treeless fen, and transitional lagg zones in fall (October 1, 2011). The DOC samples were filtered through a 0.7- μm glass fiber filter. The different ecohydrological zones are presented by a representative point within each sub-unit: N 2 (bog) N 6 (fen), N 20 (lagg). The errors bars represent standard deviations based on field-replicated absorbance and DOC measurements.

6.4.3 Micro- and macro-elements

The ion hydrochemistry at all sampling sites within the mire at the end of the snowmelt period and during the fall are presented in Table 6.1. The ion concentrations (apart from K^+ , SO_4^{2-} , and PO_4^{3-}) were found to increase in the order of bog < fen < lagg and were higher during the fall than during the spring. All inorganic nitrogen species exhibited low concentrations during both measurement periods ($C_{NH_4^+} < 0.03\ mg\ L^{-1}$; $C_{NO_3^-} < 0.04\ mg\ L^{-1}$; and $C_{NO_2^-} < 0.03\ mg\ L^{-1}$). Additionally, C_{As} and C_{Hg} were detected in the outflow water, and C_{Cu} and C_{Pb} were not detected (Table 6.1).

Table 6.1 The hydrochemical properties in different ecohydrological zones across the mire after the snowmelt and at the end of the senescence period. The standard deviation was calculated based on two spatial replicates values. The sampling dates were May 9, 2011 for the end of the snowmelt and September 28, 2011 for the fall sampling. * Indicates that the measured value is below the detection limit.

Chemical Species	Lagg		Treeless Fen		Treeless Bog		Outflow
	End of the snowmelt (SD)	Fall (SD)	End of the snowmelt (SD)	Fall (SD)	End of the snowmelt (SD)	Fall (SD)	End of the snowmelt (SD)
pH	n/a	4.7	n/a	4.4	n/a	3.4	n/a
PO ₄ ³⁻ conc., mg L ⁻¹	0.06 (0.02)	0.04 (0.02)	< 0.03	< 0.03	0.05 (0.01)	0.04 (0.01)	n/a
SO ₄ ²⁻ conc., mg L ⁻¹	2.2 (0.07)	1.3* (0.02)	1.0* (0.1)	1.2* (0.1)	0.4* (0.02)	0.4* (0.02)	n/a
K ⁺ conc., mg L ⁻¹	0.4 (0.01)	0.07 (0.08)	0.9(0.06)	0.9 (0.2)	0.5 (0.1)	0.07 (0.02)	0.7
Ca ²⁺ conc., mg L ⁻¹	4.9 (0.03)	7.7 (0.9)	2.2 (0.3)	3.5 (0.1)	0.2 (0.4)	0.7 (0.2)	3.04
Mg ²⁺ conc., mg L ⁻¹	1.2 (0.6)	1.8 (0.1)	0.7 (0.1)	0.9 (0.05)	0.1 (0.001)	0.2 (0.003)	0.9
Fe ²⁺ conc., mg L ⁻¹	0.2 (0.01)	0.5 (0.6)	0.2 (0.02)	0.3 (0.06)	0.02 (0.01)	0.1 (0.03)	0.54
Na ⁺ conc., mg L ⁻¹	0.9 (0.01)	0.9 (0.4)	0.8 (0.1)	1.3 (0.02)	0.5 (0.12)	0.5 (0.02)	n/a
Cl ⁻ conc., mg L ⁻¹	1.3 (0.05)	3.1 (1.6)	0.75 (0.1)	2.6 (0.1)	0.77 (0.3)	2.8 (1.4)	n/a
As conc., µg L ⁻¹				n/a			0.42*
Hg conc., µg L ⁻¹				n/a			0.02 (0.01)

The ion concentrations used for the agglomerative hierarchical clustering method during the snowmelt period are presented in Table 6.2. Agglomerative hierarchical clustering analyses during the snowmelt period showed that the outflow water was most similar to the fen water with respect to the hydrochemistry (Figure 6.15). C_{Fe} at the outflow was found to be higher than that of the peatland sites between April 18 and May 9.

Table 6.2 The ion concentrations during the snowmelt period at different ecohydrological zones across the mire complex. n/a: not available. All standard deviations for the duplicate samples are less than 0.01 mg L^{-1} . The different ecohydrological zones are presented by representative points within each sub-unit: N 2 (bog) N 6 (fen), N 20 (lagg).

Chemical species	Date	Outflow	Lagg	Treeless Fen	Treeless Bog
C_{DOC} , mg L^{-1}	Apr 18	32	10	13	9
	Apr 28	32	34	22	14
	May 9	35	37	28	17
C_K , mg L^{-1}	Apr 18	0.97	2.79	1.70	0.96
	Apr 28	1.02	0.47	2.05	0.68
	May 9	0.67	0.41	0.81	0.62
C_{Ca} , mg L^{-1}	Apr 18	2.03	1.93	0.92	0.06
	Apr 28	2.3	7.8	2.9	0.08
	May 9	3.04	5.0	1.9	0.1
C_{Mg} , mg L^{-1}	Apr 18	0.73	0.68	0.47	0.01
	Apr 28	0.71	1.77	0.90	0.02
	May 9	0.93	1.24	0.67	0.06
C_{Fe} , mg L^{-1}	Apr 18	0.38	0.07	0.1	0.03
	Apr 28	0.26	0.28	0.39	0.03
	May 9	0.54	0.17	0.2	0.02

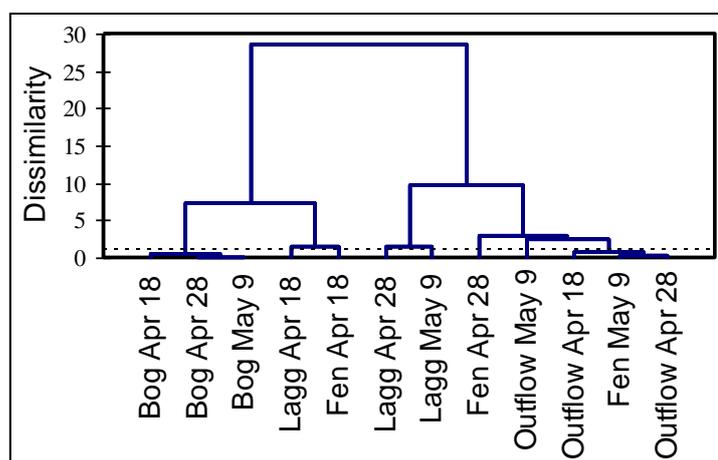


Figure 6.15 Dendrogram based on the agglomerative hierarchical clustering analysis, which was performed based on the data in Table 6.2.

C_{SiO_2} measurements that were taken during the first phase of the snowmelt period showed dynamic changes at all sites (Figure 6.16). The C_{SiO_2} was below the detection limit in the snowmelt water. The SiO_2 concentration was 1.8 mg L^{-1} in the

surface water samples collected from small localized ponds in the lagg zone. During the intensive snowmelt period, excess meltwater from the bog and fen sites discharged into the lagg zone, and the SiO_2 content decreased to 0.6 mg L^{-1} . During the first phase of snowmelt, the fen and bog sites exhibited low SiO_2 concentrations of 0.7 and 0.2 mg L^{-1} , respectively. After the initial flush, the SiO_2 concentrations increased to 2.1 and 1.2 mg L^{-1} in the surface waters of the fen and bog, respectively, due to the thawing of deeper layers. The SiO_2 content in the outflow water decreased from 5 mg L^{-1} , which is comparable with the SiO_2 content of $5.0 \pm 1.4 \text{ mg L}^{-1}$ during the baseflow period of July 2010 (Chapter 5), to 2.1 mg L^{-1} . This indicates that during the first phase of the snowmelt the “old water”, which takes its hydrochemical signature from the previous year, was flushed from the system; subsequently, a mixture of surface and soil pore waters with snowmeltwater from the mire was discharged.

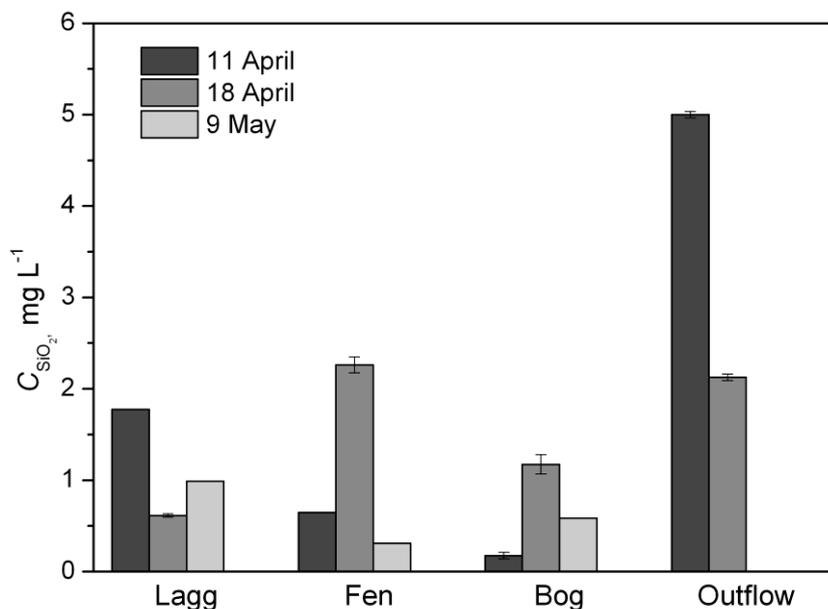


Figure 6.16 The SiO_2 concentrations during the first phase of the snowmelt period in different ecohydrological zones across the study site. The ecohydrological zones are presented by a representative point within each sub-unit: N 2 (treeless bog) N 6 (treeless fen), N 20 (lagg). The error bars represent the standard deviations based on replicate measurements

During the last week of the snowmelt (May 9), the 10, 30, and 60 cm C_{SiO_2} measurement depths (at 5 sampling sites along the transect) demonstrated that the fen and bog sites were hydrologically connected and that the C_{SiO_2} at the 10 cm depth was low ($1\text{-}1.3 \text{ mg L}^{-1}$), whereas C_{SiO_2} concentrations were higher at the 30 cm ($2.4\text{-}2.7 \text{ mg L}^{-1}$) and 60 cm ($2.1\text{-}2.9 \text{ mg L}^{-1}$) depths. In contrast to the fen and bog sites, water samples derived from the lagg zone significantly differed from other sites at the 10 cm

depth (3.1 mg L^{-1}). Increases of C_{SiO_2} with depth were also evident at the lagg site, where the C_{SiO_2} at 30 cm was 5.6 mg L^{-1} . At the lagg zone, measurements at 60 cm were not possible because of the frozen ground. The difference observed at 10 cm in the lagg zone demonstrates that the lagg zone was not hydrologically connected with the rest of the mire. The C_{SiO_2} concentrations at 10 cm and 30 cm in the lagg zone were similar to the summer mean monthly values of 3.9 and 4.4 mg L^{-1} , respectively (Chapter 5). This finding may indicate that no percolation of snow water into groundwater occurred at the lagg zone.

6.5 Discussion

6.5.1 Sampling methodology

The reliability of lateral carbon flux estimates depends on the sampling frequency, analytical precision, and accuracy of the flow measurements (Laudon et al. 2004). Estimates of DOC export fluxes from peatlands, which are based on infrequent sampling, could easily overlook high-flux events (Grayson & Holden, 2012). Therefore, studies that consider only the growing season without including the highly dynamic snowmelt period are likely to lead to underestimates of annual carbon fluxes (Dyson et al., 2011). In the current study, an adaptive sampling strategy was implemented that performed the highest frequency of observations during high-flow events such as the snowmelt period and the lowest frequency of observations during the base flow period. The use of a high sampling frequency during the snowmelt period allowed for the capture of dynamic changes in DOC concentrations in surface waters across the peatland and in the outflow stream.

The use of conventional catalytic combustion oxidation or wet-heated persulfate oxidation techniques to determine the DOC content is not efficient when a large number of rapid analyses are required particularly in remote areas. In contrast, high-resolution monitoring with a UV-Vis field-based spectrophotometer facilitated the detection of dynamic changes in DOC concentrations across the site and at the outflow stream, leading to improved flux estimates. Moreover, the additional use of a portable UV-Vis spectrophotometer for DOC content determination allowed qualitative evaluations of the DOM (e.g., with respect to molecular size, aromaticity and humic to fulvic acids dominance) to be conducted simultaneously for filtered samples.

6.5.2 DOC variability and loss

In the current study, the spectrophotometric measurements demonstrated that TOC was comprised mostly (90 %) of DOC. These findings are comparable to the findings of other studies reporting that DOC is the dominant form of carbon export from boreal catchments (e.g., Mattsson et al. 2005; Köhler et al., 2008; Dinsmore et al. 2011). This study demonstrated that the DOC concentrations in surface and soil

pore waters in a heterogeneous mire landscape exhibits substantial spatial and temporal variability which has also been observed in other studies (e.g., Moore 1987).

Qualitative changes in the DOM are shown in Figure 6.12 and Figure 6.13 and demonstrate that there was a significant variation in DOM quality during the snowmelt period. The spectrophotometric measurements indicated that the outflow water of the mire complex investigated in this study contained lower proportions of aromatic and high-molecular-mass DOM compared with outflow water from a wetland-dominated (> 40 %) catchment discharged during the transition between winter and summer, as studied by Ågren et al. (2008). During the study period of Ågren et al. (2008), the ranges of $SUVA_{254}$ and A_{254}/A_{365} were 4.6-4.5 L mg⁻¹ m⁻¹ and 3.7-3.9, respectively. In contrast, the current study demonstrated that by the end of the snowmelt period, the $SUVA_{254}$ values varied between 3.9 and 4.1 L mg⁻¹ m⁻¹, while A_{254}/A_{365} ranged from 4.0 to 4.7.

The DOC concentrations in the outflow stream were lower during the spring melt period compared with the baseflow period due to the snowmelt dilution effect (Chapter 6.5). The negative correlation between the discharge rates and the organic carbon content as a result of dilution is consistent with observations reported at other peatland-dominated catchments (Fraser et al. 2001; Laudon et al. 2004; Dyson et al. 2011). The upper limit of the DOC concentration in the study site's runoff water (33-45 mg L⁻¹) is comparable with that of the boreal Mer Bleue peatland in Canada (20-47 mg L⁻¹). The mean DOC concentrations in the outflow waters (35.3 ± 6.9 mg L⁻¹) were higher than those observed by Dyson et al. (2011), who reported values of 26.2 mg L⁻¹ and 17.5 mg L⁻¹ for two study sites in Finland. The elevated DOC concentration observed for the Pojog River during the snowmelt period is comparable with that of other boreal rivers (Pokrovsky & Schott 2002; Finlay et al. 2006).

The overall DOC loss during the spring snowmelt period alone (1.7 ± 0.33 g C m⁻² in 74 ± 15 mm of runoff over 28 days) is at the lower end of the wide range of previous estimates (1-48 g C m⁻² yr⁻¹) from wetland and forest-wetland catchments (as reviewed by Fraser et al. 2001). Furthermore, this carbon loss is at the lower end of the range (< 10 g C m⁻² yr⁻¹) for peatland-dominated areas with negligible relief and/or runoff of less than 250 mm (Fraser et al., 2001). The total DOC loss is also consistent with the results of Dyson et al. (2011) for the Suoporo study site, which was covered by 70 % peatlands (1.78 ± 0.94 g m⁻² month⁻¹), and is lower than that

found at the Väipuro study site, which was covered by 56 % peatlands ($2.87 \pm 1.91 \text{ g m}^{-2} \text{ month}^{-1}$). The DOC export relative to the runoff from the Ust Pojieg mire complex was larger than estimates for that from subarctic peatlands (Moore 1987) but similar to estimates from other boreal catchments (Table 6.3). It could also be expected that 11.6-17.6 % of the total exported DOC would be further removed from streamwater by in-stream processes that would lead to increased CO_2 outgassing (Dawson et al., 2001).

Table 6.3 A summary of the DOC export and runoff measurements from boreal and sub-arcticpeatland-dominated catchments.

Type of catchment, location	Carbon loss, g m^{-2}	Runoff, mm	Carbon loss/Runoff, $\text{g m}^{-2}/\text{mm}$	References
Boreal mire-forest complex, Russia	1.7 ± 0.33	74	0.022	Current study, see Haupt (2012) for further details
Subarctic peatland, Canada	1.1-4.9	302-389	0.0036-0.012	Moore (1987)
Boreal, bog, Canada	8.3 ± 3.7	222	0.037	Fraser et al. (2001)
Boreal bog, Canada	16.4 ± 3.4	391 ± 67	0.041	Roulet et al. (2007)
Minerogenic oligotrophic mire, Sweden	11.9-14.0	343-369	0.034-0.037	Nilsson et al. (2008)*
Boreal peatland, Finland	4.2-11.3	194-387	0.021-0.029	Jager et al. (2009)
Peatland-dominated (56 %) catchment, Finland	15.5	515	0.03	Dyson et al. (2011)
Peatland-dominated (70 %) catchment, Finland	7.9	461	0.017	Dyson et al. (2011)

* In this study, the lateral organic carbon export is estimated for TOC, whereas it was estimated for only DOC in all other studies.

In the current study, the total lateral carbon loss was approximately 5.6-8.5 % of the average ($20\text{-}30 \text{ g C m}^{-2} \text{ yr}^{-1}$) long-term C sequestration in peatlands (Gorham 1991). The overall estimate of DOC export in the current study can be considered a conservative estimate, and it can be assumed that the actual amount of DOC lost from the peatland is underestimated because it was not possible to capture diffuse or subsurface DOC losses. Similarly, Dyson et al. (2011) have also acknowledged the complexity of lateral carbon flux measurements during snowmelt periods and the consequent possibility of underestimating the flux. Furthermore, it was observed that the topography of the catchment plays an important role in DOC flux variation (Andersson & Nyberg, 2008). The weak slopes between the current study site and the river could be one reason for the relatively low DOC lateral export. It can also be assumed that some of the DOM content within the mire was used as a substrate for methane and carbon dioxide production during the freeze-thaw cycle and did not reach the stream. As was demonstrated by Gažovič et al. (2010), a strong diurnal

variability in CH₄ flux was previously detected (CH₄ fluxes: ~0.8 mg m⁻² h⁻¹ during the night peak efflux and ~3 mg m⁻² h⁻¹ during the day peak efflux) during the freeze-thaw cycle of the snowmelt at the same study site where the current study was performed.

6.5.3 Hydrological flowpaths

The annual average organic carbon export from different catchments is usually positively correlated with the percentage of wetland coverage in the catchments (Laudon et al. 2004; Mattsson et al. 2005; Buffam et al. 2007). However, Laudon et al. (2004) observed that the organic carbon export is negatively correlated with the proportion of wetlands during the snowmelt period. This difference was explained by differences in flow paths during the snowmelt period compared with the baseflow periods in summer and fall. During the snowmelt, lateral water fluxes in boreal wetlands are dominated by surface flow over the frozen soils and surface waters; in contrast, the lateral water fluxes from boreal forested areas typically occur via subsurface flow paths. The current study showed that the water that flowed over the frozen ground in the mire zones primarily carried mobile DOC from the surface. The limited interaction with the underlying peat soils may result in reduced DOC export during an abrupt snowmelt period compared with that exported during a gradual snowmelt. It can be expected that a slower snowmelt proceeds the thawing of underlying soil during the slow snowmelt period, leading to increased surface water and soil pore water mixing and thus a higher DOC export. The deeper soil layers of the lagg zone can be assumed to increasingly and substantially contribute to the lateral carbon flux of the outflow during the later stages of the snowmelt period.

Due to the mosaic pattern of many mire, it was expected that the differences in the vegetation cover and hydrological regimes can lead to varying qualitative and quantitative properties of the DOM in soil pores and surface waters. Thus, the DOC export may vary in heterogeneous catchments and may present separate signals of ecohydrological landscape sub-units. In the current study, variation between the qualitative DOM characteristics of different ecohydrological mire zones (as presented e.g. in Figure 6.11) can be explained by different soil and vegetation characteristics between these zones, whereas temporal variation in the outflow spectrophotometric characteristics were likely driven by changing hydrological pathways and by changes

in water and DOM source areas within the mire complex. The increase in aromatic DOM in the outflow over the snowmelt period (Figure 6.12) may indicate that deeper soil layers with higher contents of recalcitrant DOM in their pores become increasingly hydrologically connected during the later stages of snowmelt. The presence of high values of A_{465}/A_{665} during the first flush (Figures 6.11 and 6.12) in the discharged water indicate higher amounts of low-molecular-size fulvic acids that were likely conserved from the fall and were also derived from the destruction of root cells during freeze-thaw cycles. The depletion of the DOC content in the outflow water could be caused by not only changes in the hydrological pathways but also depletion in the reserves. Similarly, Worrall et al. (2002) observed that the character of the DOC and the A_{465}/A_{665} ratio changes during storm events were due to the exhaustion of the reserves rather than changes in the flow paths used by runoff.

Hydrochemical tracers, such as SiO_2 (Figure 6.16) and ion content (Table 6.2), demonstrated significantly different concentrations at the different ecohydrological mire zones and provided additional insights regarding the flow dynamics of these zones. Due to the high concentrations of SiO_2 (Figure 6.16) in the first flush of water discharge in the outflow stream, it can be suggested that the “old carbon” from the previous year (stored near the origin of the stream) is discharged during the early phase of snowmelt and that the pore water is replaced by fresh water. Similar observations were made by Ågren et al. (2010a), who observed that as new water (e.g., snowmelt or precipitation) enters the system, it recharges the peatland and pushes out older stored water into the stream. This annual recharge with new water and thus new DOC, is supported by radiocarbon studies that have shown that the DOC exported from boreal wetlands is composed of materials of relatively recent origin (Palmer et al., 2001; Raymond & Hopkinson, 2003). Additionally, agglomerative hierarchical clustering analysis using hydrochemical variables (i.e., ion concentrations) separated measurement sites and sampling dates into groups and demonstrated that after the second snowmelt period, the outflow water chemistry was most closely related to the fen chemistry (Figure 6.15). Agglomerative hierarchical clustering analysis is a robust and effective method for the classification of groundwater quality and the interpretation of temporal trends (Daughney & Reeves, 2005, 2006; Güler et al., 2002). Agglomerative hierarchical clustering is also an advantageous tool for distinguishing between water types because it includes different types of variables, such as chemical, physical, and biological factors (Daughney &

Reeves, 2005). However, this method does not provide the significance of these differences; therefore, supplementary statistical and graphical methods must be applied (Daughney & Reeves, 2005).

6.5.4 Snowmelt hydrology

Based on our hydrochemical measurements, the snowmelt period can be described by the following steps. The first wave of melting occurred at the bog site, where snow meltwater partially replenished the depleted water content after the extreme drought period of the previous summer, and the rest of the water contributed to surface and interflow runoff toward the fen and lagg zones. The water flowed through a channel in the lagg zone (where the ground was still frozen) toward the outflow and the river. This water flushed away the snowmelt water and, in turn, removed the “old carbon” from the mire.

Later, the soil in the fen and forested patches began to thaw. At the later stages of snowmelt, the differences in DOC concentration with soil depth reflect the effects of surface dilution and removal from snow meltwater runoff (Figure 6.9). Additionally, this increase of DOC concentration with soil depth indicates that different layers become hydrologically connected during different stages of snowmelt. The higher concentrations of DOC at lower depths in all zones (except the bog) can be explained by the fact that the spring melting of snow occurs relatively quickly and most of the snow meltwater is unable to completely penetrate the soil. Therefore, the flushed DOC is primarily from the surface, and the DOC in the lower peat depths remains unaffected. In contrast, the DOC concentrations within the treeless bog were similar for all depths, which indicate less ice in the ground and a better mixing of pore waters. After the snowmelt period, the water supply reduces due to decreased precipitation and inflow, and DOC export is consequently reduced. The amount of runoff during the snowmelt may be affected by the hydrological conditions at the end of the previous year (prior to the ground freeze and start of the snow season). For example, the summer of 2010 (immediately previous to the study year) was the second hottest summer over the previous 510 years in the studied region (Barriopedro et al., 2011), resulting in a significant drought in the studied mire complex. Therefore, it can be assumed that a significant amount of the snowmelt recharged the water deficit of the mire soils rather than contributing to the lateral outflow and river flow.

The reduced levels of discharge into the fluvial system during the post-snowmelt can affect the geochemical parameters (acidity, UV light penetration rate, availability of nutrient sources for microorganisms, etc.) of the aquatic system. After entering the streams, organic carbon may accumulate for long-term storage in sediments or may be respired as CO₂ or CH₄; the fate of this carbon depends on its quality and the hydro-biogeochemical characteristics of the drainage system (Laudon et al. 2004).

6.5.5 Micro- and macro-elements

As presented in Table 6.1, the ion concentrations increased along the lagg-fen-bog transect in the following order: bog < fen < lagg. All concentrations, apart from those of K⁺, SO₄²⁻, and PO₄³⁻, increased during fall probably because of the cumulative effect of summer evapotranspiration and decreased precipitation rates during summer. Significantly higher concentrations of most ions in the lagg zone are evidence for the greater influence of mineral soils in this transition zone of the mire complex. Therefore, the variability in hydrochemistry in the lagg zones is strongly susceptible to influence from the mineral inflow water. Similarly, Vitt et al. (1995) found that seasonal variations in magnesium and calcium contents were increasingly greater in poor fen, moderately rich fen, and extremely rich fen sites, which implies that the groundwater determines the temporal variation in cation concentrations at the minerogenic mire sites. The K⁺ concentration decrease observed after snowmelt over the summer towards fall was likely due to depletion by plant uptake (Proctor, 2003). Howie & Van Meerveld (2012) suggested that K⁺ content variation is due to not only differences in plant intake but also precipitation and evapotranspiration differences.

6.6 Conclusions

This study represents a step toward differentiating the main contributing ecohydrological zones to the overall discharge from a heterogeneous forest-mire landscape as well as quantification of DOC loss in boreal Russia. The integrated effect of the mosaic-type landscape, with its various soil, vegetation, and hydrological regimes, was evident as the DOC content and water-chemical properties across the mire complex varied substantially during and after the snowmelt. The major findings of the present study are summarized below:

1. During the snowmelt period, approximately 1.7 g C m^{-2} of DOC was transferred in the approximately 74 mm of runoff from the catchment into the river.
2. The snow pack and the top soils of the bog, fen, and lagg ecohydrological zones thaw at different times as a result of differences in exposure to the sunlight, vegetation cover, and soil structures. Within a short period of time, variations in the thawing periods led to differences in the inputs and relative contributions of each ecohydrological zone of the mire complex to the change in outflow DOC content. During the first week of the snowmelt period, carbon accumulated in the area near the stream flow during the previous year was discharged, while during later stages the fen and the surface layer of the lagg site were the main contributors to carbon flux.
3. The DOC concentrations of surface and soil pore waters vary seasonally, increasing during the summer and reaching a peak concentration during the fall before decreasing again during the winter and early spring.
4. The quality of DOM varied over time and space. In particular, the humification index A_{465}/A_{665} demonstrated that during the first stage of the snowmelt in the transitional lagg zone, a higher amount of low-molecular-size organic carbon is observed in the surface water. During the snowmelt, the proportion of high-molecular-size DOM increased in the lagg zone. In contrast, during the fall, the proportion of low-molecular-size carbon was the highest in the lagg zone.

Further research is important for developing an improved understanding of the spatial and temporal dynamics of DOC in boreal catchments and is vital to predicting the response to expected climate changes in this region.

6.7 Appendix

Table 6.4 The C_{DOC} across the peatland after the snowmelt period 2011.

Site	Long utm	Lat utm	May 25	Jun 2	Jun 9	Jun 16	Jul 1	Jul 6	Aug 4	Aug 10	Aug 19	Aug 26	Sep 1	Sep 28	Oct 1
Treeless taiga bog C_{DOC} , mg L ⁻¹	459586	6867192	18.9	22.7	23.7	24.6	23.7	21.4	22.9	24.9	24.2	21.8	25.3	29.5	n/a
	459575	6867178	27.5	22.2	22.0	22.4	24.6	22.2	24.1	23.5	22.4	22.1	22.1	32.1	26.2
	459551	6867151	19.6	21.4	22.5	22.7	19.8	19.9	19.6	18.8	20.5	24.4	23.5	28.5	27.6
	459489	6867109	16.0	21.5	19.3	20.9	20.7	20.8	20.7	19.8	21.8	22.1	24.0	19.4	n/a
	459427	6867069	19.3	22.9	23.2	23.5	21.5	19.8	19.7	20.0	19.8	20.3	20.6	31.6	28.0
Treeless taiga fen C_{DOC} , mg L ⁻¹	459401	6867030	30.6	37.1	32.9	32.3	32.5	32.6	33.1	32.7	33.4	33.3	33.3	36.1	35.2
	459390	6866989	35.7	40.8	36.0	35.3	36.7	35.2	36.7	38.2	37.0	36.4	36.7	39.4	38.5
	459363	6866926	38.1	40.0	41.4	45.6	42.8	49.0	50.9	49.6	49.3	48.2	43.5	56.4	64.9
	459327	6866837	36.1	38.4	38.7	44.2	47.6	48.5	50.6	51.8	51.4	49.9	46.6	55.5	n/a
	459304	6866781	35.5	38.7	39.6	45.2	45.6	46.6	45.7	48.5	45.6	46.5	43.5	n/a	58.9
Pine fen C_{DOC} , mg L ⁻¹	459266	6866701	37.6	41.2	42.1	39.6	41.8	42.3	44.4	45.1	43.5	42.9	42.7	n/a	n/a
Pine bog C_{DOC} , mg L ⁻¹	459234	6866624	36.4	39.3	40.8	52.6	46.6	49.0	n/a	56.8	52.4	52.3	51.7	n/a	59.6
	459206	6866561	39.2	43.9	45.2	42.5	47.4	58.0	65.0	54.2	51.5	50.8	47.9	n/a	59.7
	459194	6866527	36.1	40.8	41.5	46.7	48.2	50.9	64.0	51.6	52.7	51.9	47.7	n/a	56.9
Pine fen C_{DOC} , mg L ⁻¹	459177	6866476	27.4	29.8	31.1	45.2	42.3	46.1	50.2	47.4	45.3	46.6	46.6	56.7	n/a
	459157	6866448	32.2	35.0	36.2	33.8	35.4	44.0	46.3	40.1	45.1	54.5	37.6	n/a	n/a
	459128	6866391	39.2	42.9	43.5	37.7	36.7	34.8	52.7	38.5	38.2	38.3	35.9	47.2	51.1
Forested peatland/ Lagg zone C_{DOC} , mg L ⁻¹	459113	6866347	39.6	44.3	44.8	43.9	44.7	49.6	36.6	45.5	46.7	44.0	44.6	57.3	n/a
	459104	6866328	40.4	45.5	44.7	44.6	48.0	48.2	46.5	48.8	49.4	48.9	48.4	n/a	n/a
	459085	6866256	40.4	45.5	46.6	46.4	50.1	50.7	51.4	50.3	50.9	51.0	49.3	n/a	56.0
	459086	6866238	40.7	45.4	61.2	47.3	67.5	51.2	51.1	49.6	51.9	48.7	48.9	64.5	n/a
	459068	6866210	45.0	54.5	17.2	62.8	10.4	68.3	55.8	51.7	49.8	50.0	52.0	n/a	54.4

Table 6.5 The aromaticity index values (SUVA₂₅₄) across the peatland after the snowmelt period 2011. The standard deviation for replicate measurements was always less than 0.4 L mg⁻¹ m⁻¹, n/a stands for not available.

Site	Long utm	Lat utm	May 25	Jun 2	Jun 9	Jun 16	Jul 1	Jul 6	Aug 4	Aug 10	Aug 19	Aug 26	Sep 1	Sep 28	Oct 1
Treeless taiga bog SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	459586	6867192	3.57	3.82	3.81	3.83	3.68	3.63	3.66	3.68	3.67	3.63	3.69	3.74	n/a
	459575	6867178	3.74	3.73	3.76	3.82	3.69	3.64	3.67	3.65	3.63	3.63	3.62	3.78	3.71
	459551	6867151	3.68	3.69	3.73	3.81	3.60	3.61	3.66	3.57	3.60	3.72	3.70	3.73	3.73
	459489	6867109	3.60	3.69	3.69	3.77	3.62	3.66	3.64	3.58	3.66	3.65	3.70	3.55	n/a
	459427	6867069	3.70	3.90	3.87	3.80	3.66	3.67	3.66	3.61	3.61	3.68	3.62	3.77	3.73
Treeless taiga fen SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	459401	6867030	3.80	3.86	3.87	3.85	3.81	3.81	3.83	3.81	3.83	3.83	3.81	3.86	3.83
	459390	6866989	3.84	3.87	3.87	3.87	3.97	3.84	3.89	3.89	3.88	3.86	3.84	3.86	3.85
	459363	6866926	3.87	3.91	3.90	3.96	3.88	3.91	3.91	3.91	3.91	3.90	3.88	3.93	3.97
	459327	6866837	3.86	3.89	3.88	3.92	3.90	3.90	3.91	3.91	3.92	3.91	3.90	3.93	n/a
	459304	6866781	3.84	3.86	3.90	3.93	3.91	3.89	3.89	3.91	3.89	3.91	3.88	n/a	3.95
Pine fen SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	459266	6866701	3.85	3.86	3.91	3.91	3.88	3.89	n/a	3.90	3.89	3.89	3.88	n/a	n/a
Pine bog SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	459234	6866624	3.85	3.89	3.92	3.96	3.91	3.93	3.89	3.96	3.93	3.93	3.93	n/a	3.95
	459206	6866561	3.85	3.88	3.95	3.93	3.91	3.94	3.96	3.93	3.93	3.92	3.92	n/a	3.95
	459194	6866527	3.88	3.90	3.91	3.95	3.91	3.92	3.99	3.92	3.92	3.93	3.90	n/a	3.94
Pine fen SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	459177	6866476	3.86	3.90	3.84	3.92	3.88	3.91	3.93	3.90	3.92	3.90	3.91	3.94	n/a
	459157	6866448	3.79	3.81	3.92	3.89	3.83	3.90	3.90	3.87	3.91	3.93	3.86	n/a	n/a
	459128	6866391	3.82	3.86	3.92	3.91	3.84	3.84	3.93	3.85	3.88	3.85	3.85	3.90	3.92
Forested peatland/ Lagg zone SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	459113	6866347	3.88	3.90	3.91	3.91	3.90	3.93	3.89	3.90	3.93	3.89	3.90	3.94	n/a
	459104	6866328	3.88	3.91	3.91	3.91	3.92	3.93	3.92	3.93	3.94	3.91	3.92	n/a	n/a
	459085	6866256	3.88	3.91	3.92	3.91	3.93	3.94	3.96	3.92	3.94	3.93	3.93	n/a	3.96
	459086	6866238	3.88	3.92	3.97	3.92	4.01	3.94	3.94	3.92	3.95	3.91	3.92	3.97	n/a
	459068	6866210	3.88	3.91	3.58	3.98	3.24	3.99	3.97	3.94	3.94	3.93	3.93	n/a	3.95

Table 6.6 The C_{DOC} in the pore-waters at different depths along the transect (May 9). Deeper measurements in the lagg zone (forested table) were not possible because these layers remained frozen. Standard deviation was calculated based on duplicate measurements.

Site	N	lonData	latData	Surface (SD)	10 cm (SD)	30 cm (SD)	60 cm (SD)
Treeless taiga bog C_{DOC} , mg L ⁻¹	1	459591	6867194	16.1 (0.04)	20.5 (0.01)	20.7 (0.03)	22.4 (0.08)
	2	459576	6867178	17.2 (0.01)	20.7 (<0.01)	21.2 (0.01)	22.5 (0.02)
	3	459552	6867151	15.3 (0.08)	18.0 (<0.01)	21.4 (0.05)	17.8 (0.03)
	4	459488	6867108	13.2 (0.14)	14.7 (0.01)	21.4 (0.01)	11.4 (0.03)
	5	459427	6867071	16.3 (0.09)	22.2 (0.06)	19.7 (0.07)	16.1 (0.01)
Treeless taiga fen C_{DOC} , mg L ⁻¹	6	459403	6867030	27.6 (0.02)	29.3 (0.04)	36.3 (0.04)	35.5 (0.03)
	7	459388	6866988	32.4 (0.07)	32.4(0.05)	28.7 (0.05)	29.2 (0.01)
	8	459364	6866923	36.1(<0.01)	39.4 (0.09)	49.7 (0.01)	46.6 (0.03)
	9	459328	6866834	34.1 (0.04)	34.5 (0.05)	48.2 (0.03)	46.3 (0.04)
	10	459303	6866781	31.4 (0.05)	27.0 (0.04)	44.1 (0.06)	43.9 (0.15)
Pine fen C_{DOC} , mg L ⁻¹	11	459265	6866698	33.0 (0.01)	39.3 (0.01)	43.7 (0.04)	40.1 (0.12)
Pine bog C_{DOC} , mg L ⁻¹	12	459232	6866623	34.9 (0.04)	40.5 (0.11)	51.6 (0.03)	62.1 (0.02)
	13	459205	6866564	30.8 (0.02)	31.3 (0.07)	66.4 (0.06)	44.5 (0.12)
Pine fen C_{DOC} , mg L ⁻¹	14	459175	6866492	32.3(<0.01)	32.8 (0.07)	45.4 (0.07)	41.8 (0.06)
	15	459156	6866448	28.4 (0.07)	31.0 (0.01)	37.1 (<0.01)	49.5 (0.13)
	16	459133	6866391	28.9 (0.13)	28.3(0.09)	34.5 0.03)	34.4 (0.07)
Forested peatland/ Lagg zone C_{DOC} , mg L ⁻¹	17	459110	6866345	37.0 (0.02)	36.9 (<0.01)	42.3 (0.04)	43.4 (0.01)
	18	459108	6866332	37.5 (0.08)	37.6 (0.04)	37.4 (0.08)	n/a
	19	459102	6866320	36.5 (0.03)			
	20	459094	6866288	37.6 (0.02)			
	21	459088	6866256	37.0 (0.04)			
	22	459081	6866237	38.3 (0.02)		n/a	
	23	459072	6866214	43.1			

7 Characterization of truly dissolved and colloidal matter in a boreal mire-forest-river system in the Komi Republic, Russian Federation

7.1 Abstract

There is an increasing effort to characterize dissolved organic matter (DOM) dynamics in the connected terrestrial, limnic and marine ecosystems. This characterization is important for the understanding of biogeochemical matter transport from the continents to the ocean. However, most studies focus on the quantitative aspect without characterizing the qualitative properties of DOM. Knowledge concerning the qualitative characteristics of DOM in different compartments of the hydrosphere is necessary for evaluating the fate of terrestrial DOM and its potential biodegradability. Additionally, knowledge concerning high molecular organic matter provides information about preferentially bonded heavy metals and contaminants. Mire ecosystems are important sources of DOM, especially in the vast, but understudied, regions of boreal Russia. This study presents the abundance, distribution and qualitative differentiation of different organic carbon size fractions in the natural waters of a boreal mire-forest-river system in Northwest Russia. To investigate how the qualities of DOM change in time and space, a complex of physical analyses (fractionation by means of tangential flow filtration and spectroscopic UV-Vis absorbance measurement) and chemical analyses (measurement of the concentrations of dissolved organic carbon (DOC) and ions, and detection of stable carbon isotope signatures) were performed. Sampling was performed at five sites within the mire-forest-river landscape i.e., at bog, fen and lagg zones of the mire, at one outflow creek from the forest-mire complex and in the adjacent regional Pojeg River. The results of the study demonstrate that the DOM composition, which is the proportion of each size fraction, differed significantly among the different ecohydrological units of the landscape and showed clear seasonal variability. During all seasons, a major proportion of the organic carbon was found in the colloidal fraction. The “truly” dissolved organic carbon fraction showed a seasonal pattern. The lowest concentration of the truly dissolved size fraction was detected during the snowmelt period, whereas the highest concentration was detected during the summer period. During the summer period, the highest relative contribution of the truly dissolved organic carbon to the bulk DOC was detected at the fen and bog

sites. After the snowmelt period, the highest relative contribution was at the transitional lagg site. During fall, the proportion of the truly dissolved organic carbon was lower than in the summer period and was relatively equal at all studied sites. The differences in the proportions of the size fractions indicate that, depending on the season and sub-unit, the mires produce qualitatively variable DOM. Furthermore, the lagg zone was identified as a main path for the outflow. This work also provides a conceptual understanding of five possible routes for low molecular weight carbon production: leachates from vegetation, microbial decomposition of high molecular size organic compounds, dieback of microorganisms due to nutrient deficiency, UV degradation and physical degradation of high molecular size organic compounds because of freeze-thaw cycles.

7.2 Introduction

To evaluate the future of terrestrial dissolved organic matter (DOM) and its potential impact on greenhouse gas production, its biogeochemical characteristics and potential biodegradability must be quantified (Wickland et al., 2007). However, the analysis is complicated by the fact that DOM is not composed of a single substance but rather includes a broad spectrum of organic compounds (Reddy and Delaune, 2008). Operationally, it is possible to separate DOM into two size-based groups corresponding to the low-molecular-size and high-molecular-size organic carbon fractions. The two groups demonstrate different biogeochemical activities, levels of decomposition, and availability for microorganisms. Generally, high-molecular-size organic carbon, or colloidal organic carbon, include fractions between 1 kDa and 1 μm (Guo & Santschi, 1997a). Various studies have also used different membranes to separate the colloidal fraction with sizes ranging from 10 kDa-0.4 μm , 3 kDa-0.4 μm , 1 kDa-0.4 μm , 10 kDa-0.45 μm , and 1 kDa-0.22 μm (Guo & Santschi, 1997a; Sigg et al., 2000; Wells, 2002; Pokrovsky et al., 2010). A fraction below 1 kDa is referred to as a low-molecular-size, or truly dissolved fraction (Riise et al., 2000; Pokrovsky et al., 2010). Truly dissolved organic carbon compounds (0.5-1 kDa) can be transferred through the microbial cell membrane and metabolized; in contrast, extracellular enzymes are necessary to hydrolyze colloidal compounds and POC for microbial metabolism (Battin et al., 2008).

The labile, truly dissolved DOM fraction is typically composed of simple carbohydrate monomers, amino acids, amino sugars, and other low-molecular-mass compounds (e.g., Guggenberger et al., 1994; Küsel & Drake, 1998; Kaiser et al., 2001; Koivula & Hänninen, 2001; Marschner & Kalbitz, 2003). The colloidal fraction can consist of macromolecular organic matter, microorganisms, viruses, and nanoparticles (e.g., oxides of iron, aluminum, or manganese bound to organic matter) (Buffle et al., 1998; Gustafsson et al., 2000; Guo & Santschi, 2007). In contrast to the slowly degradable and relatively stable colloidal fraction, which is composed of polysaccharides and other organic derivatives from biota that require special enzymes for further decomposition, the terrestrial export of bioavailable labile truly dissolved organic carbon can be an important resource for aquatic bacterial metabolism (e.g., Qualls & Haines 1991; Tranvik & Jørgensen, 1995; Marschner & Kalbitz, 2003; Berggren et al., 2010). The colloidal fraction of DOM exhibits selective binding to

heavy metals and contaminants, and most trace elements are transported via organic and organo-mineral colloids (Guo & Santschi, 2007; Reddy and Delaune, 2008; Pokrovsky et al., 2010). Thus, a better understanding of the structural and functional properties of natural organic matter as well as of the partitioning of chemical species between truly dissolved and colloidal phases is important for the evaluation of biogeochemical cycles and the fate (mobilization, transport, solubility, and bioavailability) of chemical species, such as natural macromolecular organic matter, metals, radionuclides, and hydrophobic organic pollutants (Chen et al., 2002; Guo & Santschi, 2007; Pokrovsky et al., 2012).

Several techniques can be employed to separate DOM into its truly dissolved and colloidal fractions. Conventionally, XAD resin columns have been used for different types of size fraction separation. However, because of the limitation of this method (which separates only 10-15 % of the DOM and requires a pH adjustment), tangential flow filtration (*i.e.*, cross-flow ultrafiltration) is often preferred. This method does not require pH adjustment and is able to extract a higher amount of DOM while separating it based on size rather than chemical properties. This method is widely used for size fractionation and analysis of the environmental behavior of these fractions (Guo & Santschi, 2007). Additionally, bulk DOM can be characterized using absorbance measurements, such as A_{254}/DOC (*i.e.*, SUVA_{254}), A_{254}/A_{365} , and A_{465}/A_{665} . SUVA_{254} , which correlate strongly with aromatic carbon content (Marschner & Kalbitz 2003; Weishaar et al., 2003; Roehm et al., 2009). DOM with a low aromatic content is more bioavailable (Kaushal & Lewis, 2005), whereas aromatic structures are highly stable and more resistant to biodegradation. This is in contrast to carbohydrates, which are easily available substrates for microorganisms (Kalbitz et al., 2003b). However, a strong negative correlation between SUVA_{254} and bioavailability may not always be a reliable predictor of biodegradability because non-aromatic compounds can also demonstrate variable biodegradability rates (Weishaar et al., 2003). A low biodegradability of aliphatic compounds may be a result of complexation with aromatic structures or from a high rate of polymerization or oxidation (Guggenberger et al., 1994); however, these differences cannot be assessed using simple spectrophotometric methods (Marschner & Kalbitz, 2003). Another ratio, A_{254}/A_{365} , is used to provide information concerning molecular size (*e.g.*, De Haan, 1993; Ågren et al., 2008), whereas A_{465}/A_{665} provides information concerning the proportions of humic and fulvic acids (Thurman 1985; Peuravuori &

Pihlaja, 1997). Thurman (1985) assigned A_{465}/A_{665} ranges for humic and fulvic acids. Mature humic acids have an A_{465}/A_{665} ratio ranging from 2 to 5, whereas less mature fulvic acids have a ratio of 8 to 10 (Thurman, 1985). Another characteristics that can differentiate DOM is the $\delta^{13}\text{C}$ signature, which provide evidence for decomposition processes through isotope fractionation by the preferential microbial consumption of ^{12}C (e.g., Novák et al., 1999; Kalbitz & Geyer, 2002). The $\delta^{13}\text{C}$ signature can also show the DOM source. For instance, terrestrially derived organic matter from C-3 plants has a $\delta^{13}\text{C}$ value close to -28 ‰ (Fry, 2008). Marine macroalgae exhibit a wider range (e.g., from -10.5 to -29.5 ‰) of stable carbon isotope signatures (Wang & Yeh, 2003).

Currently, the sources, chemical characteristics, and environmental behavior of the different size fractions of DOM remain poorly understood (Guo & Santschi, 2007). Moreover, the following types of aquatic samples are mostly used for ultrafiltration: estuarine surface waters (Martin et al., 1995; Guo & Santschi, 1997b; Minor et al., 2002), marine surface waters (Carlson et al., 1985; Brownawell, 1991; Buesseler et al., 1996; Guo & Santschi 1996), sediment pore waters (Burgess et al., 1996; Chin & Gschwend, 1991), and river surface waters (Eyrolle & Benaim 1999; Sigg et al. 2000). Soil pore waters tended to receive less attention than waters from the fluvial systems (Menziés et al. 1991; Gooddy et al. 1995; Riise et al. 2000; van Hees et al. 2000; Pokrovsky et al. 2005, 2010).

Furthermore, the size fraction distributions of organic compounds, major ions, and trace elements in wetlands (Dupré et al., 1999) and organic-rich boreal peatlands have not been studied extensively (Pokrovsky et al., 2005). The seasonal and temporal variation of the different DOM size fraction proportions in the boreal peatlands of Russia, where more than 50 % of global peatlands are located (Apps et al. 1993), is especially poorly characterized. Investigating the qualitative characterization of peatland DOM is particularly important, because it has been demonstrated that peatlands have a great impact on aquatic systems and that peatland coverage of catchment areas is positively correlated with DOM concentrations (Kortelainen et al., 2006), aromaticity (Ågren et al., 2008; Olefeldt et al., 2012), and molecular mass (Olefeldt et al., 2012) in draining streams. Therefore, it is important to characterize the structure of DOM in mire inflow, peat pore, and mire outflow waters to gain new insights into the processes that control the generation, transport, and transformation of DOM in boreal mires. This characterization will help to evaluate the potential impact

of boreal peatlands on aquatic systems and greenhouse gas emissions from the mire ecosystems as well as from the aquatic ecosystems.

It can be hypothesized that because of the heterogeneous pattern of the hydrology and vegetation communities in peatlands (Bridgham, 1998), the DOM produced should vary structurally, both quantitatively and qualitatively, across different ecohydrological sub-units (e.g., lagg, fen, and bog). Differences in the DOM characteristics among these sub-units should be primarily driven by different vegetation cover, soil characteristics, and hydrological regimes. It can be assumed that the production of labile, truly dissolved compounds during summer should increase because of exudation and leaching from the fresh vegetation. The truly dissolved compounds would then be consumed rapidly; it has been demonstrated by Amon et al. (2001) that bacteria selectively remove bioreactive components, i.e., compounds such as dissolved amino acids and carbohydrates that are preferentially utilized by microorganisms, and leave biorefractory molecules. High temperatures during summer should lead to an increased rate of DOM biodegradation, which will lead to a relative enrichment of the refractory DOM compounds that are depleted in $\delta^{13}\text{C}$. Thus, during summer, the truly dissolved fraction should include not only labile DOM from exudates and recalcitrant low-molecular-size but also the products of DOM decomposition. During fall, the labile fraction from new exudates should decrease, whereas during the winter-spring period, it might increase because of frost damage to living cells (Morley et al., 1983; Tierney et al., 2001; Giesler et al., 2007) or possible physical disruption of the soil (Kalbitz et al., 2000). Additionally, the C/N ratio can be expected to change because of decomposition, where a large C/N ratio indicates a low decomposition rate and a small ratio indicates a high decomposition rate (Hornibrook et al., 2000; Broder et al., 2012). The C/N ratio is related to decomposition because microbial consumption leads to a relative decrease in carbon relative to nitrogen (Broder et al., 2012): mineralized nitrogen is retained in the microbial biomass (Damman, 1988; Hornibrook et al., 2000) while organic carbon is turned into CO_2 .

The main aim of this study is to provide a quantitative analysis of the apportionment of DOM into separate size fractions and the concentrations of associated hydrochemical species in a mire-forest-river landscape during the annual cycle. The following objectives were set:

1. Characterize the relative proportion of each of the two pools (truly dissolved and colloidal) of different size fractions of DOM within river, mire (bog, fen and lagg), and outflow waters.
2. Trace whether the size fraction proportion shows seasonal variation during the spring (snowmelt), summer (active vegetation growth period), and fall (senescence) periods.
3. Measure the $\delta^{13}\text{C}$ signature of different DOM fractions from various sites within a forest-mire system (lagg, fen, bog, river, discharge point).
4. Present the aromatic carbon content, molecular mass, and humification indexes derived using spectrophotometric measurements.
5. Distinguish, based on the chemical and physical qualitative differences of different size fractions, the main contributor to the discharge streams within the mire.
6. Characterize the ion speciation into different size fractions of DOM from the peat surface waters.

7.3 Materials and Methods

7.3.1 Study site

The study was conducted at the Ust-Pojeg mire complex (~ 25 km²) located in the Komi Republic of the Russian Federation (see chapter 3 for a detailed study site description).

7.3.2 Sampling

Water samples were collected from the surface at the forest-mire transitional zone (lagg), from fen and bog zones, and from the peatland outflow into the river fluvial system in the Ust-Pojeg mire complex. Additionally, samples were collected from the Ust-Pojeg River, located upstream from the study site, to evaluate the influence of the boreal terrestrial landscape on aquatic systems during the snowmelt period. Samples were collected from the surface in 5 L plastic bottles. Samples for ion analyses were kept in polyethylene bottles pre-rinsed with distilled water. Before sample collection, multiple rinses of the bottles were conducted using sample water. Sampling was conducted during the baseflow and high-flow periods (summer 2010: July, fall 2010: September-October, and spring 2011: April). Sampling frequency was adjusted to the flow rate and was conducted weekly during the base flow period and every 3-7 days during the high flow period.

7.3.3 Filtration

To separate the bulk DOC from particulate organic matter, samples were filtered within 24 hours after collection through pre-combusted (550 °C, 2 h) 0.7- μ m-pore-size glass-fiber filters (GF/F, Whatman, UK) using a glass filtration set (Sartorius, Germany) and a vacuum pump. To precondition the filtration system and avoid contamination from the filter before collecting the filtrate, 100 ml of sample water was processed through the filter and discarded afterward. A tangential flow filtration (TFF) system was used for fractionating the bulk DOM into different fractions.

Figure 7.1 a presents the TFF operation scheme. This filtration system was composed of ultrafiltration membranes (hydrophilic polyethersulfone (PES), Omega, Centramate, PALL Corporation, USA), a pump, a holder (Centramate, PALL

Corporation, USA), a reservoir, tubing and fittings, and containers for the water sample and permeate solutions. Two fractions were yielded during filtration: permeate and retentate. The permeate is the DOM fraction that passed through the tangential flow filtration membrane, and retentate is the DOM fraction that did not pass through the membrane.

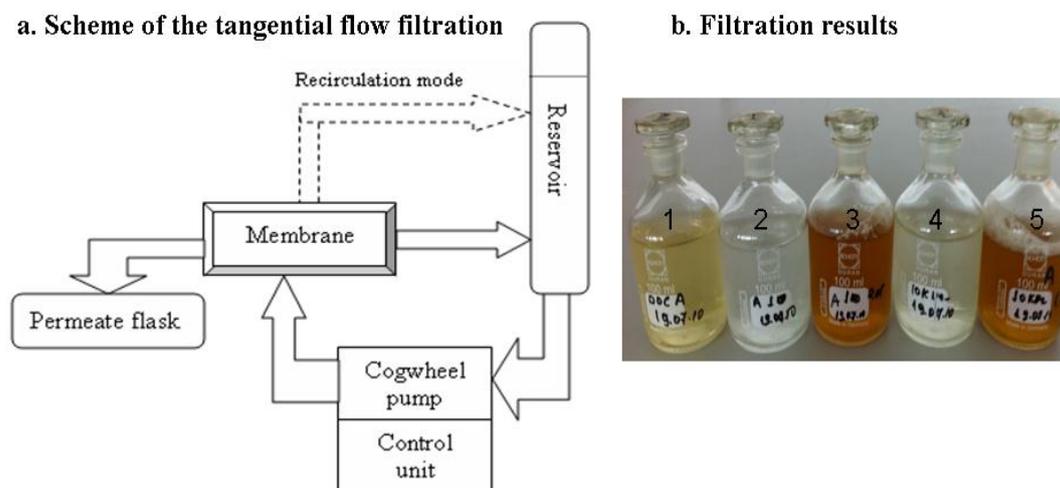


Figure 7.1 a. Schematic representation of tangential flow filtration (Drawing by B. Brockmeyer, University of Hamburg), b. the output of the filtration (1) bulk DOC (filtered with $0.7 \mu\text{m}$), (2) $\leq 1\text{kDa}$; (3) $\geq 1 \text{kDa}$, (4) $\leq 10\text{kDa}$, (5) $\geq 10 \text{kDa}$.

All tubing and fittings were made of Teflon. Two polyethersulfone membranes with different nominal molecular cut-off sizes (1kDa and 10kDa) were used to separate dissolved compounds into a colloidal fraction with high molecular size and the ‘truly dissolved’ fraction with low molecular size. The intermediate ($1 \text{kDa} \leq x \leq 10 \text{kDa}$) fraction was calculated by subtracting the DOC content of the $\leq 10 \text{kDa}$ fraction from the $\leq 1 \text{kDa}$ fraction content. The filtration and cleaning procedures followed protocols described by Schwalger and Spitzky (2009). After filtration all samples were conserved in acid-washed glass bottles. To reduce bacterial activity, the samples were acidified to pH 2 and stored at $4 \text{ }^\circ\text{C}$ until further laboratory analysis. Samples for the major ion analyses were collected in plastic bottles and frozen until analysis.

To exclude the possibility of cross-contamination, blank samples were collected after the cleaning procedure. The organic carbon blanks never exceeded 0.79 mg L^{-1} for a $\leq 10 \text{kDa}$ membrane or 0.26 mg L^{-1} for a $\leq 1 \text{kDa}$ membrane. For all other elements, the blanks were always below the analytical detection limits. Standard solutions of polyethylene glycols (PEG) 1, 10 and 35 kDa were used to evaluate the

retention performance of the used membranes. The retention coefficient (RC) was calculated based on the following estimator (Schwalger and Spitzzy, 2009) :

$$RC=1-(C_{Perm}/C_{Ret}) \quad (1)$$

where C_{Perm} and C_{Ret} are the concentrations of the standard molecule in the permeate and retentate, respectively.

In the current study, the ≤ 1 kDa filters retained 97-98 % of the 10 and 35 kDa PEG, and the 10 kDa membranes retained 93-94 % of the 10 and 35 kDa PEG.

The retentates were collected for recovery estimation. The recovery was estimated as:

$$Recov = (C_{Ret} + C_{Perm})/C_{PFW} \quad (2)$$

where C_{Perm} and C_{Ret} are the organic carbon contents in the respective volume in permeate and retentate, respectively, and C_{PFW} is the organic carbon concentration of the pre-TFF water, which was used as a bulk DOC sample (Schwalger and Spitzzy, 2009). The mean recovery was within a range of 78-114 % (96.5 ± 12.4 %).

7.3.4 Dissolved organic carbon and dissolved nitrogen content determination

The organic carbon content of each fraction was analyzed using a wet-heated persulfate oxidation method (Aurora Model 1030; O-I-Analytica, USA). The standards (potassium hydrogen phthalate: KHP, $KHC_8H_4O_4$: 5, 20, 40 mg L⁻¹) were always checked before and after the analyses to ensure that no analytical drift occurred within and between sample runs.

Dissolved nitrogen (DN) was analyzed using a thermal catalytic oxidation at 720 °C chemiluminescence method (TNM-L, Shimadzu, Japan). In the current study, preliminary screening for inorganic nitrogen species showed that the inorganic nitrogen content was very low. Thus, it can be assumed that the DN was mostly composed of dissolved organic nitrogen.

7.3.5 Stable carbon isotopes ($\delta^{13}C$) analyses

7.3.5.1 Liquid sample stable carbon isotope ($\delta^{13}C$) analyses

To characterize the stable carbon isotopes signatures of the different DOM size fractions, the $\delta^{13}C$ signatures of the organic matter in the liquid samples were analyzed through isotope-ratio mass spectrometry (Finnigan Delta V, Thermo Scientific, USA). The isotope ratios are expressed as δ -values and are reported

relative to the Vienna Pee Dee Belemnite (VPDB) standard according to the following equation:

$$\delta^{13}\text{C} = [(R_{\text{sample}}/R_{\text{VPDB}}) - 1] \times 1000 \quad (3)$$

R is the ratio of $^{13}\text{C}/^{12}\text{C}$ in the sample and the VPDB standard, respectively. The secondary standards, USGS 40 and IAEA-C6, were measured against the VPDB standard to estimate the instrument accuracy and precision. The measurement precision was within the range of 0.01 to 0.2 ‰, and the accuracy was -0.3 to 0.3 ‰. Additionally, the mass balance calculations based on the bulk, ≤ 1 kDa and ≤ 10 kDa fractions' DOC concentrations and $\delta^{13}\text{C}$ were performed in order to compare with the retentate $\delta^{13}\text{C}$ signatures (≥ 1 kDa and ≥ 10 kDa).

7.3.5.2 Plant stable carbon isotope ($\delta^{13}\text{C}$) analyses

After identifying the plant species, vegetation from each landscape type was collected during July and October 2010. The plants were pressed and dried directly after collection. To determine plant tissue $\delta^{13}\text{C}$ -content, each species was separated into stems, leaves, roots, and other parts (e.g., flowers). Afterward, the samples were ground (6 min in a vibration disk mill or by hand, depending on the sample quantity) and dried in cabinet desiccators (12 hours at 60 °C). A 0.042 μg sample was used to determine the $\delta^{13}\text{C}$ signature using a Flash 2000 organic elemental analyzer for isotope ratio mass spectrometry (Thermo Scientific, USA).

7.3.6 Absorption measurements

Spectroscopic absorbance measurements over a wavelength range of 200-742.5 nm at 2.5 nm intervals were conducted using a UV-Vis spectrophotometer (spectro::lyser, s::can, Austria). Afterward, the absorbance coefficients A_{255}/DOC (or SUVA_{255} , reported in units of $\text{L mg}^{-1} \text{m}^{-1}$), A_{254}/A_{365} , and A_{465}/A_{665} were used as proxies to characterize the aromaticity, molecular size, and humification indexes, respectively.

7.3.7 Inorganic chemical species analyses

The different size fractions were analyzed to determine the concentrations of Na, K, Mg, Ca, Fe, Zn, and Cu using an atomic absorption spectrometer ('AAS');

1100B, Perkin-Elmer, USA). Cuvette tests (LCW 028, Hach Lange, Germany) were used to determine silica (SiO_2) content in different size-fractions in the lagg and outflow sites. Cuvette tests (LCW 341; Hach Lange, Germany) were used to determine the nitrite (NO_2^-) content within the different size fractions for the following sampling dates: lagg zone on July 17 and 26, September 22, and October 3; fen and bog zone on July 19, September 22, and October 3; and outflow and river on April 28. The results of nitrite analyses are not presented because they were all under the measurement range ($< 0.015 \text{ mg L}^{-1}$).

7.3.8 Statistical analyses

Descriptive statistics were calculated for all chemical analyses. Pearson's correlation analysis was used to evaluate the relationships between the inorganic species concentrations and organic carbon concentrations in the size fractions. All analyses were tested at significance levels of 0.001 and 0.05 (Pearson, two-tailed). All statistical analyses were performed using the SPSS 18.0 package (IBM Corp., Chicago, USA).

7.4 Results

7.4.1 Proportion of different organic carbon size fractions

During the summer, fall and spring periods, the DOC size fractions of surface waters from different parts of the mire complex exhibited clearly different proportions (Figure 7.2). The detailed seasonal variation is presented in Table 7.1 and Appendix Table 7.10-12. Within the mire, the bog demonstrated the lowest bulk DOC concentration; while the lagg demonstrated the highest bulk DOC concentration. During all seasons, the predominant size-fraction was the total colloidal fraction (≥ 1 kDa). The highest proportion of truly dissolved organic carbon was detected during summer, while the highest proportion of the total colloidal fractions occurred during the fall season. During the snowmelt period, all sites demonstrated lower DOC concentrations in the surface waters.

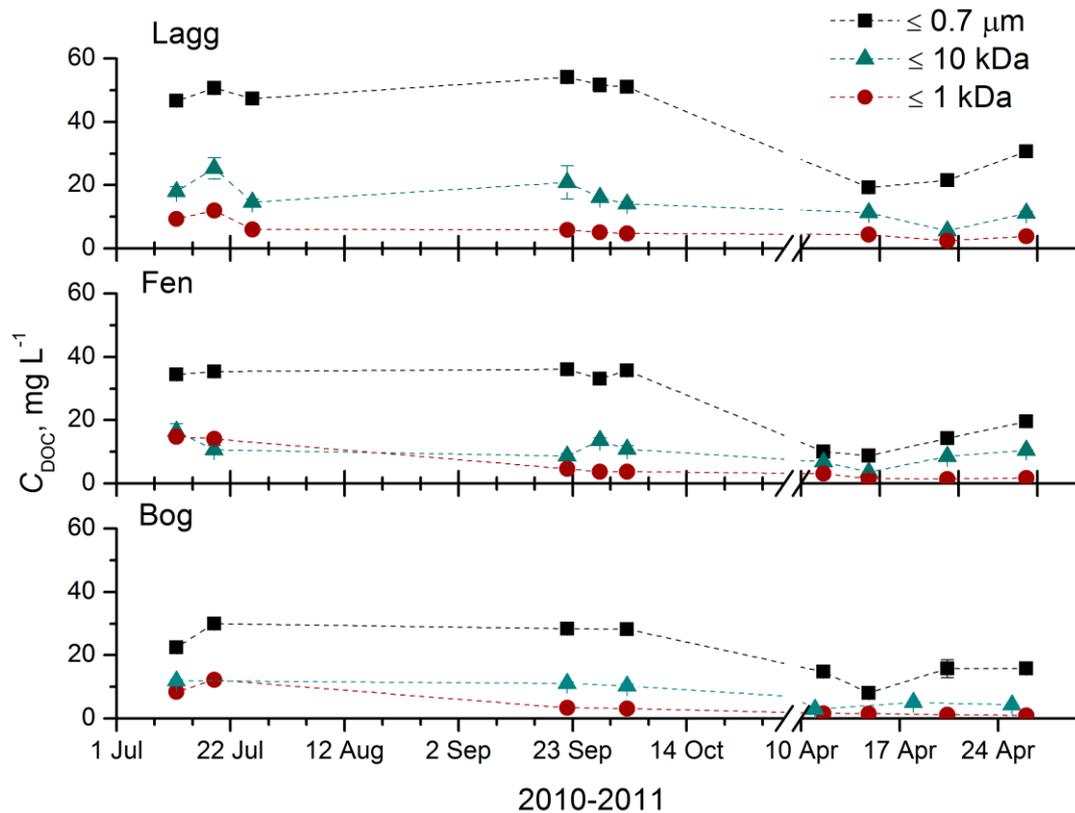


Figure 7.2 The bulk ($\leq 0.7 \mu m$), high colloidal ($\leq 10 kDa$), and truly dissolved ($\leq 1 kDa$) fraction dynamics in the course of the annual cycle. Before the axis break, the intervals between major ticks on the x-axis are 3 weeks; after the break, they are 1 week.

Table 7.1 Average seasonal contribution of different size fractions (truly dissolved fractions: ≤ 1 kDa; intermediate-size colloidal: 1-10 kDa; and large-size colloidal: ≥ 10 kDa) to the bulk DOC fractions (all results of absolute organic carbon concentrations are presented in Appendix Table 7.10-7.12).

Site	$C_{\text{Bulk DOC}} (\leq 0.7\mu\text{m}),$ mg L^{-1} (SD)	≤ 1 kDa, % (SD)	1-10kDa, % (SD)	≥ 10 kDa, % (SD)	Season
Lagg	48 (2)	19 (6)	21 (5)	60 (10)	Summer
	52 (2)	10 (1)	23 (5)	68 (6)	Fall
	24 (6)	16 (6)	25 (11)	60 (17)	Spring
Fen	35 (1)	36 (9)	7 (3)	56 (6)	Summer
	35 (2)	11 (1)	20 (9)	68 (9)	Fall
	13 (5)	17 (10)	39 (12)	45 (12)	Spring
Bog	26 (5)	39 (2)	16*	47*	Summer
	28 (0)	11 (1)	26 (1)	62 (2)	Fall
	14 (4)	10 (5)	25 (8)	64 (9)	Spring
Outflow	50 (2)	16 (1)	5 (3)	79 (1)	Summer
	37 (10)	10 (3)	27 (19)	63 (17)	Spring
River	22 (1)	17 (3)	33 (25)	50 (23)	Spring

* during summer, only one sample was filtered through a ≤ 10 kDa filter at the bog site

Lagg

At the lagg site, the seasonal concentration of the bulk DOC concentration during summer (47-50 mg L^{-1}) was slightly lower than during the senescence period (51-54 mg L^{-1}), whereas the concentration was the lowest (19-31 mg L^{-1}) during snowmelt. During summer, the truly dissolved organic carbon concentration in the lagg zone was within the range of 6-12 mg L^{-1} , while it decreased during fall (5-6 mg L^{-1}) and snowmelt (3-4 mg L^{-1}). During the first week of the snowmelt period, the lagg's truly dissolved fraction concentration (4.3 mg L^{-1}) was closer to the concentrations during the end of fall (4.7 mg L^{-1}), before subsequently decreasing (2.5- 4.4 mg L^{-1}). The truly dissolved fraction in the lagg zone composed 13-24 % of the bulk DOC fraction carbon during summer. This proportion decreased during fall (9-11 %), whereas during spring the proportion (12-23 %) was similar to summer. The total colloidal fraction at the lagg zone constituted a substantial part of the bulk DOC (summer 76- 87 %; fall 89- 91 %; spring 77-88 %), from which predominantly organic carbon was in the form of large-size colloidal fraction.

Fen

At the fen, the mean surface DOC concentration during summer (34-35 mg L⁻¹) and fall (33-36 mg L⁻¹) was similar, whereas during spring (9-20 mg L⁻¹), the concentration was lower compared to other seasons. During summer, the mean truly dissolved fraction concentration was 14-15 mg L⁻¹, which constituted more than 39-42 % of the bulk DOC fraction at the fen site. During fall, the truly dissolved fraction's concentrations decreased (4-5 mg L⁻¹), constituting 10-13 % of the bulk fraction. During spring, 9-31 % of the bulk was in the form of the truly dissolved fraction (1-3 mg L⁻¹). The total colloidal fraction comprised the main part of the bulk DOM fractions (summer: 57 - 70 %; fall: 87 - 90 %, spring: 69 - 91 %), while the large-size colloidal fraction was the dominant form in the total colloidal fraction.

Bog

The mean bulk DOC concentration at the bog site was substantially lower than at the fen and lagg during all seasons (summer 22-29 mg L⁻¹; fall 28 mg L⁻¹; spring 8-16 mg L⁻¹). During summer, the truly dissolved fraction (12 mg L⁻¹) constituted 40-52 % of the bulk DOC; however, owing to the low water table levels, it was difficult to collect water from this site during the later periods of the summer season. During the fall period, the truly dissolved fraction (3-3.4 mg L⁻¹) proportion decreased and constituted 11-12 % of the bulk DOC fraction, while during snowmelt, the truly dissolved (1-2 mg L⁻¹) constituted 6-19 % of the bulk DOC fraction. Similarly to the lagg and fen site the total colloidal fraction comprised the most of the bulk DOM.

Outflow

During summer, the concentrations of all fractions in the outflow site were stable (48 - 52 mg L⁻¹), with the truly dissolved fraction comprising 15-27 % of bulk DOC (Figure 7.3). Due to the severe drought during summer, the above-surface discharge during fall ceased and could no longer be detected. During the snowmelt period, the bulk DOC concentration was only close to the summer concentration during the first week (51 mg L⁻¹); thereafter, it was within a constant lower range (30-34 mg L⁻¹). The truly dissolved fraction was within the range of 2-5 mg L⁻¹ and

comprised 7-14 % of the bulk (Figure 7.3). Similar to the other sampling sites, the colloidal fraction comprised the major form within the bulk DOM fraction.

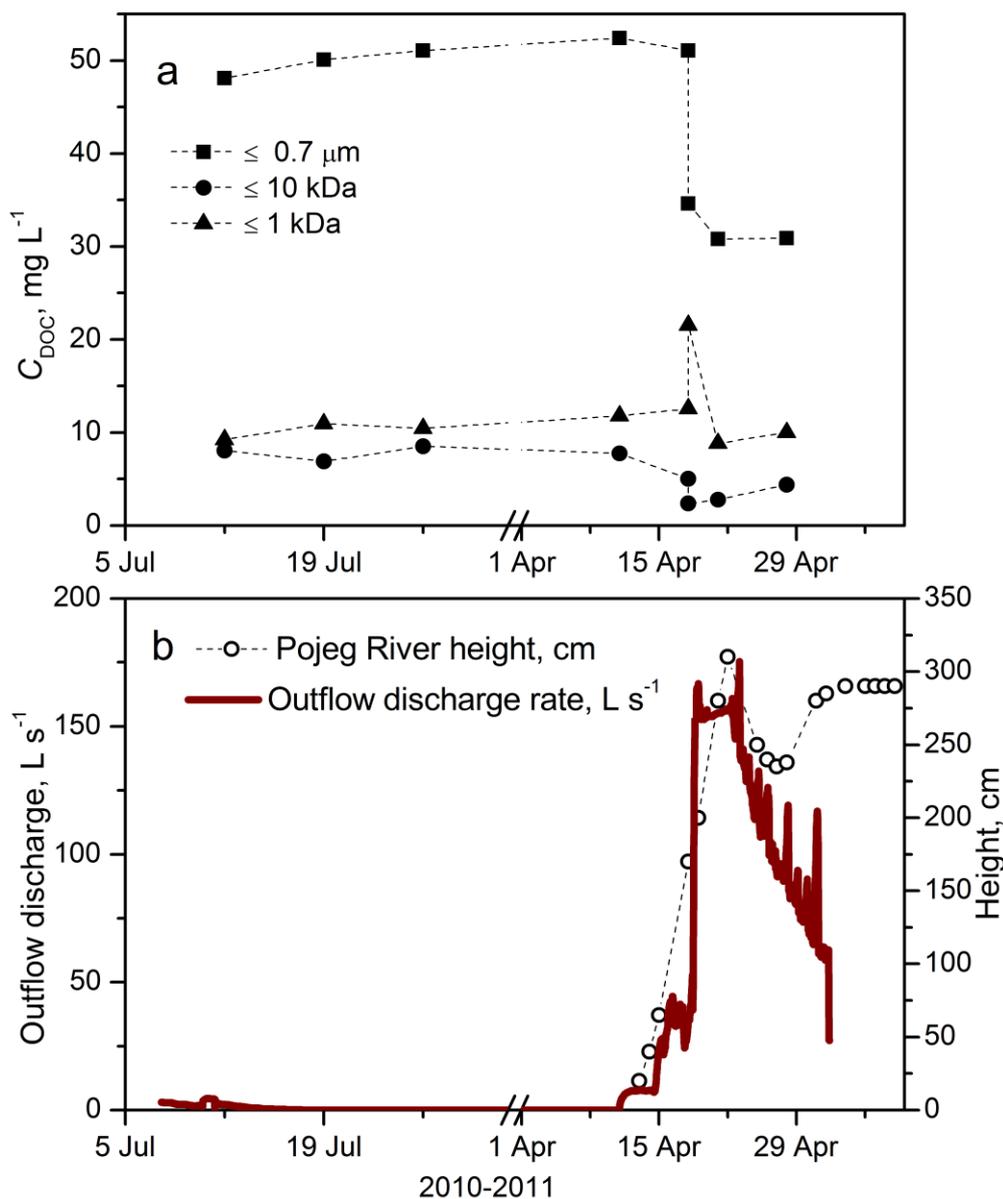


Figure 7.3 a. Seasonal dynamics of different organic carbon size fractions in the mire outflow during the summer and snowmelt periods. Standard deviation values for the duplicate samples were always lower than 1.57 mg L^{-1} . b. Discharge time series and Pojeg River height* (Data source for the figure b: personal communication Benjamin Runkle, University of Hamburg). *height-discharge relationship is probably not constant due to thawing/melting in the river banks. Thus, the decrease after April 22 may be because the ice on the bottom of the river melted so the water height fell.

River

The different dissolved organic carbon size fraction dynamics of the boreal Pojeg River are presented in Figure 7.4. During snowmelt, the bulk DOC

concentration was within the range of 20-23 mg L⁻¹ and was thus significantly higher than the fall concentration: 4.5 mg L⁻¹. The truly dissolved fraction contributed 14-20 % of the bulk DOC during the snowmelt. The total colloidal fraction comprised that main part of the bulk. However, variations were also detected between the high-size and intermediate size colloidal fractions (Figure 7.4).

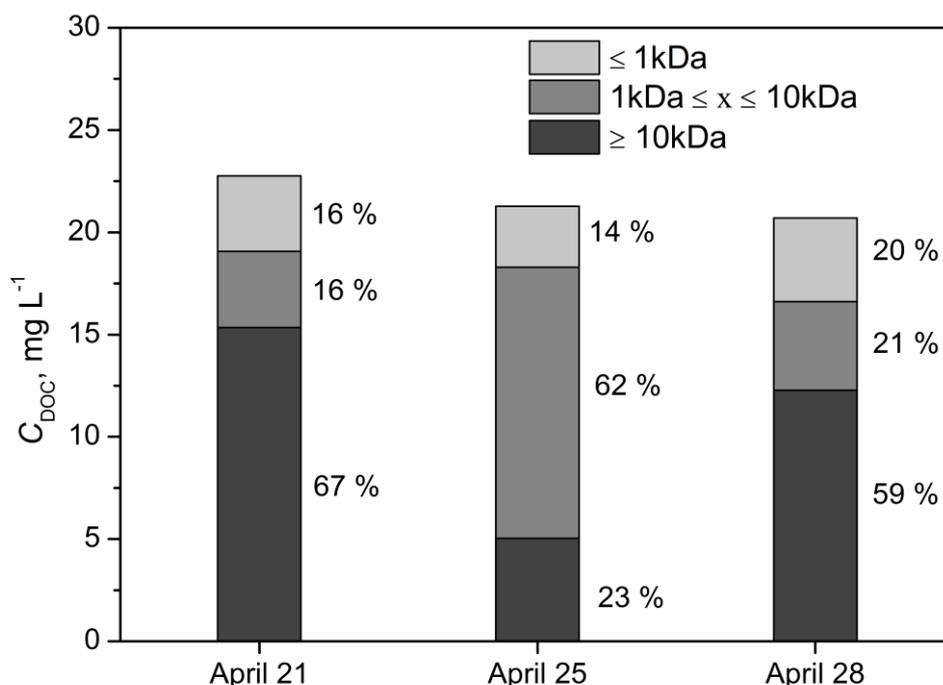


Figure 7.4 Dissolved organic carbon concentrations of different organic carbon size fractions distributions in the Pojieg River during the snowmelt period.

7.4.2 Stable carbon isotope ($\delta^{13}\text{C}$) signatures

Table 7.2 presents the $\delta^{13}\text{C}$ values for the different plant species and parts. The stable carbon isotope signature of the plants was within the range for plants utilizing the C-3 photosynthetic pathway (-26 to -32 ‰). The stems and stalks nearly always exhibited a depleted stable carbon isotope signature showing a lower $\delta^{13}\text{C}$ value when compared to the leaves and roots. The most enriched values of $\delta^{13}\text{C}$ were detected in the plant material of *Sphagnum spp.* (-24 ‰). *Sphagnum spp.* also demonstrated a wide range of $\delta^{13}\text{C}$ values, ranging from -24.0 to -31.3 ‰.

The stable carbon isotope ($\delta^{13}\text{C}$) values of the pore water samples at different depths (July 7 and 26, August 8, October 9) ranged from -28.2 to -29.2 ‰ and varied little with depth. Table 7.3 presents the depth measurements for the samples collected on July 7. Also the table shows very slight enrichment in lagg > fen > bog.

Table 7.2 Stable carbon isotope signatures for the plant materials across the study site (Forested area- 1, lagg- 2, fen- 3, bog- 4).

Species	Site	Stem/stalk, $\delta^{13}\text{C}$, ‰	Leaf/needles $\delta^{13}\text{C}$, ‰	Other parts $\delta^{13}\text{C}$, ‰
<i>Aconitum vulparia</i>	4	-29.9	-30.4	
<i>Andromeda polifolia</i>	1	-27.6	-28.8	
<i>Andromeda polifolia</i>	2	-27.6	-28.7	
<i>Andromeda polifolia</i> *	3	-27.1	-27.6	root -27.8
<i>Andromeda polifolia</i> *	4	-26.9	-27.2	
<i>Angelica sylvestris</i>	1	-27.9	-29.8	
<i>Betula nana</i>	1	-28.6	-29.7	
<i>Betula nana</i> *	3	-27.7	-29.5	
<i>Betula pendula</i> *	2	-32.8, -30.8 ¹		bark -34.5; root -31.4, flower -27.9
<i>Calamagrostis canescens</i>	2	-26.8		root -26.1; blade -26.8
<i>Carex rostrata</i> *	3	-26.2		branch -29.4
<i>Chamaedaphne calyculata</i> *	3	-30.5	-29.4	
<i>Chamaedaphne calyculata</i> *	4	-28.0	-29.4	
<i>Equisetum pratense</i>	1	-27.2	-28.8	
<i>Equisetum sylvaticum</i>	3	-26.8	-27.5	
<i>Equisetum sylvaticum</i>	4	-26.1	-27.9	
<i>Eriophorum angustifolium</i>	1	-27.6		flower -27.3
<i>Eriophorum angustifolium</i>	2	-28.8		flower -29.1
<i>Eriophorum angustifolium</i> *	3			root -24.4
<i>Lathyrus pratensis</i>	4	-26.5	-26.7	
<i>Lathyrus vernus</i>	4	-29.3	-30.1	
<i>Menyanthes trifoliata</i>	2	-27.5		
<i>Oxycoccus macrocarpus</i>	1	-28.6	-28.3	
<i>Oxycoccus palustris</i>	1	-27.3	-28.2	
<i>Oxycoccus palustris</i>	2	-32.3	-32.7	
<i>Picea obovata</i> (1.3 m)*	1	-29.0	-30.3 ² , -31.3 ³	branch -29.4; root -27.9
<i>Picea obovata</i> (10 m)*	1		-29.8 (2 m) ⁴	branch -29.1; bark-27.3; root 27.9
<i>Pinus sylvestris</i> *	4	-29.5	-28.6	
<i>Pinus sylvestris</i> *	4	-30.8		bark -31.1
<i>Pyrola rotundifolia</i>	3	-31.4	-28.0	flower -31.1
<i>Ranunculus repens</i>	1	-32.3	-28.6	
<i>Ranunculus tripartitus</i>	1	-31.2	-32.2	
<i>Salix caprea</i>	1	-31.3		
<i>Salix myrtilloides</i>	1	-30.1	-30.8	
<i>Salix repens</i>	1	-26.7	-27.9	
<i>Scheuchzeria palustris</i>	1	-26.3		fruit -24.3
<i>Sphagnum</i> ⁶	4	-29.7		
<i>Trientalis europaea</i>	1	-31.6	-33.1	
<i>Trientalis europaea</i>	2	-29.6	-31.4	
<i>Vaccinium myrtillus</i>	1	-28.7	-28.9	
<i>Vaccinium myrtillus</i>	3	-26.2	-26.9	
<i>Vaccinium uliginosum</i>	1	-29.0	-29.7	
<i>Vaccinium uliginosum</i>	2	-29.9	-30.6	
<i>Vaccinium uliginosum</i>	3	-30.6	-31.5	fruit -30.2
<i>Vaccinium uliginosum</i>	4	-30.7	-30.0	
<i>Vicia angustifolia</i>	1	-30.5	-31.0	
<i>Vicia sepium</i>	3	-30.8	-31.4	
<u>$\delta^{13}\text{C}$ signature for <i>Sphagnum</i> species for the complete plant.</u>				
<i>Sphagnum</i>	1	-31.3		
<i>Sphagnum</i>	1	-26.9		
<i>Sphagnum</i>	1	-26.4		
<i>Sphagnum</i>	2	-23.9		
<i>Sphagnum</i>	3	-24.0		
<i>Sphagnum</i> *	3	-26.7		
<i>Sphagnum</i> *	3	-26.95		

*stands if samples are collected during fall (October 2010), while all other samples were collected during summer (July 2010), ¹ sample was taken from the center of the stem; ² sample is collected from the 1.3 m height, ³ sample is taken from the 0.5 m height; ⁴ sample is taken from a 2 m height; ⁵ sample is taken from 4 cm depth; ⁶ $\delta^{13}\text{C}$ signature for *Sphagnum* species was analyzed for the complete plant.

Table 7.3 $\delta^{13}\text{C}$ isotope signature for DOC fraction at different depths across the catchment (July 7, 2010).

Depth	10 cm (SD)	30 cm (SD)	60 cm (SD)
Lagg	-28.35 (0.09)	-28.46 (0.02)	-28.62 (0.05)
Fen	-28.79 (0.01)	-28.76 (0.06)	-28.72 (0.07)
Bog	-28.91 (0.04)	-28.86 (0.07)	-28.96 (0.25)

*Pore water samples were filtered through $\leq 0.7 \mu\text{m}$ filters. The standard deviation (SD) is estimated based on the analytical replicate measurements.

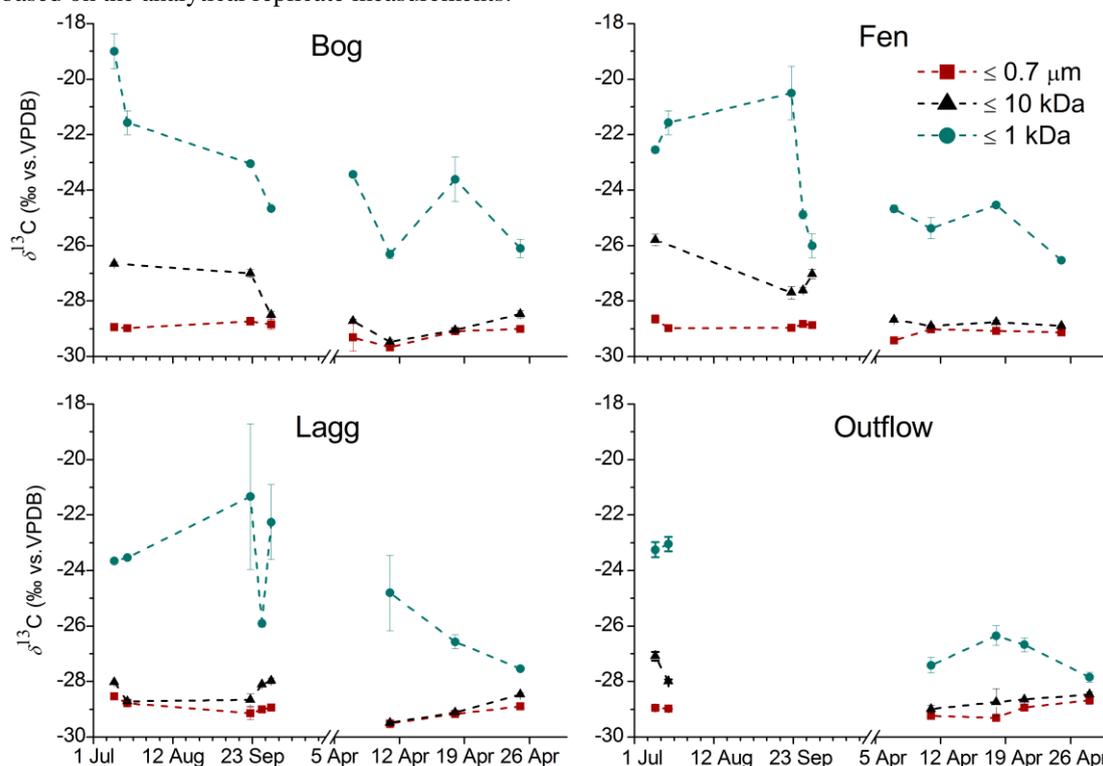


Figure 7.5 $\delta^{13}\text{C}$ isotope signature of the bulk ($\leq 0.7 \mu\text{m}$), high colloidal ($\leq 10 \text{ kDa}$), and truly dissolved ($\leq 1 \text{ kDa}$) fraction in the course of the annual cycle. Before the break, the intervals between major ticks at the x-axis are 6 weeks; after the break, they are 1 week. Error bars represent the standard deviations based on the analytical replicate measurements from two bottle measurements.

Figure 7.5 demonstrates the $\delta^{13}\text{C}$ isotope signature variation for different DOC organic carbon fractions. The heaviest $\delta^{13}\text{C}$ signature was found in the truly dissolved organic carbon fraction (Figure 7.5). The strongest variations over the sampling period were observed for the $\leq 1 \text{ kDa}$ fraction at the bog site (Figure 7.5). At the bog site during summer (July 12), the $\delta^{13}\text{C}$ signature of this fraction was $-18.9 \pm 0.6 \text{ ‰}$, whereas during fall, this value decreased to -24.7 ‰ (October 3), and fell further during the snowmelt to -26.1 ‰ (April 25). At the bog site the $\leq 10 \text{ kDa}$ fraction exhibited a similar trend: on July 12, the value was -26.7 ‰ , whereas in fall, it was -28.5 ‰ . During the snowmelt period, the values fluctuated within the range of -28.5 to -29.1 ‰ , which is very close to the bulk DOC signature range of $29.1 \pm 0.3 \text{ ‰}$. A

similar dynamic was observed at the fen site. The summer values of the ≤ 1 kDa fraction fluctuated from -20.5 to -22.5 ‰; during fall the values decreased to -26.0 ‰; and during snowmelt, they ranged from -24.5 to -26.5 ‰. The ≤ 10 kDa fraction during summer exhibited enriched values of -25.8 ‰. During fall, the values decreased to -27.0 ‰, and during snowmelt, the values were closer to the bulk values, decreasing to -28.90 ‰. The bulk DOC isotope signature had a mean value of -28.9 ± 0.2 throughout the entire sampling period. In the lagg zone, the carbon isotopic content of the ≤ 1 kDa fraction's ranged from -23.7 to -23.5 ‰; in the fall, it exhibited a wider variation, fluctuating from -21.33 to -25.90 ‰; and during snowmelt, it decreased to -27.6 ‰. In the lagg zone, the ≤ 10 kDa and bulk DOC fractions were relatively stable, with mean values of -28.6 ± 0.5 ‰ and -29.0 ± 0.3 ‰, respectively. At the outflow point, the values were higher during the summer period (bulk DOC -28.9 ± 0.02 ‰; ≤ 1 kDa -23.2 ± 0.1 ‰; ≤ 10 kDa -27.5 ± 0.6 ‰) than during the spring period (bulk DOC -29.0 ± 0.3 ‰; ≤ 1 kDa -27.1 ± 0.7 ‰; ≤ 10 kDa -28.7 ± 0.2 ‰).

The $\delta^{13}\text{C}$ values of the DOC fractions sampled in the river during the snowmelt period showed differing stable carbon isotope signatures (Figure 7.6). In the river samples, the $\delta^{13}\text{C}$ values did not strongly vary during the snowmelt period (bulk DOC -28.5 ± 0.1 ‰; ≤ 1 kDa -27.3 ± 0.6 ‰; ≤ 10 kDa -28.3 ± 0.2 ‰); however, the ≤ 1 kDa fraction exhibited slightly enriched values compared to ≤ 10 kDa and bulk fractions.

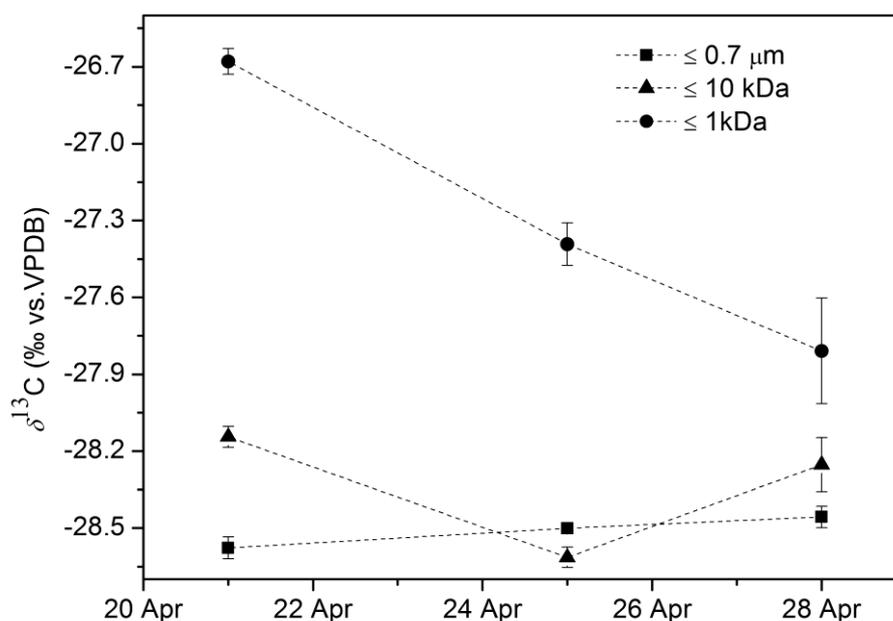


Figure 7.6 Stable carbon isotope signatures size fractions of Pojég River DOC samples during the snowmelt period. Error bars represent standard deviations calculated based on the analytical replicates of $\delta^{13}\text{C}$ measurements.

The retentate $\delta^{13}\text{C}$ signatures from all sites were relatively constant over the sampling period (Table 7.4). The values ranged from -28.3 to -29.1 ‰ and were very similar to the bulk DOC values. The retentate fractions' $\delta^{13}\text{C}$ values did not exhibit seasonal variation. The mass balance calculations demonstrated good agreement with the retentate $\delta^{13}\text{C}$ signatures (≥ 1 kDa: -29.9 ± 1.4 ‰; ≥ 10 kDa: -29.4 ± 0.7 ‰). Because the variation between values did not vary strongly and was similar to the bulk DOC fractions' $\delta^{13}\text{C}$ signatures the data is not presented.

Table 7.4 Stable carbon isotope signatures ($\delta^{13}\text{C}$) for selected retentate fractions. Standard deviations are calculated based on the mean values of the n samples

Fraction	Site	n	Mean $\delta^{13}\text{C}$ value (‰)	SD $\delta^{13}\text{C}$ value (‰)
≥ 10 kDa	Lagg	8	-29.12	0.24
	Fen	8	-28.93	0.17
	Bog	6	-28.94	0.25
	Outflow	5	-29.15	0.17
	River	1	-28.37	
≥ 1 kDa	Lagg	6	-29.11	0.27
	Fen	8	-29.08	0.34
	Bog	6	-28.89	0.30
	Outflow	6	-29.15	0.19
	River	3	-28.34	0.25

7.4.3 DOC/DN

At the beginning of the summer period, the DOC/DN ratios of the pore waters were higher compared with the later period, suggesting that with increased drought and temperature the rate of degradation increased (Table 7.5). The values at the bog sites were higher than at the other sites, which demonstrate that degradation was slower at the bog site.

Table 7.5 DOC/DN ratios of pore waters taken from different subsurface depths during the summer 2010 sampling period.

Site	Depth, cm	7-Jul	12-Jul	26-Jul	3-Aug
Lagg	10	52.1	-	45.0	-
	30	50.8	-	49.1	-
	60		-	48.8	42.2
Fen	10	48.9	40.6	37.3	41.9
	30	-	44.6	41.4	44.5
	60	52.5	46.7	41.7	45.7
Bog	10	58.7	-	-	-
	30	73.1	51.7	49.7	53.3
	60	66.6	54.3	46.6	44.9
Outflow		52.2	-	-	-

The analyses of the different fractions for the snowmelt period demonstrate that the DOC/DN concentration ratio of ≤ 1 kDa is consistently and sometimes substantially smaller than the values of the $\leq 0.7 \mu\text{m}$ and ≤ 10 kDa fractions (Table 7.6). The highest variability in the values for all fractions was observed at the bog site, which was caused by a disproportionate decrease in the carbon and nitrogen contents as a result of the snowmelt water input on April 11.

Table 7.6 DOC/DN ratio values of different size fractions during the snowmelt period 2011.

Site	Fraction size	7-Apr	11-Apr	18 and 21Apr (river, outflow)	25 and 28 Apr (outflow)
Lagg	$\leq 0.7 \mu\text{m}$	37.88	42.22	40.21	43.88
	$\leq 10\text{kDa}$	-	46.59	43.50	43.58
	$\leq 1\text{kDa}$	-	36.33	30.31	29.35
Fen	$\leq 0.7 \mu\text{m}$	71.53	35.64	19.84	39.98
	$\leq 10\text{kDa}$	21.83	32.14	36.04	48.00
	$\leq 1\text{kDa}$	14.17	27.13	16.00	16.60
Bog	$\leq 0.7 \mu\text{m}$	81.93	-	30.16	39.91
	$\leq 10\text{kDa}$	17.85	62.25	40.73	21.36
	$\leq 1\text{kDa}$	16.78	57.00	9.49	27.50
Outflow	$\leq 0.7 \mu\text{m}$	57.99	49.10	43.52	52.92
	$\leq 10\text{kDa}$	-	46.97	43.45	44.12
	$\leq 1\text{kDa}$	-	27.43	21.29	29.93
River	$\leq 0.7 \mu\text{m}$	14.75	-	33.00	-
	$\leq 10\text{kDa}$	-	-	33.83	-
	$\leq 1\text{kDa}$	-	-	19.36	-

7.4.4 Spectrophotometric measurements of different size fractions

During snowmelt, variations in the spectrophotometric properties were detected for all DOM fractions at the outflow, river, fen, bog and lagg sites (Figure 7.7). After the first week of snowmelt, the bulk DOM fraction exhibited lower values of SUVA_{254} in the bog region compared to the fen and lagg zones, thus indicating relatively higher proportions of recalcitrant aromatic structures. SUVA_{254} increased during this period, indicating a higher proportion of aromatic compounds. The SUVA_{254} values in the ≤ 10 kDa fraction were relatively similar for all sites, apart from the outflow and river sampling points during the first week of the snowmelt, which demonstrated a higher amount of aromatic carbon. During the snowmelt period, an increase in aromatic carbon content period was also detected in the ≤ 1 kDa fraction, accompanied by a decrease in the A_{465}/A_{665} ratio. This indicates an enrichment of high-molecular-size humic acids, given that the value of A_{465}/A_{665} ratio < 5.0 indicates

the presence of humic acids, whereas the values for 6.0 to 8.5 demonstrate the presence of fulvic acids (Thurman 1985). Similar to the results of the TFF size fractionation, the A_{465}/A_{665} ratio demonstrated that the bulk DOM at the outflow and lagg zones had a higher proportion of low-molecular-size organic matter compared with the fen and bog sites. During the subsequent periods, the A_{465}/A_{665} ratio was relatively similar at all sites and indicated the presence of humic acids.

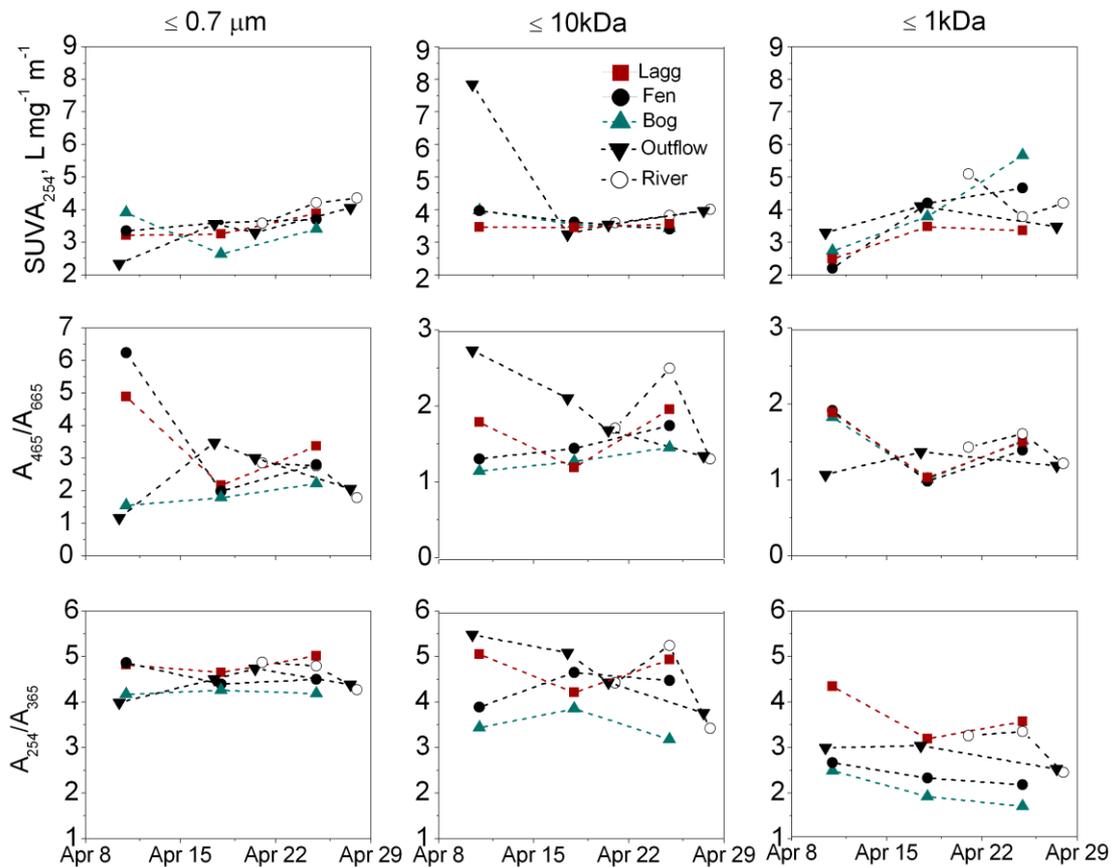


Figure 7.7 Absorbance ratios (SUVA_{254} , A_{465}/A_{665} and A_{254}/A_{365}) for the different size fractions ($\leq 1\text{ kDa}$, $\leq 10\text{ kDa}$, and $\leq 0.7\ \mu\text{m}$) during the snowmelt period.

The absorbance ratio values for the $\leq 10\text{ kDa}$ fraction demonstrate that the water samples at the outflow point had highest aromatic content during the first days of the snowmelt, while it subsequently decreased and was similar to other sites. The A_{254}/A_{365} ratio demonstrated that outflow had a higher proportion of low-molecular size organic carbon during the first days of the snowmelt period before later decreasing, and was relatively similar at all sites. The lower values of the absorbance ratio A_{254}/A_{365} for the $\leq 1\text{ kDa}$ fractions indicate that the bog has a higher average molecular size organic carbon in this fraction than at the other sites. SUVA_{254} values demonstrate that all sites had a relatively similar amount of the aromatic carbon

during the first phase of the snowmelt, in ≤ 1 kDa fraction, while bog demonstrated the highest proportion of low molecular organic carbon compared to all other sites during the later phase. However, the results of A_{465}/A_{665} ratio for ≤ 1 kDa can be disputable, given that only a low amount of light was absorbed at this wavelength, and thus the produced ratio can result in error.

7.4.5 Inorganic species differentiation in the different size fractions

Figure 7.8 presents the variation of C_K , C_{Ca} , C_{Mg} and C_{Fe} among the sites (presented sampling date: July 19 for the lagg, fen, and bog; and April 28 for outflow). The different sites exhibited distinctly different concentrations of inorganic species. The highest concentration of C_{Ca} , C_{Mg} and C_{Fe} was observed at the lagg site, whereas the highest concentration of C_K was at the bog site. The strong variation in inorganic species indicates the possibility of tracing the rather diffuse water flows within the mire complex. Variation not only exists in the concentrations but also in the proportion of the ions associated with the different DOM size fractions. The colloidal fraction generally exhibits the following trend: $C_{Fe} < C_{Mg} < C_{Ca}$.

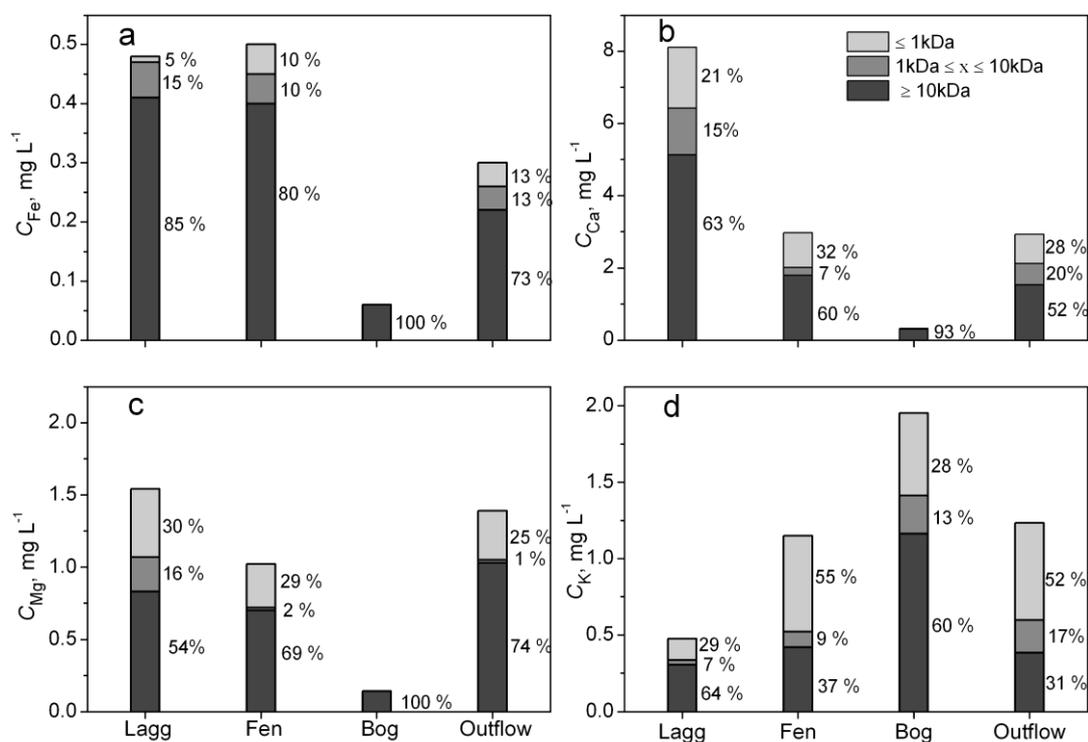


Figure 7.8 Ion distribution among intermediate-size and large-size colloidal (1-10 kDa and ≥ 10 kDa) and truly dissolved (≤ 1 kDa) fractions within the bulk DOC fraction at different sites in the mire complex (a) iron concentration C_{Fe} , (b) calcium concentration C_{Ca} , (c) magnesium concentration C_{Mg} , (d) potassium concentration C_K . (sampling was conducted on July 19: lagg, fen, and bog; and on April 28: outflow).

Figure 7.9 shows the variation of species distributions in the different fractions in the Pojeg River, in contrast to the mire and outflow sites (Figure 7.9) the C_{Ca} and C_{Mg} contents are much higher in the truly dissolved DOM fraction than in the other DOM fractions. The seasonal variability and distribution of inorganic elements across the DOM size fractions are presented in Table 7.7.

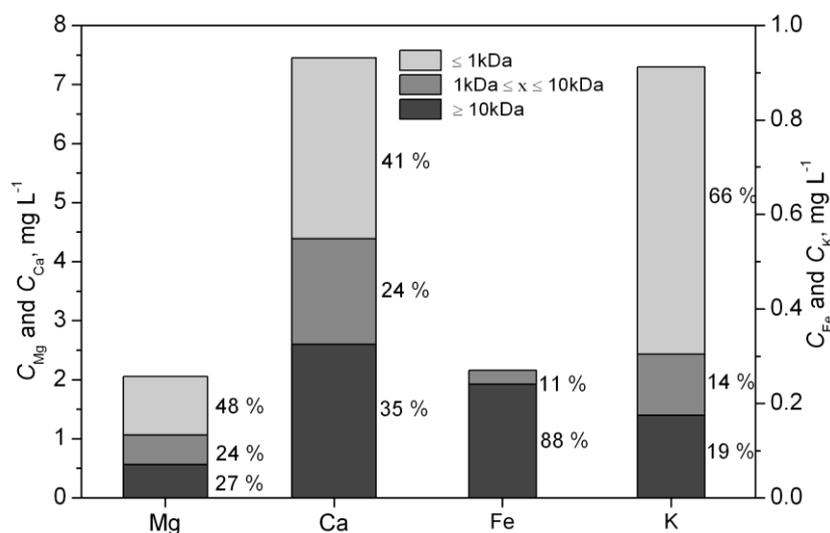


Figure 7.9 Concentrations and proportions of selected ions associated with different DOM size fractions in the Ust Pojeg River sample (April 28).

Based on the tangential flow filtration size fractionation, C_{Fe} , C_{Ca} , C_{Zn} , and C_{Mg} were present predominantly in the large colloid (≥ 10 kDa) fraction. C_K at the lagg and fen was abundantly present in both low molecular mass and high molecular mass, whereas at the bog site, it was mostly present in the colloidal form. C_{Mn} was only detected in the lagg (0.04 ± 0.02 mg L⁻¹) and fen (0.06 ± 0.02 mg L⁻¹) sites and only in the high molecular mass (≥ 10 kDa) fraction. The silica concentrations in the bulk fraction ranged from 3.7 to 4.4 mg L⁻¹ at the lagg site, and 4.1-6.8 mg L⁻¹ at the outflow site. Silica content in the bog and fen sites was analyzed only for the bulk fraction at the bog and fen sites (see Chapter 6 for further details). The silica analyses demonstrated that most of the silica content is in the truly dissolved form at the lagg (88-97 %) and outflow (98-100 %) sampling points (July 7 and 19).

Thus, based on the DOM size fractionation results, all of the sites' elements can be separated into three groups: 1. elements that are not influenced by filtration and are present in a truly dissolved phase (SiO_2); 2. elements that are partially present in all fractions (Ca, Mg, K); and 3. elements that are strongly (≥ 85 %) associated with the colloidal fraction (Fe, Zn, Mn).

Table 7.7 Major cation distribution across truly dissolved intermediate-size colloidal and large-size colloidal DOM fractions related to the bulk concentrations.

Element	Site	Mean concentration (SD) mg L ⁻¹	% ≤1 kDa fraction	% in 1-10 kDa fraction	% in ≥10 kDa fraction
C_{Ca}	Lagg	8.1 ± 0.2	22 ± 5	16 ± 4	63 ± 1
	Fen	1.7 ± 0.5	15 ± 15	20 ± 12	65 ± 11
	Bog	0.2 ± 0.3	3 ± 3	0	95 ± 2
	Outflow	2.9	27	20	52
	River	5.2	41	24	34
C_{Mg}	Lagg	1.7 ± 0.1	24 ± 9	24 ± 8	51 ± 4
	Fen	0.9 ± 0.08	14 ± 15	17 ± 13	69 ± 8
	Bog	0.2 ± 0.04	0	14 ± 21	86 ± 21
	Outflow	1.39	24	1	74
	River	2.06	48	24	27
C_{Fe}	Lagg	0.4 ± 0.2	3 ± 2	15 ± 6	82 ± 8
	Fen	0.5 ± 0.04	5 ± 5	11 ± 2	84 ± 5
	Bog	0.07 ± 0.02	5 ± 10	11 ± 19	83 ± 17
	Outflow	0.3	13	13	73
	River	0.3	0	11	88
C_K	Lagg	0.5 ± 0.07	47 ± 16	8 ± 9	45 ± 17
	Fen	2.37 ± 1.4	46 ± 13	20 ± 16	35 ± 3
	Bog	2.53 ± 0.9	27 ± 3	25 ± 11	48 ± 10
	Outflow	1.23	52	17	31
	River	0.91	66	14	19
C_{Zn}	Lagg	0.05 ± 0.01	n/d ^o	n/d ^o	76 ± 12
	Fen	0.17 ± 0.01	n/d ^o	n/d ^o	76 ± 11
	Bog	0.11 ± 0.09	n/d ^o	n/d ^o	90 ± 14

* Sampling weeks: lagg: July 19 and 26, September 22, October 3; fen and bog: July 19, September 22, October 3; outflow and river: April 28. “n/d^o” not detected.

Table 7.8 Pearson correlation (*r*) coefficients between absolute carbon content and different elements in various fractions.

Elements	≤0.7 μm n = 22	≤10 kDa n = 19	≤1 kDa n = 19
C_{Mn}	0.62**	0.18	n/a
C_{Mg}	0.73**	0.42	0.13
C_K	-0.26	-0.23	-0.20
C_{Ca}	0.77**	0.49*	0.12
C_{Fe}	0.67**	0.28	0.38

* significant at the 0.05 level; **significant at the 0.01 level

The Pearson correlation coefficients presented in Table 7.8 reveal a strongly significant correlation between the organic carbon concentrations and all element concentrations except for C_K in the bulk fraction, whereas in the ≤10 kDa fraction, only C_{Ca} exhibited a significant relationship with the organic carbon content. No significant correlation was detected between the concentration of any element and the organic carbon content in the ≤1 kDa fraction.

7.5 Discussion

7.5.1 Proportion and dynamics of the different organic carbon size fractions

This study was the first to investigate the different size fraction distributions of DOM compounds throughout an annual cycle in surface waters of different ecohydrological sub-units in a Russian boreal mire complex. The highest DOM concentrations were detected during the summer and fall seasons. It can be assumed that the low water tables and high temperatures during summer and fall increased the rate of peat decomposition and, therefore, increase the quantity of DOM that is available for release. However, DOM production may only partially explain the high concentrations during summer and fall because high concentrations tend to coincide with periods of low rainfall and may also be related to evaporative enrichment or increased accumulation of DOM during longer water residence times (Scott et al. 1998). Across the mire, significant differences in the bulk DOC concentrations at different ecohydrological sites were detected. This variation is most likely a result of differences in vegetation cover. It is likely that the DOM at the bog site was predominantly derived from the *Sphagnum* moss species, which are dominant in this landscape unit. In contrast, a mix of different vascular and bryophyte species was present in the fen and lagg zones. In the lagg zone, tree species were dominant. The increased temperature and dry conditions during the summer likely accelerated DOM production; as a result, the highest DOC accumulation was identified in the peat pore waters during fall. During the snowmelt period, the concentration significantly declined because of dilution by the melted snow. In contrast to the bulk DOC concentration, variations in the proportions of the different DOM size fractions were much more pronounced during different seasons. In the current study the tangential flow filtration can potentially underestimate the proportion of the truly dissolved organic carbon because easily biodegradable compounds, such as carbohydrates, can bind to refractory DOM compounds (Guggenberger et al., 1994; Jandl & Sollins, 1997) and stop their degradation (Kalbitz et al., 2003a). Thus, formation of truly dissolved organic carbon with colloidal fraction complexes can lead also artifact during the ultrafiltration and underestimate amount of low molecular size organic carbon availability.

During the different seasons, structural transformation of the DOM was detected. The highest mean proportions of truly dissolved organic matter at the lagg, fen, and bog sites were observed during summer. At all sites, the proportion of truly dissolved fraction decreased during fall and increased during spring. Generally, the truly dissolved fraction is more bioavailable than high molecular mass carbon. As reviewed by Pokrovsky et al. (2011) and referenced therein, low-molecular-size complexes are potentially bioavailable because they are comparable in size to the pore sizes of the cell wall transport channels. In a study by Bengtsson & Törneman (2004), DOC with a molecular size < 0.1 kDa was mineralized faster by stream water bacteria than DOC with a molecular size < 3.5 kDa. Similarly, in soil samples collected during spring, Marschner & Kalbitz (2003) found that the biodegradability of the <1 kDa fraction was three to four times higher than the <10 kDa fraction; however, in the samples collected during summer, the biodegradability of DOM was much lower, with no differentiation among size fractions. This difference was explained by the probable depletion of biodegradable compounds by the activated microorganisms during late spring and summer (Marschner & Kalbitz, 2003). In contrast, other studies (e.g., of samples from the Gulf of Mexico, the Amazon River, and nearby coastal ocean waters) have demonstrated, that the biodegradation rate was higher in larger DOM size fractions (Amon & Benner, 1994, 1996). These results were explained by differences in structural characteristics, as larger compounds were most likely fresher and less diagenetically altered; therefore, they were more bioreactive than the small fractions. Thus, size is only a secondary factor in DOM biodegradability; the primary factor is the structural characteristics (Marschner and Kalbitz, 2003).

Furthermore, in contrast to the assumption that easily degradable DOM should be depleted preferentially in soils, Marschner & Bredow (2002) observed that DOM not only decreased with increasing temperature but also became more biodegradable. These results could be explained by high microbial activity leading to a reduction of substrates and nutrients; in turn, mortality in the microbial population releases easily degradable cell constituents (Marschner & Bredow, 2002; Marschner & Kalbitz, 2003). Thus, to explain the results of this study and sources of the truly dissolved fractions, five production routes should be considered.

A conceptual illustration (Figure 7.10) reveals probable main sources of low molecular size compounds during different sampling seasons. The first route includes truly dissolved fraction derived from exudates of roots and mycorrhizal fungi and

leachates from, for example, leaves and stems; which most likely was highest during the summer period. This group includes labile truly dissolved organic carbon fraction (e.g., root exudates composed of ethanol, carbohydrates, and amino acids), which are easily biodegradable under aerobic and anaerobic conditions (Reddy & Delaune, 2008). The biodegradation rate of leachates varies depending on the plant species. Wickland et al. (2007) observed that the leachates of *Sphagnum* and feather mosses were rapidly biodegraded and that a higher amount of the DOM in these leachates was mineralized (90 %) compared to leachates from *Eriophorum* (20 %) and *Picea* needles (10 %). In contrast, the litter of *Sphagnum spp.* is poor in nutrients, inhibits microbial activity and is more resistant to decay than vascular plant litter (Rydin & Jeglum 2006). Thus, it can be expected that leachates at the bog site will be mineralized faster, which can lead to a significant decrease in the truly dissolved fraction proportion during senescence at the bog site.

Summer	Fall	Winter
<ul style="list-style-type: none"> • exudates and leachates from the vegetation • microbial degradation of high molecular size organic carbon compounds • die-back of microorganisms due to nutrient deficiency • degradation due to UV radiation. 	<ul style="list-style-type: none"> • leachates from a senescent vegetation and leaf fall • microbial degradation of high molecular size organic carbon compounds. 	<ul style="list-style-type: none"> • physical degradation of high molecular size organic compounds because of freeze-thaw cycles.

Figure 7.10 Conceptual illustration of potential main sources of truly dissolved DOM fractions during different seasons.

The second route includes the end product of the decomposition of high-molecular-size organic compounds. A temperature increase can not only stimulate DOM production but also the decomposition rate. Thus, the high temperatures during summer can stimulate microbial activity and the breakdown of larger insoluble compounds (Christ & David, 1996), which can serve as an additional source of truly dissolved compounds during summer. If this process dominates over the bioavailable truly dissolved organic carbon production from exudates and leachates, it will eventually lead to the net depletion of the bioavailable fraction and the accumulation

of recalcitrant truly dissolved compounds. Decomposition can not only increase because of temperature but also the prolonged residence time, which may provide time for extracellular enzymes to decompose high molecular mass fraction. Because the water flow is very low and the residence time is greater during summer, it can be expected that the absolute degradation rate of DOM will be higher. Thus, a long residence time allows DOC to be recycled and released as CO₂ within the mire (Bengtson & Bengtsson, 2007); with high flow, the DOC can be transferred into the aquatic system, where its fate will depend on the ability of the local microorganisms to enzymatically consume organic carbon. Moreover, the differences in residence time can also lead to different proportions of the size fractions at different depths. Pokrovsky et al. (2005) found that the peat soil solutions collected from 10-40 cm depths in Russia during September demonstrated a higher proportion of a truly dissolved fraction (more than 50 % of the bulk fraction) compared to the current study. This difference most likely occurred because of the longer decomposition and residence period.

The third truly dissolved organic carbon source is the “dieback” of microorganisms due to nutrient deficiency (Marschner & Bredow, 2002). Increasing temperatures and low nutrient availability can lead to the starvation and dieback of microorganisms, which may be the source of easily degradable carbon compounds (Marschner & Bredow, 2002). This route might also have increased the truly dissolved fraction’s proportion during the extremely hot summer of 2010. This assumption is supported by the nutrient analyses during the summer of 2010 (see Chapter 5, section 5.4.3). In particular, the lower concentrations of nitrogen and phosphorous could have led to a stronger starvation effect at the bog site than in the fen and lagg zones.

The final two potential processes are driven by environmental conditions that may be especially pronounced in open, northern wetlands. The fourth route of truly dissolved organic carbon production is caused by photodegradation, which leads to a breakup of larger to smaller DOM compounds (Bertilsson & Tranvik, 2000; Ma & Green, 2004), thus contributing to the truly dissolved fraction proportion during the summer period. In the current study, a higher proportion of truly dissolved fraction was observed during summer, when the highest photodegradation was likely. The fifth route includes truly dissolved organic carbon production through freeze-thaw cycles during the winter-spring period. Frost increases the DOM content through the

possible physical disruption of the soil (Kalbitz et al., 2000), lysis of the cells of soil microorganisms (Morley et al., 1983; Giesler et al., 2007), and increased fine root mortality (Giesler et al., 2007; Tierney et al., 2001).

In summary, a high truly dissolved fraction proportion during summer may be linked to increased root exudation, photodegradation, decomposition, and the die-back effect. The high values of the truly dissolved DOM fraction may indicate the presence of a significant amount of recalcitrant end-products of decomposition because, according to Kalbitz et al. (2003b), DOM extracted from peats and forest floor layers has a lower proportion of labile DOC content (3-6 %). Therefore, the proportion of the bioavailable truly dissolved fraction should be expected to be much less than the total truly dissolved fraction detected in the current study. It can also be expected that during summer the newly produced labile hydrophilic compounds in the DOM mixture are quickly metabolized and respired because the half-life of the labile DOM can be very short (2-5 days), whereas the half-life of the stable DOM may range from 0.2 to 8.6 years (Kalbitz et al., 2003b). These factors lead to more recalcitrant hydrophobic acids and DOC compounds altered by microbial metabolisms remaining in the soil pore waters, with possible accumulation until and during the fall period.

Based on the seasonal DOM size fraction distribution, it can be suggested that increased vegetation growth, water residence times, high temperatures, and stronger photodegradation lead to a higher proportion of the truly dissolved organic carbon fraction during the summer period. Because of the multiple routes and causes of truly dissolved production, not all truly dissolved compounds should be considered highly biodegradable, as some of them may be the recalcitrant end products of degradation.

For the potential evaluation of DOM conversion to greenhouse gases such as CO₂ and CH₄, it is necessary to conduct incubation experiments with different phylogenetic groups of bacteria, because the utilization rate of DOM and even truly dissolved DOM varies across the phylogenetic groups of bacteria (Cottrell & Kirchman, 2000). The same organic matter can be preferentially decomposed by the microorganism community of one ecosystem over others because of the differences in enzymes produced. It was demonstrated that even ancient terrestrial origin (1000-5000 years old) carbon may be decomposed in the river system in a matter of weeks (Cole et al., 2001). Thus, the incubation experiments with microorganisms from different environments (soils, lakes, rivers, oceans, etc) may provide information concerning the potential outgassing rate of DOM.

The proportion of different fractions can also be used to determine the main contributor to the outflow in landscapes like the studies typical boreal mire complex with diffuse surface flow paths. The proportion of different size fractions in the outflow water during summer and the final weeks of snowmelt were similar to the proportion in the lagg zone. Thus, the lagg zone appears to be an important contributor to the outflow water from the mire complex to the river. Additionally, the similarity of DOM in the outflow during the first week of the snowmelt period compared to the previous season may indicate that during the first phase of snowmelt, the meltwater pushes the old subsurface carbon from the catchment into the river. During the summer period, the decrease in the truly dissolved fraction compared with the high molecular mass fraction of the outflow point and compared with the truly dissolved concentrations in the lagg zone's surface waters could have been caused by the biodegradation of the organic matter during transportation, whereas an increase in the high colloidal fraction may be caused by soil erosion during flow.

The ≤ 1 kDa fraction contribution to the bulk DOM in the Pojeg River is comparable with the results obtained for other rivers, e.g., the Amazon River (Benner & Hedges, 1993) and the Yukon River (Guéguen et al., 2006). The bulk DOC concentration of the Pojeg River is also comparable to that of other boreal rivers (Pokrovsky & Schott 2002; Finlay et al. 2006). The dominant proportion of the colloidal fraction in the bulk of the DOM fraction in the river samples is also comparable to the results for 22 boreal streams reviewed by Pokrovsky et al. (2012). During the snowmelt period, the DOC mean concentrations in the Pojeg River (22 mg L^{-1}) were higher than in another Russian river, Severnaya Dvina (12 mg L^{-1}), whereas the proportion of the colloidal fraction was in the range described by Pokrovsky et al. (2010). The difference in the bulk C_{DOC} can be caused by the used filter size differences, as Pokrovsky et al. (2010) used the filter size $0.22 \text{ }\mu\text{m}$, whereas in the current study, filters with the nominal cut-off size of $0.7 \text{ }\mu\text{m}$ were used. Furthermore, the study by Pokrovsky et al. (2010) presents the results for the period from December to March, while in the current study, results are presented only for April, when a high discharge from the peatlands was observed due to snowmelt.

7.5.2 Stable carbon $\delta^{13}\text{C}$ isotope signature and DOC/DN ratio

Table 7.2 indicates that different plant species and parts of plant species demonstrate various $\delta^{13}\text{C}$ signatures. The stem $\delta^{13}\text{C}$ signatures were generally higher compared to the leaves. Similar observations have been conducted by a number of studies arguing that such differences are caused by post photosynthetic fractionation processes and environmental factors such as light availability, humidity and water availability (Farquhar et al., 1989; Dawson et al., 2002b; Badeck et al., 2005; Bowling et al., 2008). Owing to the dominant vegetation differences, the $\delta^{13}\text{C}$ values of the organic soil carbon content also differed among the various sites (Table 7.9).

Table 7.9 Soil organic carbon $\delta^{13}\text{C}$ values for the first surface soil horizon samples (sampling in July 2010). The standard deviation is calculated based on the laboratory replicate measurements. Data source: Langer, 2012.

Site	$\delta^{13}\text{C}$, ‰	SD, ‰
Forest	-28.68	0.03
Lagg	-29.64	0.19
Fen	-27.80	0.09
Bog	-27.88	0.05

The predominant vegetation was *Sphagnum spp.* in the fen and bog zones, and the bulk fraction of soil organic matter at these sites exhibited enriched ^{13}C values compared with the forest and lagg zones. In contrast to *Sphagnum* species litter, it was reported that vascular plant litter is composed of true lignin, which tends to be depleted in $\delta^{13}\text{C}$ (Kracht & Gleixner 2000; Gogo et al. 2012 and references therein). Accordingly, the observed differences between the forested zones and the peatland areas may reflect a relative enrichment of lignin-derived aromatic compounds with depleted values of $\delta^{13}\text{C}$ in the forested zone. Therefore, slight differences in the $\delta^{13}\text{C}$ of the organic fractions may reflect variable vegetation cover, and sites rich in vascular plant cover may lead to ^{13}C -depleted DOM. Furthermore, a decrease in the $\delta^{13}\text{C}$ values can be expected during decomposition, given the relatively higher proportion of isotopically depleted lignin (Fernandez et al., 2003; Preston et al., 2006). The bulk DOM $\delta^{13}\text{C}$ signature demonstrates that the dominant organic carbon source during snowmelt in the Pojeg River, where the river DOM $\delta^{13}\text{C}$ signature is a function of the source $\delta^{13}\text{C}$ signature, was an allochthonous source from terrestrial C-3 plants.

In contrast to the bulk DOM fractions, the truly dissolved size fractions demonstrated a significant difference in $\delta^{13}\text{C}$ content (Figure 7.5). The same sub-fraction (e.g., ≤ 1 kDa) demonstrated significantly different values for different sub-units in the mire complex. Differences in the $\delta^{13}\text{C}$ signature across a similar range of size fractions (e.g., 1 kDa-0.2 μm) at different sites have also been recorded in other studies (Guo & Santschi, 1996; Wang et al., 2004; Zou et al., 2004). Based on the review by Guo & Santschi (1996), the $\delta^{13}\text{C}$ signature of the colloidal fraction demonstrates an increase from terrestrial/freshwater (e.g., from -23 to -27 ‰ for rivers) to marine environments (from -23 to -21 ‰). The detected differences in isotopic signature can reflect different molecular compositions (Kracht & Gleixner, 2000). For example, in terms of coniferous plants, Gleixner et al. (1993) found that lignin and lipids were depleted in ^{13}C by 1 to 2 ‰ compared with carbohydrates from the same origin. Macko et al. (1990) demonstrated that $\delta^{13}\text{C}$ values vary for different monosaccharides of *Sphagnum*; for instance, glucose has a value of -26.1 ‰, whereas rhamnose has a value of -29.0 ‰. In this study, the bulk fraction's $\delta^{13}\text{C}$ was -27.5 ‰, with this variation potentially explained by the individual mechanisms of biosynthesis of the monosaccharide or its polymer (Macko et al. 1990). Therefore, glucose exhibited an enriched value compared with the bulk value, whereas rhamnose exhibited a depleted value (Macko et al. 1990). Thus, the difference in $\delta^{13}\text{C}$ of ≤ 1 kDa within different sites can be caused by the specific site vegetation individual biosynthesis mechanisms of the monosaccharides.

Seasonal variation in $\delta^{13}\text{C}$ in different size fractions was also detected. The observed strong enrichment of ^{13}C evident in the ≤ 1 kDa fraction during the summer period might reflect the discrimination of ^{13}C isotopes by decomposing microorganisms. Consequently, degradation increases the $\delta^{13}\text{C}$ signature of the remaining carbon, owing to the microbial metabolic preference for lighter isotopes. This is particularly evident during the summer period at the bog site, with the $\delta^{13}\text{C}$ enriched values in ≤ 1 kDa fraction suggesting that the bog acted as an emitter of CO_2 . This assumption can be supported by Schneider et al. (2012) demonstrating that bog sites covered with ombrogenous hummocks and lawns were sources of CO_2 at the same study site.

High temperatures can also lead to $\delta^{13}\text{C}$ enrichment in plant tissue. For instance, in the case of *Sphagnum* species, Skrzypek et al. (2007) showed that a 1 °C

increase in air temperature during the growing season resulted in a -1.6 ‰ decrease in $\delta^{13}\text{C}$. Therefore, the enriched values of the $\delta^{13}\text{C}$ analyses may also indicate that the high temperature and low water table conditions during the summer period increased the decomposition of organic matter, which may contribute to the large CO_2 emissions during the hot season. During fall, the decrease in $\delta^{13}\text{C}$ can be related to the cumulative preferential removal of labile hydrophilic compounds of the DOM fraction, leaving recalcitrant material enriched in lignin-derived carbon compounds with depleted ^{13}C values (Benner et al., 1987). In the study by Badeck et al. (2005), it was demonstrated that lignins have around 3.2 ‰ lower $\delta^{13}\text{C}$ values compared to cellulose.

Additionally, the decreased microbial metabolism reduces the production of ^{13}C -enriched compounds. Due to increased precipitation, discrimination against ^{13}C declines occurs under wet conditions, given that water increases the resistance to carbon dioxide uptake by creating a barrier to CO_2 diffusion (Farquhar et al., 1989). Overall, the interpretation of $\delta^{13}\text{C}$ with respect to decomposition should be performed with caution (Broder et al., 2012), because it can be changed not only by the preferential loss of ^{12}C due to the mineralization of DOM but also by the presence of different molecular compounds (Kracht & Gleixner, 2000), vegetation (Hornibrook et al., 2000), moisture (Farquhar et al., 1989; Loisel et al., 2010) and climatic factors (Jedrysek & Skrzypek, 2005; Skrzypek et al., 2007). In the current study, the $\delta^{13}\text{C}$ content can be used as a tracer of the hydroflow paths, demonstrating that the signatures revealed in the outflow water were closely related to the lagg zone, which, in turn, demonstrates the importance of the lagg zone in organic matter transport. The presence of recalcitrant end products in the truly dissolved fraction can be supported by the DOC/DN ratio being the lowest in this fraction (Table 7.6).

7.5.3 Spectrophotometric absorbance measurements

The spectrophotometric absorbance measurements support the assumption that the ≤ 1 kDa and ≤ 10 kDa fractions had accumulated recalcitrant end products or were produced through the physical degradation of high molecular size fractions during the frost-thaw cycles. As observed in Figure 7.7, both kDa fractions exhibit values below 5, which is within the range for mature humic acids (Thurman, 1985). Accordingly, these fractions were likely to have been mostly composed of mature humic acids. Additionally, SUVA_{254} , which is a proxy of aromaticity, increased over the snowmelt

period in the truly dissolved fraction, which could indicate that the consumption of easily bioavailable low molecular size organic carbon was higher than its production. Furthermore, it can be also expected that A_{465}/A_{665} ratios may not produce valid results for the organic matter fractions with high quantity of low colored organic matter. Consequently, the sole reliance on ratio values without further additional structural DOM analyses may lead to a misrepresentation of the proportion of the low molecular organic carbon fraction.

7.5.4 Inorganic species speciation in different size fractions

The characterization of organo-mineral colloids is important, given that they likely control the transport of many elements (Pokrovsky et al., 2005). However, the ultrafiltration behavior of different chemical species is remains under investigation (e.g. Guo & Santschi, 2007; Pokrovsky et al., 2010). In the current study, the silica presence in the dissolved form is comparable with other studies and indicates the absence of small-sized clays, phytoliths or silica-rich organic debris (Pokrovsky et al., 2005; Pokrovsky et al. 2006; Pokrovsky et al. 2011). A dominating presence of silica presence in the truly dissolved fraction can be explained by the ability of acidic, anoxic, and organic-rich environments to rapidly dissolve quartz and aluminosilicates (Bennett et al., 1991). The predominant Fe presence the colloidal fraction is comparable with that of other studies; for instance, Guo & Santschi (2006) stated that 70-100 % of Fe was found in the colloidal fraction. The Pearson correlation (Table 7.8) shows that only C_{Fe} demonstrated a good positive correlation with the organic carbon concentration in all fractions. The positive correlation between the iron and carbon contents in the ≤ 1 kDa fraction may indicate that the low molecular size fractions have active zones for binding with Fe. Therefore, considering all the elements in low molecular size fractions to be in the truly dissolved or free form can be misleading. In contrast to iron, none of the other elements in the ≤ 1 kDa fraction show a positive correlation with carbon content, and thus it can be assumed that they are present in free dissolved forms. A positive correlation between organic carbon content and C_{Mn} , C_{Mg} , C_{Ca} and C_{Fe} may indicate the importance of colloidal DOM in these elements' speciation in mire soils. Variations in the C_{Ca} and C_{Mg} fraction distributions have been observed in previously published studies. In a study by

Pokrovsky and Schott (2002), Ca and Mg elements were sorted into groups where species are present in the form of truly dissolved inorganic species or weak organic complexes. In a study by Pokrovsky et al. (2005), C_{Ca} and C_{Mg} were largely (>50-80 %) present in the form of dissolved inorganic species in a peat soil solution, with some proportion found in small (1-10 kDa) organic complexes. Dupré et al. (1999) showed that ≤ 5 % of Ca^{2+} and Mg^{2+} were bound to organic carbon in wetland waters. By contrast, Hill & Aplin (2001) showed that 15 % of K^+ and 25 % of Ca^{2+} and Mg^{2+} were found in the colloidal fractions, whereas Pokrovsky et al. (2010) detected a higher proportion of colloidal Ca and Mg in an ombrotrophic bog (30-60 %). Relatively high contents of C_{Ca} , C_{Mg} , and C_K in an high molecular size fractions can be caused by ultrafiltration artifacts. Generally, owing to its low complexation potential, K is in a free ionic form and thus exhibits permeation behavior, whereas C_{Ca} and C_{Mg} can be found in the retentate, due to ion rejection or complexation to humic substances (Garrels & Thompson, 1962; Viers et al., 1997; Dupré et al., 1999; Guo et al., 2001; Guo & Santschi, 2007). Ion rejection occurs because the surface of organic colloids is negatively charged in natural waters where the pH ranges from 4 to 8. Therefore, organic colloids may cover the membrane during the ultrafiltration process, which will disturb the charge equilibria (Dupré et al. 1999). This process will lead to the oppositely charged cations binding to the colloid surface to accommodate the modified retentates and the filtrates' charge equilibria (Dupré et al., 1999). The authors suggested that negatively charged sites of humic compounds should be neutralized by complex-forming elements in order to avoid this phenomenon (Dupré et al., 1999). Guo et al. (2001) also demonstrated that increasing permeate contents for Ca and Mg during filtration reflect evidence of the retention of these ions, owing to electrostatic interaction between species and the membrane surface. Therefore, selective retention and artifacts should be considered in terms of characterizing different size fractions by means of ultrafiltration (Guo & Santschi, 1996).

7.6 Conclusions

This study presents the following main conclusions:

- (1) The highest proportion of the truly dissolved fraction was detected at all sites during summer. Based on the seasonal changes in the fraction distribution, it can be suggested that increased vegetation growth and water residence times, high temperatures and stronger photodegradation led to a higher proportion of the truly dissolved organic carbon fraction during the summer period. A generally high colloidal DOM proportion indicates that in case if these pristine peatlands are polluted, the contaminating heavy metals will be bound to the colloidal fraction and subsequently transferred into the aquatic system.
- (2) A significant difference was detected in $\delta^{13}\text{C}$ values for all fractions, with the most enriched $\delta^{13}\text{C}$ values observed in the truly dissolved fraction. The $\delta^{13}\text{C}$ values were the lowest during the summer period and increased during the fall and snowmelt periods. However, interpretation with respect to decomposition based solely on $\delta^{13}\text{C}$ should be performed with caution because the $\delta^{13}\text{C}$ values can vary due to presence of different molecular compounds, vegetation cover and climatic factors. $\delta^{13}\text{C}$ signatures revealed that the outflow waters were hydrochemically closely related to the surface waters of the lagg zone.
- (3) The proportions of different size fractions, $\delta^{13}\text{C}$, DOC/DN ratios and spectrophotometric parameters indicate that the transitional lagg zone is an important contributor and main route for the organic matter transport to the outflow water from the mire complex to the river. This result further suggests that stable isotope measurements with ancillary data such as the DOC/DN ratio and spectrophotometric properties are useful tools for detecting qualitative changes of DOM along the transport from terrestrial to limnic and marine ecosystems.
- (4) Based on the tangential flow filtration results, the studied inorganic elements could be divided into three groups of different ultrafiltration behavior: 1. elements that are not influenced by filtration and are present in the truly dissolved phase (SiO_2); 2. elements that are partially present in all fractions (Ca, Mg, K); and 3. elements that are strongly ($\geq 85\%$) associated with the colloidal fraction (Fe, Zn, Mn). However, for further studies that aim to characterize the distribution of elements in different size fractions, membrane retentions should be studied in more

detail and possible remedies should be experimentally tested, e.g., adjusting pH to establish charge equilibrium for avoiding filtration artifacts.

Further investigation of qualitative properties and the degree of DOM degradation would be useful to better predict the future fate of DOM and pollutants which are preferentially binded to colloidal DOM fraction. Furthermore, incubation studies of DOM derived from the peatlands with different phylogenetic groups of bacteria from lakes, rivers and other adjacent aquatic systems will provide information concerning the mineralization rate, as well as the potential contribution to greenhouse gasses in the atmosphere while the DOM is transported from terrestrial through semi-terrestrial (wetlands) to limnic and marine ecosystems.

7.7 Appendix

Table 7.10 Dissolved organic carbon content of different size fractions for the Ust-Pojeg River samples. Standard deviations presented in brackets are calculated based on the replicate measurements results.

Season	Date	Lagg			Fen			Bog		
		≤0.7 μm	≤10 kDa	≤1 kDa	≤0.7 μm	≤10 kDa	≤1 kDa	≤0.7 μm	≤10 kDa	≤1 kDa
Summer C _{DOC} , mg L ⁻¹	12-Jul-10	46.6 (0.6)	18.0 (1.5)	9.3 (0.3)	34.4 (1.8)	16.5 (2.4)	14.7 (0.7)	22.5 (0.5)	8.4 (0.3)	11.8 (1.2)
	19-Jul-10	50.7 (0.4)	25.3 (3.4)	12.0 (0.7)	35.4 (0.4)	10.6 (1.3)	14.1 (0.9)	29.9 (0.4)	-	12.2 (0.4)
	26-Jul-10	47.3 (0.6)	14.6 (1.0)	6.0 (0.6)	-	-	-	-	-	-
Fall C _{DOC} , mg L ⁻¹	22-Sep-10	54.1 (0.8)	20.9 (5.3)	5.9 (0.5)	36.1 (0.8)	8.7 (0.8)	4.6 (1.5)	28.3 (0.3)	11.1 (0.4)	3.4 (0.2)
	28-Sep-10	51.7 (2.2)	16.1 (0.2)	5.0 (0.2)	33.0 (0.6)	13.5 (0.8)	3.7 (0.3)			
	3-Oct-10	51.0 (0.8)	14.0 (0.7)	4.7 (0.2)	35.7 (0.3)	10.8(1.2)	3.7 (0.7)	28.2 (0.7)	10.3 (0.5)	3.1 (0.3)
Spring C _{DOC} , mg L ⁻¹	7-Apr-11	-	-	-	10.0 (0.1)	6.8(0.2)	3.1 (0.1)	14.8 (1.2)	6.9 (0.1)	1.6 (1.0)
	11-Apr-11	19.2 (0.7)	11.3 (0.1)	4.4 (0.5)	8.7 (0.2)	3.5(0.2)	1.5 (0.3)	8.1(0.1)	2.9 (0.1)	1.5 (0.3)
	18-Apr-11	21.5	5.6 (0.2)	2.5 (0.1)	14.3 (0.2)	8.5(0.2)	1.3 (<0.01)	15.7(2.8)	5.1 (0.2)	1.2 (0.3)
	25-Apr-11	30.7 (0.3)	11.1(0.6)	3.8 (0.1)	19.6 (0.1)	10.5(0.2)	1.7 (0.1)	15.8(0.2)	4.2 (0.1)	0.9 (<0.01)

Table 7.11 Dissolved organic carbon concentrations in different size fractions of the outflow water samples. Standard deviations presented in brackets are calculated based on the replicate measurements results.

Season	Date	≤0.7µm (SD)	≤10 kDa (SD)	≤1 kDa (SD)
Summer C_{DOC} , mg L ⁻¹	12-Jul-10	48.1 (1.5)	9.2 (0.6)	8.1 (1.2)
	19-Jul-10	50.1 (0.9)	11.0 (0.4)	6.9 (0.3)
	26-Jul-10	51.1 (1.3)	10.4 (0.3)	8.5 (1.0)
	3-Aug-10	52.4 (1.0)	11.8 (0.2)	7.7 (0.2)
Spring C_{DOC} , mg L ⁻¹	11-Apr-11	51.1 (0.5)	12.6 (1.6)	5.0 (0.2)
	18-Apr-11	34.6 (0.1)	21.5 (1.4)	2.4 (0.3)
	21-Apr-11	30.8 (4.8)	8.8 (0.1)	2.8 (0.4)
	28-Apr-11	30.9 (0.9)	10.0 (0.1)	4.4 (0.3)

Table 7.12 Dissolved organic carbon content of different size fractions for the Ust-Pojeg River samples. Standard deviations presented in brackets are calculated based on the replicate measurements results.

Season	Date	≤0.7 µm (SD)	≤10 kDa (SD)	≤1 kDa (SD)
Spring C_{DOC} , mg L ⁻¹	21-Apr-11	22.8 (2.8)	7.4 (0.2)	3.7 (0.1)
	25-Apr-11	21.3 (0.4)	16.2 (0.2)	3.0 (<0.01)
	28-Apr-11	20.7 (0.3)	8.4 (0.1)	4.1 (0.3)

Table 7.13 Major ion concentrations in different size fractions at the study site.

	Date	Outflow			Lagg			Fen			Bog			River		
		≤0.7 μm	≤10 kDa	≤1 kDa												
C_K mg L ⁻¹	19-Jul-10	-	0.1	0.1	0.5	0.2	0.1	1.2	0.7	0.6	1.5	-	0.5	-	-	-
	26-Jul-10	0.3	0.1	0.1	0.5	0.2	0.3	-	-	-	-	-	-	-	-	-
	22-Sep-10	-	-	-	0.6	0.4	0.3	2.1	1.3	1.1	3.6	2.2	1.1	-	-	-
	3-Oct-10	-	-	-	0.4	0.3	0.3	3.9	2.7	1.2	2.0	1.1	0.5	-	-	-
	28-Apr-11	1.0	0.6	0.4	0.5	0.2	0.2	2.1	1.3	0.7	-	-	-	0.9	0.7	0.6
C_{Ca} mg L ⁻¹	19-Jul-10	-	1.2	0.5	8.1	3.0	1.7	3.0	1.2	1.0	0.3	-	n/d	-	-	-
	26-Jul-10	5.0	1.1	0.9	8.0	3.1	2.2	-	-	-	-	-	-	-	-	-
	22-Sep-10	-	-	-	8.4	3.1	1.4	3.6	1.5	0.4	0.8	-	n/d	-	-	-
	3-Oct-10	-	-	-	7.9	3.5	1.4	2.5	0.5	0.1	0.3	0.1	n/d	-	-	-
	28-Apr-11	2.3	0.8	0.2	7.8	2.6	1.6	2.9	0.8	0.1	-	-	-	7.5	4.9	3.1
C_{Mg} mg L ⁻¹	19-Jul-10	-	0.4	0.2	1.5	0.7	0.5	1.0	0.3	0.3	0.1	-	n/d	-	-	-
	26-Jul-10	1.4	0.4	0.3	-	0.9	0.5	-	-	-	-	-	-	-	-	-
	22-Sep-10	-	-	-	1.8	0.8	0.2	1.0	0.4	0.1	0.2	n/d	n/d	-	-	-
	3-Oct-10	-	-	-	1.8	0.9	0.4	0.9	0.2	n/d	0.2	0.1	n/d	-	-	-
	28-Apr-11	0.7	0.3	0.1	1.8	0.8	0.4	0.9	0.3	n/d	-	-	-	2.1	1.5	1.0
C_{Fe} mg L ⁻¹	19-Jul-10	-	0.1	n/d	0.5	0.1	n/d	0.5	0.1	0.1	0.1	-	n/d	-	-	-
	26-Jul-10	1.3	0.2	0.1	0.7	0.1	n/d	-	-	-	-	-	-	-	-	-
	22-Sep-10	-	-	-	0.3	0.0	n/d	0.5	0.1	n/d	0.1	n/d	n/d	-	-	-
	3-Oct-10	1.7	-	-	0.2	0.1	n/d	0.4	n/d	n/d	0.1	n/d	n/d	-	-	-
	28-Apr-11	0.3	n/d	n/d	0.3	0.1	n/d	0.4	0.1	n/d	-	-	-	0.3	n/d	n/d

* “-” stands if no sample was available for analyses, whereas n/d stands in case if measured value was under the analytical detection limit.

8 Synthesis of major findings and recommendations for further studies

This thesis contributes to the present gap in the literature and limited data available on small-scale spatial variability and seasonal dynamics of dissolved organic matter (DOM) in surface and soil pore waters in the mire-forest landscapes in the Komi Republic of Northwest-Russia. The following section describes some of the key findings and notes important follow-on questions based on the results.

The study focused on the following questions:

1. How do the temporal and spatial dynamics of DOM vary in a boreal mire complex in northwest Russia?

The DOC concentrations of surface and pore waters vary seasonally, increasing during the summer and reaching a maximum during the fall, before subsequently decreasing again during the winter and early spring (Chapter 5-7). The DOC content ranged from 19-74 mg L⁻¹ during fall (Chapter 6), which is higher than the range of the values described for other northern peatlands. The current study also demonstrates that the lagg, bog and fen zones that typically occur within a mire complex (Chapter 5-7) represent distinctly different hydrological and biogeochemical units within single mire. Furthermore, the results also highlight that changes in hydrochemical gradients are closely related to vegetation and hydrological changes, which will be important for future climate models to take into account. The lowest DOC content was observed within the bog, whereas intermediate concentrations were detected in the fen zone. The transitional lagg zone, which is poorly characterized in the literature, demonstrated the highest DOC concentration. Further investigation of the carbon cycle in the boreal region is important because this region has a stronger greenhouse gases global warming potential compared with the soils in the tropical and temperate regions (Jungkunst & Fiedler, 2007). In particular, additional investigation of the heterogeneous sites is necessary to improve the understanding of the effects of boreal peatlands on the biogeochemistry of fluvial systems, and especially the fluxes of carbon, nutrients, and heavy metals. In a follow-on study, sampling will be

necessary during all seasons to capture the spatial and temporal variation of DOM variation across high-resolution transects. The collection and frequency of these samples should be adapted to the hydrological conditions, with more samples during high flow (hourly, daily) and fewer during baseflow (weekly, biweekly). Samples from the mire should be collected from undisturbed sites to avoid interference from disturbances caused by trampling.

Given that the heterogeneous pattern for greenhouse gas emissions has also previously been demonstrated (Schneider et al., 2012), it is important to investigate greenhouse gas emissions intensity in connection with changes in DOM. Qualitative and quantitative characterization of DOM, serving as a substrate for both CH₄ and CO₂, can subsequently be used as a predictor for these emissions.

It is also recommended that for regional assessment and upscaling, at least three (lagg, fen and bog) areas should be spatially distinguished. This allows assessing the dynamics of DOM in surface and pore waters of mire soils, as well as the biogeochemical processes that rely on them. In particular, lagg zones should be delimited by remote sensing and studied in greater detail in the future, given that they can lead to high CO₂ and CH₄ emissions owing to the nutrient supply from the mineral soil and high organic carbon content intake from the vegetation could lead to higher emissions compared with the other parts of the peatland. From this perspective, lagg zones may act similarly to the wet forested zones in terms of being strong CH₄ producers (Fiedler et al., 2005; Christiansen et al., 2010; Grunwald et al., 2012).

2. Is there a structural difference in DOM content among different ecohydrological sub-units?

The study demonstrates that the relative proportion of the two pools (truly dissolved and colloidal) of different size fractions of DOM differs within river, mire (bog, fen and lagg) and outflow waters (Chapter 7). The highest proportion of the truly dissolved organic carbon fraction was detected at all sites during summer, thus resulting from increased vegetation growth and water residence times, high temperatures and stronger photodegradation. A generally high colloidal DOM proportion indicates that in the case if these pristine peatlands would be polluted, the contaminating heavy metals would be bound to the colloidal fraction and

subsequently transferred into the aquatic system. The negative environmental impact is important to note.

A significant difference was detected in $\delta^{13}\text{C}$ values for all fractions, with the most enriched $\delta^{13}\text{C}$ values observed in the truly dissolved fraction. The $\delta^{13}\text{C}$ values were the lowest during the summer period and increased during the fall and snowmelt periods. However, interpretation with respect to decomposition based solely on $\delta^{13}\text{C}$ should be performed with caution, because the $\delta^{13}\text{C}$ values can vary owing to the presence of different molecular compounds, vegetation cover and climatic factors. Furthermore, $\delta^{13}\text{C}$ can also be used as a tracer for detecting organic matter transport.

Further investigation of qualitative properties and the degree of DOM degradation would be useful to better predict the processes affecting DOM and pollutants that preferentially bind to colloidal DOM fraction. The characterization of DOM is particularly important, because the conventional perception that terrestrial organic matter is recalcitrant and contributes little to the aquatic metabolism was proven wrong recently (Battin et al., 2008). Furthermore, incubation studies of DOM derived from the peatlands with different phylogenetic groups of bacteria from lakes, rivers and other adjacent aquatic systems will provide information concerning the mineralization rate, as well as the potential contribution to greenhouse gases in the atmosphere, while the DOM is transported from terrestrial through semi-terrestrial (wetlands) to limnic and finally marine ecosystems.

3. How does the ion speciation into different size fractions of DOM vary between different size fractions?

Based on the tangential flow filtration results, the studied inorganic elements could be divided into three groups of different ultrafiltration behavior: 1. elements that are not influenced by filtration and are present in the truly dissolved phase (SiO_2); 2. elements that are partially present in all fractions (Ca, Mg, K); and 3. elements that are strongly ($\geq 85\%$) associated with the colloidal fraction (Fe, Zn, Mn) (Chapter 7). However, membrane retentions should be studied in greater detail in further studies that aim to characterize the distribution of elements in different size fractions, while possible remedies should be experimentally tested, e.g. adjusting pH to establish charge equilibrium for avoiding filtration artifacts. To predict the potential transport

of colloidal associated pollutants (metals and pesticides) to the ocean, the amount of colloidal OM must be determined.

4. How much loss of DOC from a Northwest Russian boreal mire-forest-river landscape occurred during the snowmelt period, and which sub-units contribute most to the DOC content in the outflow stream?

In the current study, 1.7 g C m^{-2} in the form of the DOC was transferred in the 74 mm of runoff from the catchment into the river during the snowmelt period (Chapter 6). The bog, fen and lagg sites thaw at different times owing to differences in exposure to the sunlight, vegetation cover and soil structures, leading to variation in the inputs and relative contribution of variable sub-units to outflow DOC content change over a short period of time. During the first week of the snowmelt, the old carbon have discharged after being conserved from the previous year, while during later stages the fen site and the surface layer of the lagg site weres the main contributor to the carbon flux. After the snowmelt period the lagg zone was the main contributor to the outflow DOM (Chapter 5).

The transition zones between peatlands and the surrounding mineral soils (lagg zones) appear to be of major importance not only as a hotspot within the mire and act as a major CO_2 and CH_4 emitter, but it also regulates the export of matter from boreal mire-forest landscapes into the fluvial system during all seasons. Accordingly, the lagg zone is the mire zone that determines the quantity and quality of organic matter exported from boreal mire-forest landscapes to the limnic systems (lakes and rivers). The lagg zone topography should be determined, given that it may reflect the most important regulatory factor in the variation of DOM fluxes among catchments. After thorough observations, it is important to integrate the results into process-based models to present the temporal and spatial DOM dynamics.

Furthermore, it was estimated that the terrestrial system transforms almost 2 Pg of organic carbon into the aquatic systems. However, DOM exported from the terrestrial systems and carbon dioxide outgassing from freshwater ecosystems are currently underestimated, which leads to the errors in the carbon budget estimation (Worrall et al., 2007; Battin et al., 2008; Lauerwald et al., 2012). Consequently, total exports of DOC from the terrestrial system into streams should be counted to reduce the error in the estimates, in order to assess additional in-stream/in-river DOC losses.

DOM discharged from the terrestrial system should not only be evaluated for the carbon content but also for its potential effect on biochemical processes in the aquatic systems, such as the solubility, transport and toxicity of heavy metals and organic pollutants, light attenuation, the acidification of aquatic systems and ecosystem nutrient availability.

5. Which methods produce rapid and accurate DOC estimates in remote field conditions?

Finally, this thesis demonstrates that it is possible to conduct rapid (< 1 minute) and accurate measurements in remote locations by means of a portable high-resolution UV-visible light spectrophotometer (Chapter 2). Furthermore, it is also demonstrated that studies using absorbance values as a proxy for DOC-content determination should include more than one wavelength in their absorbance-concentration models. Moreover, the study shows that if different methods are employed for DOC content determination during long time series then results from different methods should be inter-calibrated, given that variations in the instrument's performance could be misinterpreted as a change in the environmental conditions. It is also suggested to use absorbance values as proxies for DOC concentrations, with the necessity of creating site-specific calibration models that include more than one absorbance value at different wavelengths, in order to achieve the optimal explanatory power and increase the accuracy of the proxy-based DOC estimates.

In order to predict how peatlands will respond to climate change, an integrated approach to the process-level understanding of carbon cycles, especially DOM studies, should be included in the total carbon budget estimations. Accordingly, this will improve our understanding of important reservoirs of terrestrial organic carbon in remote boreal mires and better anticipate potential responses to climate change and its influence on aquatic systems.

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A Author's contributions

The author designed the interdisciplinary studies together with Professor Dr. Lars Kutzbach, Professor Dr. Jens Hartmann, Dr. Benjamin Runkle and Dr. Alejandro Spitz. Author reviewed the relevant literature, collected most of the samples, and performed all laboratory and data analyses as well as data interpretation. Drafts were commented by Professor Dr. Lars Kutzbach (all chapters), Professor Dr. Jens Hartmann (chapter 5), Dr. Benjamin Runkle (all chapters). All additional information concerning the guidelines, mentoring, assistance and help during this PhD study period is presented in the acknowledgements sections. Submitting the chapters to peer-reviewed journals after additional contributions of the co-authors is planned.

Ich versichere an Eides statt, dass ich bisher weder an der Universität Hamburg noch an einer anderen Universität einen Versuch zur Promotion unternommen habe.

Weiterhin erkläre ich an Eides statt, dass ich die vorliegende Dissertationsschrift selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Hamburg, den 12 May 2013

Armine Avagyan