Dissolved organic matter across terrestrial and aquatic systems

sources, chemistry and microbial processing

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Abstract

The movement of DOM from terrestrial to aquatic systems is a globally significant flux affecting both carbon sequestration and CO_2 emissions. Here, DOM dynamics were investigated in terrestrial and aquatic systems within the context of this carbon flux. The overall aim was to investigate the source and chemistry of DOM and determine how chemistry is affected by microbial processing of DOM.

In the boreal forest, understory vegetation produced more than 80 % with the species *V. myrtillus* contributing more than 50 % of litter derived DOM at the forest stand level. Litter reactivity was linked to greater chemical changes in the DOM produced at different decay stages. High reactive species (*V. myrtillus*, birch, alder) initially produced DOM with a higher lability rich in oxidized phenolic compounds, indicating lignin degradation of the source litter. As the DOM was microbially processed the similarity between litter species increased as oxygenated phenolic compounds from high reactive litter leachates were degraded and stable aliphatic secondary microbial compounds created.

Of the DOM extracted from podzols roughly a third consisted of aged (1000 yr) labile carbon as indicated by depleted ^{14}C concentrations in Keeling plot intercepts. This fraction cannot be readily detected by bulk radiocarbon measurements without further incubation of the DOM. As such, the mobilization of aged carbon might have gone on undetected. This has important implications for *e.g.* predicting the future carbon balance of the boreal forest.

Severe drought resulted in strongly decreased CDOM concentrations of lakes as a result of hydrological disconnection. This effect was more pronounced in large lakes. During normal conditions, temperature was a positive driver of CDOM in lakes. Drought systematically weakened the regulation of CDOM by the surrounding area. Furthermore, microbial processing of DOM in lakes with little terrestrial influence show that CDOM is systematically microbially produced while at the same time DOM is degraded. The strength of CDOM production is dependent on CDOM concentrations in these lakes.

Combined these results highlight that future DOM regulation might change unexpectedly as temperatures rise, drought becomes more prevalent, understory vegetation composition changes and precipitation and runoff patterns will become more variable.

Key words

dissolved organic matter, carbon, leaching, decay, chemistry, terrestrial, aquatic

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Dissolved organic matter dynamics across terrestrial and aquatic systems

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A doctoral thesis at a university in Sweden is produced either as a monograph or as a collection of papers. In the latter case, the introductory part constitutes the formal thesis, which summarized the accompanying papers already published or manuscripts at various stages (in press, submitted or in preparation).

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MADE IN SWEDEN

Tiger got to hunt, bird got to fly;
Man got to sit and wonder 'why why why?'
Tiger got to sleep, bird got to land;
Man got to tell himself he understand.

Kurt Vonnegut, Cat's Cradle

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Contributions

I GH designed the study together with supervisors. GH performed the research, analysed the data and led the writing of the manuscript.

II GH designed the study together with supervisors. GH performed the research, analysed the data and led the writing of the manuscript.

III GH designed the study together with supervisors. GH performed the research, analysed the data and led the writing of the manuscript.

IV GH carried out most of the statistical analysis and was involved with the writing of the manuscript.

V GH was involved with data analysis and contributed to the writing of the manuscript

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Popular summary in English

Forests and lakes are connected through the movement of water. Following rainfall, water moves through litter and soils to streams, rivers and lakes. Similar to how water turns brown in a coffee filter, rainwater picks up materials from organic particles along its path towards inland waters. These particles dissolve in water through a process called leaching, creating dissolved organic matter (DOM). The movement of DOM from land to water fulfils key processes in the global carbon cycle, contributing both to atmospheric emissions of greenhouse gases and to so-called carbon sequestration, which means that carbon is stored stable forms and thereby prevented to enter the atmosphere through CO_2 and CH_4 emissions.

In this thesis DOM dynamics were investigated in terrestrial and aquatic systems within the context of this carbon flux from land to inland waters. The overall aim was to investigate the source and chemistry of DOM and determine how chemistry is affected by microbial activities. Studies were done on terrestrial and aquatic systems at different scales in order to provide a broad representation of DOM dynamics in northern boreal and subarctic regions.

The first part of the project was carried out in the softwood forest surrounding river Krycklan, northern Sweden. It was found that the understory ground vegetation beneath the tree canopy produced more than 80 % of litter derived DOM. The blueberry species (*V. myrtillus*) alone was responsible for more than half of the fresh litter leaching. Higher rates of litter decay and DOM leaching were linked to greater chemical changes over time in the DOM that was released from the decaying litter. High reactive species that decayed fast (*V. myrtillus*, birch and alder) initially produced DOM with a high biodegradability, rich in phenolic compounds with high oxygen content. These compounds are produced during breakdown of the generally hard-to-degrade litter tissue lignin, indicating that lignin degradation occurs at great rates in high reactive litter. The difference in the chemistry of leachates decreased as litter or DOM was decomposed by microbes. Over time, the oxygenated phenolic compounds from high reactive litter were further broken down by microbes into new stable non-phenolic compounds. These stable compounds are found in soil and associated with long term preservation of carbon. In this regard, the results show that the composition of the understory (high vs. low-reactive species) may play a bigger role in long term soil carbon sequestration than previously thought. As a result of climate change, the understory might see a decrease in moss and increase in high-reactive shrubs such as *V. myrtillus*. The carbon sequestration of boreal soils and long term DOM dynamics might thus change as litter DOM production of the understory increases.

Of the DOM extracted from podzols – the dominating soil type in the boreal forest – roughly a third consisted of aged (1000 yr) biodegradable carbon. This fraction cannot be readily detected by conventional radiocarbon measurements because it is mixed with

modern more radioactive matter that hides the signal of the aged carbon. As such, the mobilization of aged carbon might have gone on undetected. The loss of old organic carbon from soils can be seen as equivalent to the burning of fossil fuels, which are similarly composed of aged (albeit much older) carbon. While our results don't imply an increased loss of aged soil carbon, other studies have shown that with increasing temperatures and human influence, more aged carbon can be lost from soils in a large variety of ecosystems. The fact that it is so hard to measure might mean that the loss of aged carbon in general, and the increased loss due to human influence, might have been underestimated.

In the second part of the project, the presence and fate of DOM in lakes across northern Sweden were studied. The fraction of the DOM that stains the water brown is called coloured DOM (CDOM). Concentrations of CDOM in widely distributed lakes could be predicted to a high degree by temperature, land cover and variations in land forms during a wet year. However, drought systematically made the CDOM more difficult to predict from information about the surrounding land area. Severe drought resulted in strongly decreased CDOM concentrations of lakes as land got disconnected from lakes with decreasing water flow. This effect was the strongest in large lakes. Thus, drought not only changes the lake CDOM concentrations as such, but it also changes the way that the landscape controls variations in CDOM. Furthermore, a separate study showed that CDOM in lakes is not only received though incoming water from land, but is also systematically microbially produced within the lakes. This internal production, however, only appears to be important in clear water lakes that don't already receive large amounts of CDOM from land. This means that the origin of CDOM in lakes can shift fast from internally produced to externally imported if the flux of DOM from land to water increases. As more variability in rainfall, increased droughts and higher temperatures are expected in the future, both the terrestrial export and internal dynamics of CDOM in lakes might change unexpectedly.

Combined the results of these studies highlight the complexity of DOM dynamics in terrestrial and aquatic ecosystems. The studies presented here show numerous ways in which DOM dynamics might change in a future of progressively increasing climate change. These changes may cause an intensified DOM cycle, leading to increases in both greenhouse gas emissions and carbon sequestration, at the same time as DOM concentrations in recipient waters can be expected to get more variable.

Populair wetenschappelijke samenvatting in Nederlands

Bossen en meren zijn met elkaar verbonden door de stroming van water. Na regenval beweegt water zich door bladafval en de bodem naar rivieren en meren. Net zoals water bruin wordt wanneer je koffie zet, verkleurt ook het regenwater doordat organisch materiaal wordt meegenomen richting het oppervlakte water. Dit materiaal lost op in water in een process dat 'leaching' wordt genoemd. Dit opgelost organisch materiaal wordt in het engels dissolved organic matter (DOM) genoemd. De verplaatsing van DOM door grond en water is een belangrijke koolstofflux in de wereldwijde koolstofkringloop bepalend voor zowel de koolstofvastlegging als CO_2 emmissies.

In dit proefschrift is de DOM dynamiek van terrestrial en aquatische systemen binnen de context van deze koolstofflux onderzocht. Het algemene doel was om te onderzoeken wat de bron en chemie van DOM is en hoe de chemie wordt veranderd door de microbiele verwerking van DOM. Individuele studies zijn gedaan in terrestrial en aquatische systemen op verschillende niveaus om een brede representatie van DOM dynamiek in de taiga en subarctische regio vast te leggen.

Struikgewas produceerde meer dan 80 % van het bladafval gerelateerde DOM. De blauwe bes plant (*V. myrtillus*) alleen was verantwoordelijk voor meer dan de helft van het bladafval DOM. De reactiviteit van bladafval, dat wil zeggen snel massaverlies en een hoge mate van DOM leaching, was gerelateerd aan een grotere verandering in chemie van het DOM tijdens verschillende fases van de afbraak van bladafval. Reactieve soorten (*V. myrtillus*, berk, els) produceerde in het begin van de blad afbraak DOM met een grotere biologische beschikbaarheid, rijk aan geoxideerde phenolen. Deze phenolen worden geproduceerd als de, in het algemeen hard te verteren, blad weefsel lignine wordt afgebroken. Dit wijst erop dat lignine afbreek in hogere maten plaats vindt in reactief bladafval. De verschillen in chemie tussen reactieve en niet-reactieve soorten nam af naarmate bladafval of DOM microbieel werd afgebroken. Tijdens de DOM afbraak werden de phenolen die vrij kwamen bij reactief bladafval afgebroken, terwijl stabiele aliphatische verbindingen werden geproduceerd. Deze moleculaire verbindingen worden veelal in de bodem gevonden en worden geascocieerd met de vastleggen van koolstof in de grond. Deze resultaten laten dus zien dat de compositie van grondgewassen een grote rol in de koolstof beslaglegging van de grond kan hebben. Door klimaatverandering kan de compositie veranderen van mos naar struikgewas, waaronder *V. myrtillus*. Hierdoor kan de koolstof vastlegging van de grond dus veranderen doordat de DOM productie van bladafval van het struikgewas toeneemt.

Het DOM dat uit de bodem kan worden gehaald bestaat voor een derde uit oud (1000 jaar) biologisch beschikbaar koolstof. Dit kan niet makkelijk worden vastgesteld door metingen die gebruikelijk worden gedaan in rivieren. Hierdoor kan het zo zijn dat het verlies van oud organisch koolstof van bodems onopgemerkt is verlopen. Dit verlies kan worden

gezien als gelijkwaardig aan het verbranden van fossiele brandstoffen, dat ook bestaat uit oud (welliswaar veel ouder) koolstof. Hoewel onze resultaten er niet op duiden dat er een toename is van het verlies van oud organisch materiaal, zijn er andere studies die hebben aangetoond dat toenemende temperatuur en menselijke verstoringen leiden to een groter verlies van oud koolstof in de bodem van verschillende ecosystemen. Het feit dat het zo moeilijk te meten is, duidt er wellicht op dat het verlies van oud koolstof en de toename hierin mogelijk wordt onderschat.

Het onderdeel van DOM dat de rivieren bruin maakt wordt gekleurd (coloured) DOM (CDOM) genoemd. Onze resultaten laten zien dat concentraties van CDOM in meren normalitair grotendeels kunnen worden voorspeld door temperatuur, hydrologie en de grote van het meer. Tijdens een droogte daalt de CDOM concentration sterk doordat het land niet meer in connectie staat met het water. Dit effect is sterker in grote meren. Droogte zorgt ervoor dat de regulatie van CDOM in meren in mindere maten verklaard kan worden door het omliggende gebied. De microbiele verwerking van DOM in meren met weinig aardse invloed laat zien dat CDOM systematisch geproduceerd wordt door microben terwijl DOM verteerd wordt. Dit proces hangt af van hoevel CDOM er in het water is. Doordat er meer droogte en hogere temperaturen zijn verwacht in de toekomst kan zowel de aardse export en de interne regulatie van CDOM in meren onverwachts veranderen.

Gecombineerd laten de resultaten van deze studies de complexiteit van DOM dynamiek in aardse en aquatische systemen zien. De studies gepresenteerd in dit proefschrift tonen meerdere manieren waarop de DOM dynamiek in de toekomst kan veranderen in een gebied dat is onderheven aan progressief toenemende klimaatverandering.

Foreword

Rationale and thesis structure

Large parts of the inland waters in the northern hemisphere are increasingly under pressure of climate and environmental change. This significantly affects the carbon regulation of aquatic ecosystems. These systems are not isolated, but in close relationship with the terrestrial environment through the export of dissolved organic matter (DOM). In this thesis I take an integrated approach to understanding the DOM regulation of the boreal and subarctic region of Scandinavia through a selection of detailed studies in different landscapes intimately connected by the flow of water.

In **part I**, I look at the terrestrial components in DOM leaching from vegetation and soils. As photosynthesis is the ultimate source of terrestrial DOM, I start with vegetation litter leaching processes (**paper I & II**). The leaching of DOM from litter is known to be an important factor in the carbon sequestration of mineral soils. Although the direct influence of litter on riverine DOM might be small in the boreal region, by affecting carbon sequestration of soils any litter DOM dynamics can have long term effects not only on the carbon balance of the boreal forest, but also the terrestrial export of DOM to headwater streams. In **paper III** the potential release of aged DOM from soils is investigated. At any given time, terrestrial DOM is lost from soils and exported to the aquatic system. The loss of aged DOM indicates that carbon that has been long term preserved is re-introduced into the modern carbon cycle. While increases in DOM export might reflect a general increase in terrestrial carbon and DOM production, the loss of aged DOM can be problematic as it could indicate a positive feedback loop on climate.

In **part II**, the aquatic components of DOM and its regulation by terrestrial and internal processes are discussed. On a larger scale, land cover and climate have an important effect on lake DOM concentrations. During the coming decades, extreme droughts might become more prevalent. Droughts can significantly affect DOM regulations as export of terrestrial DOM is related to the flow of water from land to lakes. As such, **paper IV** explores the effect of drought on the regulation of DOM in lakes.

In sub-arctic lakes an increase in the runoff of terrestrial DOM is expected and as such the lakes might undergo a browning effect in the future. This might change the internal DOM regulations in these lakes, as the production and degradation of certain DOM elements can depend on the amount of terrestrial DOM in the system. In **paper V** the microbial processing of DOM is investigated as related to the DOM concentrations of over 100 sub-arctic lakes.

Taken together, the articles discussed in this thesis illustrate DOM dynamics across terrestrial and aquatic systems in a region prone to progressively increasing climatic change. While the explicit effects of climate change on the processes described here have not been part of this research, results and conclusions carry important information for the future carbon balance of the terrestrial and aquatic systems in these northern regions.

Introduction

Defining Dissolved Organic Matter

Dissolved organic matter (DOM) is an operational term describing a continuum of organic molecules dissolved in solution ranging from simple sugars and amino acids to complex humic acid structures (Kalbitz et al., 2000; Kögel-Knabner, 2002; Kellerman et al., 2014). Defined as organic matter that can pass through a 0.45 - 0.7 µm filter (Kalbitz et al., 2000), DOM is usually quantified as the amount of carbon per liter and as such often used interchangeable with dissolved organic carbon (DOC; the carbon partition of DOM). The molecular size of DOM molecules as measured in weight ranges typically between 100 and 1000 Dalton (Aitkenhead-Peterson et al., 2003; Stubbins et al., 2014). Dissolved organic matter is an important link transferring energy, carbon and nutrients between different ecosystem components: from vegetation to soils (Kalbitz et al., 2000; McDowell, 2003), soils to inland waters (Pace et al., 2004; Kortelainen et al., 2006; Von Wachenfeldt and Tranvik, 2008; Battin et al., 2009; Tranvik et al., 2009; Aufdenkampe et al., 2011) and finally inland waters to oceans (Tranvik and Jansson, 2002; Burd et al., 2016). Fundamentally, DOM is the only organic fraction that is biologically respired, as exclusively carbon in a soluble form can pass the cell membrane (Marschner and Kalbitz, 2003). As such it is both the most mobile and labile form of organic carbon.

DOM in the global carbon cycle

The export of carbon from terrestrial to aquatic systems is a globally significant flux (Cole et al., 2007; Tranvik et al., 2018). With estimates upward of 5.1 Pg of carbon annually (Drake et al., 2018), it might be bigger than the estimated terrestrial carbon sink of 3.1±0.9 Pg per year (Le Quéré et al., 2016). The flux is dominated by DOM, whereas relatively smaller inputs come from chemical weathering and erosion (0.8 Pg) exported as inorganic or particulate organic carbon, although this can vary significantly across different landscapes (Tank et al., 2018). Since its first calculation (1.9 Pg) in 2007 (Cole et al., 2007), the estimate

of terrestrial carbon export has more than doubled as research concerning the terrestrial – aquatic carbon flux has intensified. This can be subscribed to a better coverage of running waters and in specific the inclusion of smaller headwater streams (Raymond et al., 2013), which can make up as much as 90 % of the total river length (Bishop et al., 2008). The increasing trend in the terrestrial carbon estimate highlights both the rapidly increasing understanding, but simultaneously lack of knowledge regarding the processes involved in terrestrial carbon export.

Future research efforts might see a further increase in the estimate of the terrestrial DOM export to inland waters as CO_2 outgassing of smaller streams is still underrepresented and carbon burial rates are underestimated (Drake et al., 2018). This raises the concern that the carbon accumulation rate of terrestrial systems might be overestimated as terrestrial DOM is degraded downstream. As the terrestrial sink is thought to have sequestered roughly a third of anthropogenic CO_2 emissions since the 1960s (Quéré et al., 2014) this may have important implications for our understanding of the global carbon cycle and climate change. For example, because the terrestrial net ecosystem productivity can be calculated as the sum of organic carbon accumulation, export and non-biological degradation minus the import (Lovett et al., 2006), the global estimate of 4.5 Pg yr^{-1} should arguably be increased to 7.3 Pg yr^{-1} to accommodate recent increases in estimates of terrestrial carbon export (Hutyra, 2014; Drake et al., 2018). While this is just one of many published calculations and to some degree arbitrary as the continental net ecosystem productivity (combining terrestrial and inland waters) stays the same (Drake et al., 2018), it is this principle that highlights the importance of the terrestrial – aquatic carbon flux on a global scale.

The browning of inland waters

Over the past decades an increase in DOM has been observed in inland waters across the northern hemisphere, leading to an apparent water browning caused by the increased export of terrestrial carbon to aquatic ecosystems (Hongve et al., 2004; Evans et al., 2005; Monteith et al., 2007; Worrall and Burt, 2007; Kritzberg and Ekström, 2012). Although a moderate amount of DOM can increase primary productivity and fish production as a result of increased carbon and nutrient levels (Finstad et al., 2014; Seekell et al., 2015), at higher concentrations DOM can acidify and color the water brown and deplete oxygen through respiration of DOM to CO_2 and methane (Pace and Prairie, 2007). The browning of inland waters can lead to a decrease in the light penetration depth and reduce the productivity and diversity of the phytoplankton community, thereby decreasing the carbon sequestration and overall food web production in lakes (Jones, 1992; Karlsson et al., 2009). A rapid increase of DOM can cause anoxic conditions and a sharp decrease in fish and macroinvertebrate populations downstream (Brothers et al., 2014; Arzel et al., 2020). Moreover, when DOM rich water is chlorinated in drinking water distribution plants it

can produce carcinogenic by-products (Roulet and Moore, 2006; Lavonen et al., 2013), leading to increased water production costs (Eikebrokk et al., 2003; Lavonen et al., 2013). In addition, on both a small and large scale there exists a strong connection between water brownness and the production and outgassing of the greenhouse gas CO_2 (Lapierre et al., 2013; Brothers et al., 2014). This clearly shows the direct socio-economical and environmental stakes and urgency in understanding the terrestrial export of DOM to inland waters.

Numerous drivers have been proposed for the brownification of inland waters, including land-use change (Kritzberg, 2017), rising temperatures (Lee et al., 2001; Evans et al., 2005; Weyhenmeyer and Karlsson, 2009), greater flow through increased precipitation (Hongve et al., 2004; De Wit et al., 2007; Erlandsson et al., 2008) and a declining atmospheric deposition of sulphate (Evans et al., 2006, 2012; De Wit et al., 2007; Monteith et al., 2007). However, no consensus has been reached on what the most important driver is, and the topic remains heavily debated. Lately, research has moved away from trying to determine a singular cause for inland water brownification and instead accept that the problem is multifaceted. The co-regulation and strength of various drivers may differ per region, acknowledging a more complex and realistic view (Kritzberg et al., 2020).

Aside from the regional browning of surface waters in the northern hemisphere, the global export of terrestrial carbon to inland waters is thought to have increased by roughly 1.0 pG yr^{-1} since pre-industrial times as a result of anthropogenic influence (Regnier et al., 2013). A further increase in the export of terrestrial carbon to aquatic systems is expected in the future as climate and environmental forcing continues (Larsen et al., 2011; De Wit et al., 2016; Finstad et al., 2016; Kritzberg et al., 2020). This increase might further strain the inland waters already under stress from the environmental changes of the last decades. Moreover, as inland waters connect the land with the ocean, the effects will not be limited to freshwater sources. In the Baltic basin, for example, this increase is predicted to reduce phytoplankton and consequently fish production in the north, and increase bottom-water anoxia in the south, leading to decreased cod recruitment and stimulation of cyanobacterial blooms (Andersson et al., 2015). An increase in terrestrial carbon export could be equivalent to a loss of soil carbon, the largest terrestrial carbon pool in the global carbon cycle (Schlesinger and Bernhardt, 2013), as export has largely (0.8 Pg yr^{-1}) been related to soil erosion in the past (Regnier et al., 2013). This might exert a positive feedback loop on climate change, as is seen in *e.g.* the thawing of permafrost soils (Zimov et al., 2006; Schuur et al., 2009; Schuur and Abbott, 2011). Aside from direct CO_2 and methane emissions as a result of thawing (Schuur et al., 2009), DOM from previously frozen soil is exported to inland waters, further contributing to the re-introduction of ancient carbon to the modern carbon cycle (Neff et al., 2006; Guillemette et al., 2017). This DOM is rapidly degraded (Selvam et al., 2017) and CO_2 is emitted to the atmosphere that would have otherwise been preserved for another hundreds if not thousands of years. Research into the sources, chem-

istry and microbial processing of terrestrial DOM is thus highly relevant with regard to the past and future changes in the environment and climate of the northern hemisphere.

DOM in terrestrial systems

Ultimately, the source of all terrestrial DOM is photosynthesis of upland vegetation (McDowell, 2003). Dissolved organic matter in soils is produced as precipitation moves through vegetation and litter, dissolving and conveying parts of the carbon it passes towards the soil. Rainfall falls onto trees and transfers DOM from the leaves, through gaps in the canopy as through fall or along the stem as stemflow (Johnson and Lehmann, 2006; Van Stan and Stubbins, 2018). The magnitude of stemflow is highly variable but can be considerable and deliver DOM and nutrients directly to the rhizosphere as water follows the preferential flow path along the roots (Johnson and Lehmann, 2006). Although both fluxes can be substantial (Moore, 2003; Van Stan and Stubbins, 2018), the most important source of carbon to the forest soil is considered to be litter (Kalbitz et al., 2000). Litterfall in the boreal forest can encompass 50 % to 80 % of the aboveground net primary production (Chen et al., 2017) and as litter is decomposed 7 % to 40 % of the litter carbon can be lost as DOM (Soong et al., 2015).

The quantity and quality of DOM leached during litter decay is dependent on the litter species (Nykvist, 1963; Cleveland et al., 2004; Don and Kalbitz, 2005; Wymore et al., 2015). There is a positive relationship between initial litter decomposition rates and DOM leaching (Osono and Takeda, 2005) and both are related to the chemistry and toughness of the litter (Reh et al., 1990; Pérez-Harguindeguy et al., 2000; Lorenz et al., 2004). As litter decomposes, leachable material is depleted first (Soong et al., 2015) and the potential for DOM leaching decreases exponentially (Don and Kalbitz, 2005). The DOM leached from litter is highly labile but becomse less reactive as litter decomposition advances (Don and Kalbitz, 2005). Most studies on litter leachates have focused on differences between canopy species, while understory species have largely been ignored. In the boreal forest, the net primary production of understory species can be up to half that of the canopy (Snyder, 1961; Kolari et al., 2006; Benscoter and Vitt, 2007). However, while the canopy consists largely of stable biomass such as tree-stems, the carbon and nutrients of the understory are rapidly recycled (Snyder, 1961; Hart and Chen, 2006). Since little is known about understory litter leaching, the role of the understory as a primary DOM source is currently unknown.

Following leaching, DOM infiltrates the soil where it plays an important role in the formation of stable soil organic matter (SOM)(Kaiser and Guggenberger, 2000; Kalbitz et al., 2000). As DOM passes through the soil, it is respired, taken up and altered by microbes or stabilized through organo-mineral interactions (Moore, 2003; Kaiser and Kalbitz, 2012; Shen et al., 2015). Hydrophobic molecules are temporarily stabilized through a process

called sorption in which DOM becomes attached to mineral particles through electrostatic interactions (Kalbitz et al., 2005; Kleber et al., 2007). Although hydrophilic molecules are associated with labile carbon that is quickly taken up by microbes, both can lead to the formation of persistent SOM (Grandy and Neff, 2008; Prescott, 2010; Cotrufo et al., 2015). The combined result of these two processes can lead to a sharp reduction in litter leached DOM in the first few centimeters of the soil (Fröberg et al., 2007a,b; Müller et al., 2009; Hagedorn et al., 2015) and a change in chemistry so that the DOM in soils bear little resemblance to litter leachates (Strid et al., 2016; Thieme et al., 2019).

Sorption is generally associated with subsoil horizons, but it occurs throughout the soil profile. Dissolved organic matter cycles downwards through the soil as DOM is temporarily immobilized, altered through microbial processing and re-released only to be potentially immobilized again at lower depth (Kaiser and Kalbitz, 2012). Sorption significantly decreases the decay rates of DOM and can contribute to its stabilization (Kalbitz et al., 2005). However, the sorption complex can get saturated and desorption of DOM can occur at any time (Guggenberger and Kaiser, 2003; Kaiser and Kalbitz, 2012). The strength of the interaction between DOM and mineral particles can differ and is dependent on the sorption surface and mineral complexes (Kaiser and Guggenberger, 2000; Kleber et al., 2007). As a result, the quantity of sorbed DOM in a soil is dependent on soil structure and chemistry(Grandy and Neff, 2008).

Labile carbon is either respired or used by microbes to build biomass. Although it was once thought that the chemical preservation of recalcitrant carbon was the main process in which long term carbon sequestration was achieved, it is now realized that labile carbon may play a bigger role in the preservation process (Schmidt et al., 2011; Cotrufo et al., 2013; Lehmann and Kleber, 2015). One mechanism in which labile carbon leads to the preservation of SOM is through microbial recycling: carbon is taken up and recycled in a microbial loop for extended periods of time (Ahrens et al., 2015). Microbial products and necromass have been shown to form stable SOM (Miltner et al., 2012; Kallenbach et al., 2016). Another mechanism that has received increased attention during the last decades is the physical microbial access to carbon (Six et al., 2002). Without access, carbon will not be biologically degraded and as such intrinsic chemical recalcitrance is less important for the preservation of aged DOM in soils (Ekschmitt et al., 2005; Lützow et al., 2006; Schmidt et al., 2011; Lehmann and Kleber, 2015). Spots where physical access is denied (*e.g.* micropores) have been shown to consist of labile (Marschner and Kalbitz, 2003) and microbial carbon (Cotrufo et al., 2013). Therefore, labile DOM could be a driving force behind long term carbon preservation in soils.

The regulation of terrestrial DOM export

While the flux of DOM from forest vegetation to soils is large compared to other landscape fluxes, the export of DOM from mineral soils to inland waters can be rather low as a result of low runoff and high rates of sorption in the subsoil (Moore, 2003). In the headwater streams of the boreal forest, the chemical similarities between instream and riparian soil DOM suggest that most of the DOM originates in the rather small wetland zone next to the rivers (Ledesma et al., 2018). According to some studies there is little reason to expect a significant lateral flow of DOM from upland soils to the riparian zone (Strohmeier et al., 2013). However, this question does not seem to be completely answered. For example, the riparian zone is known to sustain a larger pool of aluminum than upland soils, while the lateral flux is lower than the flux from riparian to inland water (Cory et al., 2007). It is postulated that episodic transport might explain this discrepancy. As the transfer of metals is related to the transfer of DOM (Wu et al., 2012) this suggests that the same might be true for lateral DOM fluxes. Alternatively, it might be that the fluxes have recently changed, leading to an increased flux of aluminum to inland waters resulting eventually in the depletion of riparian concentrations (Cory et al., 2007).

Export of terrestrial DOM is governed by hydrological connectivity, which varies greatly between the seasons (Laudon et al., 2011). In most forested catchments water moves through subsoils with low organic content during low flow, resulting in low carbon export. Increased discharge results in higher water tables and forces water through high organic topsoil causing higher rates of carbon export (Barnes et al., 2018). High discharge events, such as storms and snowmelt, can explain up to 80 % of the annual DOM export in forested landscapes (Hinton et al., 1997; Laudon et al., 2004; Raymond and Saiers, 2010; Wilson et al., 2013). In temperate forests the increase in DOM with discharge is steeper during autumn, indicating the release of upland soil and particularly litter DOM in the rivers (Wilson et al., 2013). This might not be directly translatable to boreal catchments because of the differences in vegetation and hydrology. In catchments where peatlands dominate, high discharge can result in a dilution of riverine DOM concentrations, especially in winter when ice layers form on top of the peat (Laudon et al., 2004). No such dilution can be seen in forested boreal catchments, indicating that lateral transport of DOM from upland soils through the riparian zone might exist to some degree.

On a larger scale land cover or use and climate play a large role in determining the potential export of terrestrial DOM (Kothawala et al., 2015; Laudon and Sponseller, 2018). Wetlands generally see high rates of DOM export as a result of the great hydrological connectivity as well as their high organic soil content (Mattsson et al., 2005; Ågren et al., 2007). In forested areas DOM export is thought to have increased following intensification of forestry (Kritzberg, 2017). Clearcutting of these forests is known to temporarily increase the export of DOM in boreal headwater streams (Nieminen, 2004; Schelker et al., 2012). The DOM

export is generally lower in natural grasslands and agricultural landscapes, although in the latter more nutrients and DIC are exported (Tank et al., 2018; Fovet et al., 2020). Increased temperatures can lead to increased DOM export, as does increased precipitation (De Wit et al., 2007; Larsen et al., 2011). However, increased drought can lower DOM export as a result of decreased runoff and hydrologically disconnected upland areas. Exactly how the combined effect of land cover, climate and other catchment characteristics regulate the DOM of inland waters is currently unknown. Similarly, there is a large knowledge gap on how this regulation is affected by drought.

Over the past decades, the boreal region has seen the fastest increase in temperature of all global forested areas, a trend which is expected to continue (Gauthier et al., 2015). Climate models suggest that the carbon stock of the boreal and arctic might decrease in the future (Kurz et al., 2013; Bradshaw and Warkentin, 2015). With 95 % of the carbon stored in soils (Scharlemann et al., 2014), this has the potential to increase DOM export significantly. In (sub-) arctic environments, the loss of permafrost as an effect of warming can result in the delivery of aged DOM to the aquatic system (Neff et al., 2006). Increased anthropogenic disturbances as a result of forestry, agriculture and urbanization can lead to the mobilization and release of aged carbon from soils to rivers (Butman et al., 2015; Gauthier et al., 2015; King et al., 2018). Once released as DOM, the carbon becomes accessible to microbes, leading to the mineralization of aged organic carbon, which can be seen as equivalent to the burning of fossil fuels (Regnier et al., 2013). However, the potential for aged carbon leaching from mineral soils is currently unknown as research in permafrost thaw has been prioritized.

The fate of DOM in inland waters

Inland waters only occupy approximately 3 % of the global land area (Likens, 2009) but emit roughly the same amount of CO_2 as the annual CO_2 uptake by oceans (Tranvik et al., 2009). The burial of carbon in inland waters exceeds the carbon sequestration through ocean sedimentation (Tranvik et al., 2009). This shows terrestrial DOM is not only transported through inland waters to oceans, but is actively processed along the way (Cole et al., 2007) subjected to respiration, photochemical degradation (Hernes and Benner, 2003; Cory et al., 2014), flocculation and subsequent sedimentation (Von Wachenfeldt and Tranvik, 2008), and microbial uptake (Hernes and Benner, 2003; Cole et al., 2007; Aufdenkampe et al., 2011). Of the 5.1 Pg of annually exported terrestrial carbon, approximately 0.6 Pg is deposited as sediment, 3.9 Pg is returned to the atmosphere as CO_2 and 0.9 Pg is exported to the ocean (Drake et al., 2018). These are highly significant fluxes in light of the global carbon cycle.

The fate of the DOM is co-dependent on its intrinsic chemistry and the external environmental conditions. The intrinsic chemistry is to some degree related to the source of the DOM. Autotrophic DOM consists mainly of low molecular weight molecules that are prone to rapid bio-degradation, while terrestrial DOM consist for a large part of bigger aromatic molecules with a higher recalcitrance to microbial processing (Fellman et al., 2008, 2010; Murphy et al., 2008). Even between terrestrial sources, the chemistry of DOM can be different as *e.g.* forested areas are known to release lower amounts of microbial recalcitrant colored DOM as mires (Fellman et al., 2008; Li et al., 2018). However, the manner in which processes affect DOM must be seen within their environmental context. In a lake without oxygen, microbial processing will be lower even for labile autotrophic DOM. In a river with a high sediment load, interactions between terrestrial aromatic DOM and mineral particles can lead to high rates of sedimentation (Groeneveld et al., 2020). Photochemical degradation of DOM, a process by which mainly aromatic (terrestrial) DOM reacts with sunlight and is partially or completely degraded, is dependent on *e.g.* the lake depth or canopy cover. As such, the DOM regulation of lakes is to a varying degree dependent to the environmental and physical characteristics of the catchment.

The DOM in boreal lakes can consist of up to 90 % of terrestrial DOM (Algesten et al., 2003). In these lakes the terrestrial DOM provides carbon that helps support the food web through heterotrophic degradation (Karlsson et al., 2012). Changes in the source and quality of the DOM can affect the microbial community and thus the DOM processing in the lake (Karlsson et al., 2012; Berggren and Giorgio, 2015; Evans and Thomas, 2016). In sub-arctic mountainous lakes the terrestrial DOM concentrations are generally very low and thus internal DOM regulations are more important than external ones (Forsström et al., 2013). However, increased export and browning of lakes is expected in the future (Karlsson et al., 2005; Wauthy et al., 2018), possibly shifting the microbial regulation of DOM in these lakes. For example, increased terrestrial DOM export can lead to a shift from a system with low DOM concentrations with high productivity and carbon cycling to a system with high DOM concentrations and low carbon cycling (Guillemette and del Giorgio, 2011). As a result of this shift, the ability of the microbial and photosynthetic community to degrade and supply DOM changes, as well as the chemistry of the DOM. However, research in sub-arctic lakes is limited and thus it is unknown how the microbial degradation of DOM is dependent on increased browning in these ecosystems.

Aims of the thesis

The overarching purpose of this thesis is to investigate dissolved organic matter (DOM) dynamics in terrestrial and aquatic ecosystems within the context of the global carbon cycle and in specific the carbon flux from land to inland waters. Although DOM has been intensively studied both in aquatic and terrestrial systems, key knowledge gaps remain as to the source, chemistry and microbial processing of the DOM.

Throughout the studies, DOM is followed as it is first leached from litter (**paper I & II**), extracted from soils (**paper III**) and finds its way into lakes (**paper IV & V**). Along the way relevant questions are posed related to the source, chemistry or microbial processing of DOM in relation with the particular environment investigated and in context of the global carbon cycle and ongoing climate change. The main interest lies in figuring out the importance of understory vegetation and litter decay dynamics on DOM production (**paper I**) and its chemistry (**paper II**), the flux of aged DOM from boreal mineral soils (**paper III**) and the controls (**paper IV**) and microbial processing of lake DOM (**paper V**). In the thesis a variety of techniques was used ranging from ultra-precise mass spectrometry to investigate the molecular diversity of DOM, to remote sensing via satellite imagery to capture the largescale processes in lake DOM. While diverse, the topics all relate to the terrestrial – aquatic carbon flux and provide key insights into the DOM dynamics of the northern hemisphere.

Emphasis lie on the origin of DOM in soils (**paper I & III**) and lakes (**paper IV**) and the relationship between microbial processing of DOM and its chemistry (**paper II & V**). The specific objectives were:

- To quantify the role of different litter species in the production of DOM through litter leaching, in specific looking at understory species in the boreal forest (**paper I**)
- To explore the dynamics in litter DOM chemistry as related to its bioavailability and the reactivity of the litter (**paper II**)
- To investigate and quantify the potential loss of aged DOM from boreal podzols (**paper III**)
- To investigate the role climate and landscape have in regulating DOM concentrations in lakes, in specific during dry and wet years (**paper IV**)
- To investigate the microbial processing of DOM in arctic lakes and its effect on DOM chemistry, in specific as related to increased terrestrial influence (**paper V**)

With these objectives the aim is to improve the understanding of the carbon connection between vegetation, soils and inland waters in a changing environment.

Materials and Methods

Study Area

The study area of the papers discussed in **part I** of the thesis is the Krycklan catchment (64°14'N,19°46'E). The catchment is representative for large parts of the boreal landscape and has, since its establishment in the 1970s, become an increasingly research-intensive area (Laudon et al., 2013). The roughly 6800 hectare of the catchment is covered by forests (87 %), oligotrophic mires (9 %) thin soils and rock outcrops (Laudon et al., 2013). Surface waters cover 0.1 – 4.7 % of the sub-catchments (Ågren et al., 2007). The main land use is forestry. Arable land constitutes only 2 %. The forests are second growth, of which 90 % is productive forest with a potential yield capacity of 1 m^3 per year per hectare (Tiwari et al., 2016). The dominant canopy species are *Pinus sylvestris* (63 %) and *Picea abies* (26 %)(Laudon et al., 2013). The roughly 11 % of deciduous species (Laudon et al., 2013) consist mainly of *Betula spp.* and sporadically *Alnus incana* or *Salix spp.* (Andersson and Nilsson, 2002). The understory is dominated by the shrubs *Vaccinium myrtillus* and *Vaccinium vitis-ideaa* and a moss layer of *Hylocomium splendens* and *Pleuzorium schreberi* (Laudon et al., 2013).

For **paper IV** lakes and catchments have been selected across Sweden and Norway representative of the area and with a variety in catchment characteristics, suitable for studying the effects of climate, land cover and the physical variables of the catchments on lake DOM. For the last study (**paper V**) roughly 100 lakes were selected in the mountainous region of sub-arctic northern Sweden, where terrestrial DOM has little influence order to study the effect of lake DOM regulation in varying states of isolation.

Methods for measuring DOM

In **papers I-III & V** laboratory techniques were used in order to isolate and quantify the DOM from its source water. The process consists of a number of sequential steps identical for each project (Figure 1). First, DOM needs to be extracted from litter and soils (**papers I-III**) through artificial leaching. A variety of methods exist for the extraction of soil DOM, leading to different fractions of soil carbon to be released (Zsolnay, 2003). The most aggressive protocol uses an alkaline extraction in order to extract all soluble carbon (Rice 2001). However, this method has recently seen increased scrutiny as the acid environment is thought to create artificial DOM structures that have little to do with the natural leaching process in soils (Lehmann and Kleber, 2015).The most natural way of extraction might be leaching through irrigation at a minor vacuum, however this only extracts mobile available DOM in quantities that might be too small for further chemical and incubation analysis (Zsolnay, 2003). Thus, and as a way to keep consistency between projects, I used a batch extraction method for the extraction of the potential available DOM through shaking. This approach differs from other soil DOM protocols (Zsolnay, 2003) as I used pure water instead of a $CaCl_2$ solution and because leaching through shaking was extended to 48 hours. Recent literature has suggested using pure water extractions to avoid interactions between the dissolvent and the DOM (Lehmann and Kleber, 2015). The extended time was determined to achieve the maximum amount of litter DOM leaching, after which the rapid degradation of DOM from the leachates offset any additional leaching (Arellano, 2015). For soil extracted DOM this rapid degradation is of no concern as the DOM generally is less bio-reactive (Kalbitz et al., 2003; Don and Kalbitz, 2005). The dry weight to water ratio ranged between 1:20 to 1:40. This ratio has been known to not effect leaching efficiency, *i.e.* per gram of dry weight the same amount of DOM will be leached (Soong, 2014).

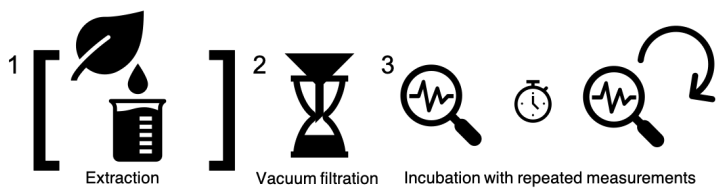

Figure 1: Overview of the lab protocol. Step 1: the DOM extraction from litter (paper I & II) or soil (paper III). Step 2: vacuum filtration (paper I-III & V). Step 3: incubation with repeated measures of dissolved oxygen and dissolved organic matter (paper I-III & V)

Following leaching the water was filtered using 0.7 µm glass fibre filters with a glass vacuum filtration setup. Typically, DOM separation with particulate organic matter is done using a 0.45 µm filter (Kalbitz et al., 2000), although different sizes are used. The pore size of the filter has been shown to not significantly affect the DOM concentrations or chem-

istry (Zsolnay, 2003). However, vacuum filtration can lead to the formation of particulate organic matter through adsorption of DOM on bubbles forming as a result of cavitation (Zsolnay, 2003). While this does not change the composition or chemistry of the DOM, the microbial availability might be slightly altered. It is unknown to what extent this is a practical difficulty for terrestrial DOM, but by keeping conditions such as vacuum pressure equal the effect should not differ between sources. In the last step following filtration, DOM samples were purged of inorganic carbon using hydrochloric acid and measured on either a Shimadzu TOC V-CPN (Herzog et al., 2017) or an OI analytical Aurora TOC analyser.

Methods for measuring DOM reactivity

The reactivity or bioavailability of DOM can be determined by measuring DOM degradation, CO_2 production or O_2 consumption over time. Given that the duration and temperature of the incubations are equal, little difference exists between different methods (McDowell et al., 2006). However, the O_2 consumption during DOM decomposition is dependent on, among other things, the oxidation state of the DOM. This is expressed as the respiratory quotient (RQ; mole of DOC lost per mole of O_2), which can vary significantly across ecosystems (Berggren et al., 2012). In **papers I-III & V**, short term incubations were done by non-intrusive high frequency (2h interval) dissolved oxygen measurements using a SensorDish Reader (SDR, PreSens, Germany) optical oxygen sensing system. Conversion to DOM was done using a RQ of 1.0, which is a reasonable assumption for arctic lakes (**paper V**)(Berggren et al., 2012). While it is unknown what the RQ for soil and litter leachates is, the average RQ reported for boreal lakes is slightly higher than 1 (?). Measurements were done at 20°C in duplicates or triplicates in 5ml bottles with butyl rubber septa screw caps for a duration of 7 (**paper I-III**) or 14 (**paper V**) days. During the first 7 days most of the bioavailable DOM is usually degraded, however for the calculation of decay kinetics it is advisable to add long term incubations of at least 42 days as related to the decay of the relatively refractory component (McDowell et al., 2006). In **paper I-III**, long term incubations were run starting simultaneously with the short-term incubations, measuring DOM concentrations at fixed intervals up to 180 days. Due to limited sample volume, in **paper V** the short-term incubation was extended. Although the short-term incubations for soil and litter leachates might have been slightly underestimated by using a lower RQ, the error was reduced through combining the data from short- and long-term incubations.

$$\text{Mineralized DOC} = \alpha(1 - e^{k1*t}) + (100 - \alpha)(1 - e^{k2*t}) \quad (1)$$

.

One frequently used kinetics model for DOM decay is the double exponential decay model (Eq. 1). This model assumes that the DOM is divided into two groups, a labile and a refractory part, with different decay rates. It has been used to calculate DOM decay in litter and soils (Kalbitz et al., 2003; Don and Kalbitz, 2005), however in comparing methods it can lead to very large differences in the decay values (McDowell et al., 2006). This might be an effect of the division between the two pools made in the model, which unless the data is high frequency and extensive, is to some degree arbitrary. That is to say, roughly the same amount and trend in DOM decay can be seen by a model with a lower percentage in the labile pool, but with a higher decay rate k1 and a model with a high percentage in the labile pool with a lower decay rate k1. At least this is what was observed while fitting the model to the data in **paper I**. In the field of limnology, the reactivity continuum model is gaining popularity (Eq. 2). This model differs conceptually from the double exponential model in that it does not assume different pools of DOM (Koehler et al., 2012). Instead, decay rates slowly decrease over time as decomposition of labile carbon will lead to increasingly lower decay rates of the remaining DOM. As such a decay rate kt can be calculated at any time during the incubation (Eq. 3). Calculation of the decay rate k0 might be less subjective to uncertainty as the DOM is not divided in two pools. In **papers II & V** the reactivity continuum model was used to calculate the decay rates of DOM at the start (**II**) and throughout (**V**) the incubation.

$$\frac{\mathrm{DOM_t}}{\mathrm{DOM_0}} = \left(\frac{\alpha}{\alpha + \mathrm{t}}\right)^{\mathrm{v}} \tag{2}$$

.

$$\mathrm{k} = \mathrm{v}(\alpha + \mathrm{t})^{-1} \tag{3}$$

.

Methods for measuring DOM chemistry

The chemistry of DOM can be measured by a variety of different techniques, ranging from simple UV light absorption to ultra-high-resolution mass spectrometry. Perhaps the most common technique is using UV-absorption parallel to fluorescence spectroscopy, as a high load of samples can be characterized in little time (Kalbitz et al., 1999; Stubbins et al., 2014). Fluorescent spectroscopy offers a low-cost evaluation of the chemistry of DOM. Data gathered with this technique can be used for simple indices relating to *e.g.* aromaticity or humification of the DOM (Zsolnay et al., 1999; Don and Kalbitz, 2005; Johnson et al., 2011), or complex multi-way (PARallel FACtor) analysis (Murphy et al., 2013). During the late 2000s the use of PARAFAC analysis has increased as software became more

readily available (Murphy et al., 2013). Fluorescence spectroscopy followed by PARAFAC analysis (**paper V**) is a powerful technique that leads to the assignment of compounds consisting of peaks occurring simultaneously throughout the samples in the emission excitation matrix (EEMs). The method is based on Beers Law (Lakowicz and Masters, 2008), which states that the concentration of a chemical solution is directly proportional to its absorption of light and allows for the calculations of the concentration of the different components. Components can be uploaded and referenced against an open database, allowing for the interpretation of the chemistry of the DOM (Murphy et al., 2014). One limitation of the technique is that with UV absorption only the light active coloured DOM (CDOM) can be measured and with fluorescence spectroscopy only the fluorescent part of the CDOM that reacts with light (FDOM) is detected (Figure 2). However, while the exact molecular chemistry of FDOM components are still largely undefined, FDOM components have been shown to relate to a large portion of the molecular diversity of the DOM (Stubbins et al., 2014). As such the method can be used to make more generalized assumptions about the DOM pool.

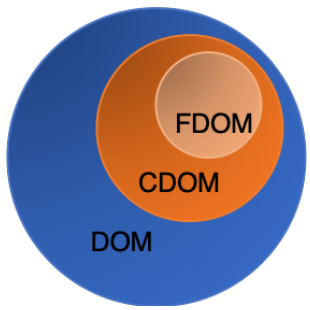

Figure 2: Relationship between DOM, CDOM and FDOM (Stubbins et al., 2014)

More advanced inclusive techniques are frequently used for the characterization of DOM, such as Fourier-transform infrared (FTIR), ^{13}C (or ^{1}H) cross-polarization magic angle spinning nuclear magnetic resonance (CPMAS-NMR) spectroscopy and FT ion-coupled resonance mass spectrometry (ICR-MS). The FTIR method is often used for litter leachates, as it has traditionally been used in litter decay studies (Gressel et al., 1995; Wershaw et al., 1996). It is somewhat comparable to the UV-absorption measurements but done on infrared spectra. It is more detailed than the UV-absorption method and can lead to the classification of compounds, however it is still a relatively unprecise measurement. The ^{13}C-CPMAS-NMR is a high precision technique used to identify, as well as provide detailed information about the structure of organic compounds. In the study of DOM, ^{13}C-CPMAS-NMR can be used to classify groups of compounds based on distinguishable NMR spectra that reflect certain detailed recurring molecular structures of the molecules (Hertkorn et al., 2013). In comparison, FT-ICR MS (**paper II**) is a high precision technique that resolves not the structure, but the formula of DOM molecules based on the measurement of its mass. With the single formulas of all detected molecules, assumptions can be made regarding its chemistry

(table 1). Both methods generally rely on a process called solid phase extraction (SPE) before running the samples. The recovery of DOM after SPE can be roughly 40 % (Hertkorn et al., 2013) and less-aromatic low-molecular weight compounds are more likely to be lost (Dittmar et al., 2008; Sleighter and Hatcher, 2008). These compounds, however, can also not be readily measured by other techniques such as fluorescence spectroscopy (Stubbins et al., 2014). As a result, there may be an inherent bias in the study of DOM chemistry against low molecular weight molecules important for bacterial degradation (Ward and Cory, 2015).

Table 1: Cutoff values for compound determination based on the aromaticity index (AI), oxygen carbon (OC) and hydrogen carbon (HC) ratio of the assigned molecular formulas (paper II)

Compound	AI	OC	HC
Condensed aromatics	>0.66		
Aromatic and polyphenolic	0.5-0.66		
Aliphatic			1.5-2
Highly unsaturated and phenolic high OC	≤0.5	<0.5	<1.5
Highly unsaturated and phenolic low OC	≤0.5	<0.5	<1.5

Radiocarbon measurements of DOM

In **paper III**, I was interested in quantifying the amount of old DOM that can be leached from boreal mineral soils. Measurements of the radioactive ^{14}C isotope can be used as a method to determine the age of organic samples. At the time of photosynthetic fixation, the atmospheric concentration of ^{14}C determines the ratio of ^{14}C to the stable ^{12}C isotope. After the organism dies, or the tissue is deposited (*e.g.* as litter), no additional ^{14}C can be added to the organic matter. Over time ^{14}C decays into ^{14}N and as such the ratio of ^{14}C:^{12}C decreases in a predictable matter. The half life time of ^{14}C is about 5730 years and thus the age of an organic sample can be relatively easily calculated based on its depletion (Godwin, 1962).

Normally, ^{14}C is constantly replenished as ^{14}N in the atmosphere reacts with neutrons produced by a cascade of reactions following the entry of cosmic rays into the upper atmosphere (Ramsey, 2008; Kovaltsov et al., 2012). Rates are known to fluctuate, mainly as a result of the strength of the Earth's magnetic field (Anderson and Libby, 1951). However, these fluctuations are almost negligible when compared to the increase in ^{14}C as a result of the atom bomb testing in the 1960s and 70s (Reimer et al., 2013). During the 60s the atmospheric ^{14}C concentrations almost doubled, but as the CO_2 in the atmosphere is exchanged with the ocean and biosphere, the ^{14}C concentrations have been falling and will soon reach pre-bomb values (Ramsey, 2008). The result is a big peak in the ^{14}C:^{12}C ratio that has both excited and frustrated carbon cycling research (Fig. 3). Although the age of young carbon samples can now sometimes be determined by comparing the ratio to the last

70 years of atmospheric concentrations, mixing of young and aged carbon can lead to the false conclusion that carbon has been recently fixed. This is especially problematic DOM studies as the source is more often than not a mix of different sources. In **paper III**, I set up an incubation experiment with the aim to split the young and aged carbon as extracted from boreal soil samples. By using the Keeling plot method (Keeling, 1958), I was able to determine the ^{14}C:^{12}C ratio of the labile DOM. This method has previously been used for the calculation of the labile 13C (Karlsson et al., 2007) as well as ^{14}C (Berggren and Giorgio, 2015) fraction of DOM. Because long term organic matter preservation in soils might have more to do with the physical exclusion of the matter from microbes than its intrinsic chemical recalcitrance, I hoped to be able to see the separated aged ^{14}C signature in the labile fraction of the DOM.

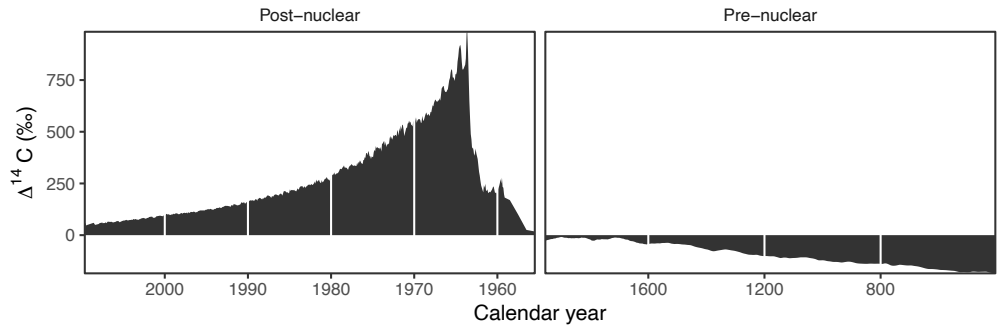

Figure 3: Historical atmospheric $\Delta^{14}C$ concentrations (Reimer et al., 2013)

The remote sensing of CDOM

Remote sensing via satellite imagery is a useful tool for measurement, observation and model building in a diverse set of studies ranging from social science to ecology. Remote sensing of CDOM is done in lakes (Kutser et al., 2005) and oceans (Aurin and Dierssen, 2012), but is not without challenges. For example, sediment loads in coastal areas can prove problematic for CDOM measurements in the ocean, although improvements are constantly being made (Aurin and Dierssen, 2012). Theoretically, the remote sensing of lakes in the boreal region should be relatively straightforward as the CDOM is the dominating absorbing compound and has a predictable effect on the reflectance spectrum (Kutser et al., 2005). However, the small lake size and low reflectance of many boreal lakes are a technical problem for satellites with a low resolution and sensitivity (Kutser et al., 2005). In addition, optically shallow lakes can affect the values of reflectance as measured by satellites, distorting the signal used for CDOM calculations (Li et al., 2017). Still, remote sensing of boreal lakes has successfully been done using satellite imagery of varying precisions and

the suitable corrections for the area (Kutser et al., 2005; Al-Kharusi et al., 2020). In **paper V**, imagery from Sentinel-2 was used and corrected for atmospheric, terrain and cirrus clouds. The CDOM of boreal lakes was calculated using the relationship (Eq.4) between the specific UV absorbance coefficient at 420 nm and the ratio of bands 2 and 3, at 490 and 560 nm respectively (Al-Kharusi et al., 2020), as suggested by earlier research (Kutser et al., 2005). The equation was developed in the same area in 2016 on a selection of 46 lakes and has been shown to accurately predict (R^2 = 0.65) CDOM concentrations across divers areas in Scandinavia (Al-Kharusi et al., 2020). Calculations for CDOM concentrations were made for 2016 and 2018 in more than 200 lakes. The calibration of CDOM can be done within 1-2 months of the sampling date (Brezonik et al., 2015), without resulting in great problems. However, because the calibration was done only in 2016 this might result in a slight bias for better CDOM estimations in 2016 as compared to 2018.

$$\alpha(420)\mathrm{CDOM} = 2.809 * (\frac{\mathrm{B3}}{\mathrm{B4}})^{-2.341} \tag{4}$$

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Part I: Terrestrial DOM dynamics in the boreal forest

Background

The future carbon balance of the boreal forest is globally important but uncertain. The warming of the past decades has been associated with increased forest fires (Flannigan et al., 2006; Astrup et al., 2018), insect herbivory and outbreaks (Niemelä et al., 2001; Bale et al., 2002; Gustafson et al., 2010), changes in vegetation composition (Ritchie, 1986; Nilsson et al., 2013), DOM export to the aquatic system (De Wit et al., 2016) and soil carbon losses (Bradshaw and Warkentin, 2015). In such shifting conditions terrestrial DOM dynamics might change unexpectedly, *e.g.* as a result of a change in species composition or increased runoff. However, while the topic of terrestrial DOM export has been rigorously investigated, there are certain knowledge gaps concerning the in and out flux of DOM in mineral soils. In the first part of this thesis I looked at two important terrestrial DOM pathways; litter leaching (**paper I, II**) and the loss of aged carbon from soils (**paper III**). Litter leaching constitutes the main DOM flux by which carbon captured by photosynthesis is transferred to the soil and plays a key role in the carbon sequestration of mineral soils (Kalbitz et al., 2000; McDowell, 2003). The loss of aged carbon from soils as DOM is an important but hard to measure flux that can be indicative of a shift in the net carbon balance of an ecosystem. Both are crucial to our understanding of the DOM dynamics and the future carbon balance of the boreal forest.

Litter leaching of DOM is a relatively well studied topic. Previous studies have been done on a large variety of species, ranging from tropical (Schreeg et al., 2013) to boreal (Wickland et al., 2007). However, the flux of DOM from litter to soils has perhaps been most intensively studied in the temperate forests. From these studies it has become clear that there exists a large variety in the potential for DOM leaching between different litter species of the same area (Cleveland et al., 2004; Hagedorn and Machwitz, 2007; Joly et al., 2016). Similarly, a large variety exists in the biodegradability and chemistry of the DOM

(Cleveland et al., 2004; Don and Kalbitz, 2005) and the ratio between CO_2 and DOM production during litter decay (Hansson et al., 2010; Silveira, 2011). Over time, the litter DOM leaching potential and biodegradability decrease, although large amounts of DOM can still be released from highly decomposed litter (Don and Kalbitz, 2005). Some coniferous species show a marginal increase in leaching as the decomposition furthers. Combined, this highlights the importance of litter species and degradation stage on the DOM dynamics of the forest. Yet, studies scaling DOM potential of litter species to forest stand level are nonexistent. Field studies are more prevalent for ecosystem DOM flux experiments. However, while field measurements are important and can help understand the fate of litter leached DOM within the forest, they are limited two ways. When measuring DOM in the field, mixing of different sources is inevitable. One method to account for this is through the isotopic enrichment of litter (Hagedorn et al., 2004), a relatively expensive and time-consuming method not realistic to do for all dominant litter types in a forest. In addition, the measurement frequency in field studies is often rather low and spikes in leaching following heavy rainfall can easily be missed.

Therefore, the studies presented in **papers I** to **III** rely on laboratory leaching experiments of litter (**I-II**) and soils (**III**) in the boreal forest, see methods. While laboratory studies cannot be directly translated to in situ conditions, the controlled environment makes structural comparisons between sources possible. As such, the absolute quantities of DOM leached from experimental studies say little about the amount of leaching taking place in the field. However, leaching potential, DOM chemistry and bioavailability are all indicatory of the role different sources play compared to each other. By combining pure water extractions with biodegradation incubations on fresh and field decomposed litter samples I aimed to establish a systematic overview and quantification of litter DOM leaching of the dominant vegetation in the study area (**paper I**). The quantification and regulation of soil DOM sources has been acknowledged as a major question in the field of soil biogeochemistry for more than 15 years (McDowell, 2003). Supplementing the laboratory approach with 3 years of litterfall data I show the strength of individual species as DOM source at the forest stand level (**paper I**). Further ultra-high-resolution chemistry measurements on the leachates show the link between DOM chemistry and bioavailability and how both are regulated by litter reactivity (**paper II**).

Unlike the temperate forests, the coniferous boreal forest has a thick understory. Although most of the ecosystem biomass consists of canopy vegetation, the understory has much higher rates of nutrient and carbon cycling (Snyder, 1961; Hart and Chen, 2006). While a large part of net primary production of canopy species is allocated to growth, the annual biomass renewal rates of certain understory species (*e.g. V. myrtillus*) can be more than 60 % (Snyder, 1961). In terms of DOM leaching, litter from evergreen species often show lower rates than deciduous litter (Don and Kalbitz, 2005; Hagedorn and Machwitz, 2007; Silveira, 2011). Furthermore, the deciduous understory species *V. myrtillus* is known have a

high soluble mass (Wardle et al., 2003). Moss biomass can be as high as 500 g m^{-2} (Stuiver et al., 2014) and while moss DOM leaching rates are low (Wickland et al., 2007) it could be a significant source through its abundance. Thus, while the DOM leaching from the canopy in the boreal forest might be limited, the understory could be a major source of litter DOM at the forest stand level.

The majority of the boreal carbon stock is stored below ground as soil organic carbon (SOC)(Scharlemann et al., 2014; Bradshaw and Warkentin, 2015). The most SOC dense areas are peatlands and organic permafrost soils (Ping et al., 2010), but podzol soils have the largest spatial extent (DeLuca and Boisvenue, 2012) and thus hold a substantial and important part of the total boreal carbon stock. The carbon stored in mineral soils can be hundreds or thousands of years old (Rumpel et al., 2002; Kögel-Knabner and Amelung, 2014) and as the area is coming under increased climate and environmental pressure the question arises how stable this carbon is. Previous research has shown that aged carbon can be exported as DOM in a number of different areas (Raymond and Bauer, 2001b; Butman et al., 2015; Barnes et al., 2018; Drake et al., 2019). However, high ^{14}C concentrations of young carbon (see methods) can hide the age of old carbon in inland waters (Dean et al., 2019). As such it is unclear to what extend old organic carbon can be laterally exported from mineral soils as DOM.

Litter leaching of DOM (papers I & II)

Leaching of DOM from fresh litter was 2-138 mg C g^{-1}, for spruce wood and *V. myrtillus* respectively (**paper I**). Over time, the rate of leaching converged at 5-15 mg C g^{-1} as DOM leaching decreased exponentially with litter mass loss for all litter species, except wood and pine litter. This is in line with previous research in temperate regions (Don and Kalbitz, 2005; Hagedorn and Machwitz, 2007) and implies that species composition of the forest has a more pronounced effect on litter DOM leaching during autumn senescence than in the following seasons. Older studies and models (*e.g.* the Century model) have linked the lignin-nitrogen ratio to the leaching of DOM (Neff and Asner, 2001; Cleveland et al., 2004). However, although the leaching of DOM in fresh litter exponentially increased as related to total litter mass loss and the total mass loss exponentially increased with the initial nitrogen content of the litter (**paper I-II**), no direct relationship was found between litter nutrient (nitrogen, phosphorus) or lignin stoichiometry and DOM leaching (**paper I**). Cleveland et al. found only a weak relationship with the lignin-nitrogen ratio, noting that the variation in DOM leaching was far greater than the variation in lignin and nitrogen content (Cleveland et al., 2004). Both nitrogen content and mass loss of *V. myrtillus* litter was roughly the same or lower than that of birch and alder litter, yet *V. myrtillus* yielded much higher DOM extractions. This is in accordance with the finding that the water-soluble fraction of *V. myrtillus* is higher despite having roughly the same chemistry and

mass loss as birch (Wardle et al., 2003) and suggests that a structural difference in the 'poorly defended tissue' of *V. myrtillus* (Snyder, 1961) results in higher DOM leaching. Previous studies have shown a relationship between lignin or the lignin-nitrogen ratio and mass loss (Melillo et al., 1982, 1984; Silveira, 2011), which could not be confirmed in this study. Bonanomi et al. found that while simple carbon-nitrogen or lignin-nitrogen ratios are able to describe the quality of undecomposed litter, they fail to predict mass loss of already decomposed material (Bonanomi et al., 2013). This might explain the lack of an overall driver of litter nitrogen and lignin on DOM leaching.

Although simple nutrient lignin ratios might fail to accurately describe litter mass loss, it is generally accepted that litter chemistry is a key regulator of initial litter decay and DOM leaching (Berg and Staaf, 1980; Melillo et al., 1982, 1984; Aber et al., 1990; Cornelissen, 1996; Pérez-Harguindeguy et al., 2000; Preston and Trofymow, 2000; Soong et al., 2015; Campbell et al., 2016). By using more advanced techniques a link has been found between litter mass loss and specific lignin and O-alkyl groups (Bonanomi et al., 2013), as well as the DOM:CO_2 production ratio of litter and the lignocellulose index (Soong et al., 2015). Over time, soluble structures such as polyphenols, certain carbohydrates and non-lignified cellulose are depleted, leading to lower rates of mass loss (Lorenz et al., 2000, 2004; Berg et al., 1982; Melillo et al., 1989). As such, the chemistry and bioavailability of litter leachates is dependent on the reactivity of the litter species and high reactive litter species should see greater changes in DOM chemistry than low reactive litter species (**paper II**). Because litter mass loss and DOM leaching are related (Osono and Takeda, 2005) high reactive litter initially deliver more DOM to soils per gram of litter. Knowledge about the chemical differences in composition between species and its relation to litter reactivity and DOM lability are thus paramount to a mechanistic understanding of soil biogeochemical and litter DOM processes.

Early mass loss is inversely related to litter toughness (Pérez-Harguindeguy et al., 2000) and as such pine, spruce and wood litter can be seen as low reactive litter species. On average, pine, spruce and wood litter saw a cumulative mass loss of 6.2 % after 180 days of litter decomposition and consistently low mean DOM leaching rates between 3.4 and 4.9 mg carbon g^{-1} over the same period (paper II). The deciduous species birch, alder and *V. myrtillus* can be considered high reactive litter species as a result of high initial mass loss rates (Berg and Ekbohm, 1991) and high soluble mass (Wardle et al., 2003). These species saw on average a cumulative mass loss of 20.6 % after 180 days and a decrease in DOM leaching rates of 81.7 to 7.4 mg carbon g^{-1} over the same period (**paper II**). This rapid reduction of the DOM leaching potential indicates the depletion of soluble compounds over time. To test whether the exhaustion of soluble compounds had an effect on the bioavailability and chemistry of DOM, dark incubations were set up and ultra-high resolution FT-ICR mass spectrometry measurements were done at the start and the end of the incubation of all litter leachates (see methods).

The leachates presented in **paper I & II** showed an overall high bioavailability. In comparison with previous studies the difference between individual species (**paper I & II**) was smaller (Don and Kalbitz, 2005), possibly due to the longer incubation time used here. High reactive litter had a relatively higher DOM reactivity that decreased as litter decay progressed, thereby eliminating the difference with low reactive litter (Figure 4). Spruce and birch wood litter showed the overall lowest biodegradability and decay rates, driving the difference between high and low reactive litter.

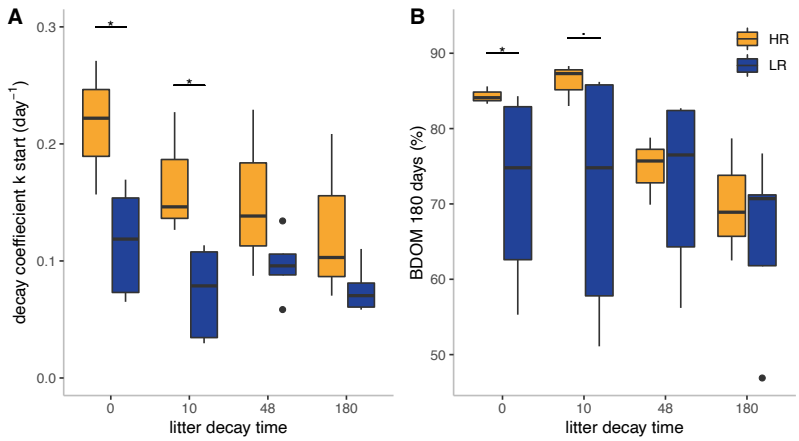

Figure 4: The decay coefficient k (A) and the total bioavailability of DOM (B) for high reactive (HR) and low reactive (LR) litter leachates related to litter decay. Significant differences between HR and LR leachates are denoted (*; $p<0.05$, •; $p<0.1$)(paper II)

In the early phase of the high reactive litter decay, a large amount of oxidized phenolic compounds was released (Figure 5). As litter decay progressed, a strong decrease in the yield of lignin-derived phenols was seen. Previous research has shown that oxidized phenolic compounds are a product of lignin degradation often seen in litter species that have a high carbon availability (Kögel-Knabner, 2002; Klotzbücher et al., 2011). Because of the high leaching rates of high reactive litter, the supply of available carbon seems not to be limited. The relative abundance of aliphatic and unoxidized phenolic compounds increased during litter decay of birch, alder and *V. myrtillus* litter, however this is arguably the result of the decreasing abundance of oxidized phenolic compounds. As litter decomposes, aliphatic compounds have been shown to accumulate (Hempfling et al., 1987; Zech et al., 1987; Bonanomi et al., 2015; Cepáková and Frouz, 2015). This indicates that aliphatics have a low relative leachability and as high leachable structures are depleted first (Lorenz et al., 2004), a proportional increase in the abundance of aliphatics is seen. No such relationship was seen for spruce, pine or wood litter, indicating that lignin is not degraded during early litter mass loss.

Microbial processing of DOM led to an increase of the chemical homogeneity between litter species. The highly oxidized phenolic compounds seen in fresh high reactive litter leachates were degraded and seemed to drive the bioavailability of the DOM (Figure 6). Stable aliphatic compounds were either created or preserved. For low reactive litter species, aliphatic compounds were degraded and phenolic compounds preserved. Thus, large interspecific differences exist in the chemistry of leachates from different litter types, however these differences diminish as a result of microbial processing. That microbial processing of DOM leads to increased chemical homogeneity has been shown before in soils (Strid et al., 2016; Thieme et al., 2019), rivers (Mosher et al., 2015) and oceans (Lechtenfeld et al., 2015; Mentges et al., 2017). Even as litter decays, its chemistry converges (Preston et al., 2009b,a) as do their leachates (**paper II**). This shows the uniform direction of carbon decay processes and indicates that the increase in molecular homogeneity in soils or surface waters is the effect of microbial DOM degradation processes and not the mixing of different chemically unique sources. As a result, using chemistry to differentiate between DOM sources might not work when the fresh DOM from *e.g.* litter or soils is compared to DOM in the aquatic system that has progressed more in its decay phase. This difficulty can be seen in the fact that the distinct chemistry of litter sources have little effect on long term evolving soil chemistry (Strid et al., 2016; Thieme et al., 2019).

Canopy litterfall in the catchment averaged 137 g m^{-2} yr^{-1}, excluding clear-cut areas and cone production (**paper I**). Needle (94 g m^{-2} yr^{-1}) and birch (25 g m^{-2} yr^{-1}) litter production was comparable and somewhat higher than the respective findings in the same area (Maaroufi et al., 2016). Regionally, needle production might differ within the range of approximately 50 and 260 g m^{-2} yr^{-1} as a result of the amount of growing days (Bhatti and Jassal, 2014) or fertilization (Leppälammi-Kujansuu et al., 2014). Understory litter production was just over 100 g m^{-2} yr^{-1}, while moss standing biomass averaged 230 g m^{-2}. This is in line with previous research showing that undergrowth layers significantly added to the total litter dry weight in pine forests (Tappeiner and Alm, 1975). The biomass estimate of *V. myrtillus* (125 g m^{-2}) was within the range of other studies in Fennoscandia (150 – 200 g m^{-2})(Atlegrim and Sjöberg, 1996) and southern Finland (0 - 210 g m^{-2})(Mäkipää, 1999). Both the rates of needle litterfall and biomass of *V. myrtillus* are dependent on fertilization (Leppälammi-Kujansuu et al., 2014), the age of the forests (Mäkipää, 1999) and the latitude (Johansson, 1993; Muukkonen and Mäkipää, 2006; Muukkonen et al., 2006). Simplified a denser canopy correlates to a sparser understory vegetation. As such, a strong north-south gradient can be seen in the boreal zone, with an increasing dominant understory going north.

Excluding moss, understory fresh litter DOM leaching per unit area was 5.3 times higher than canopy leaching at the forest stand level, even though litter production was slightly less than canopy litter (**paper I**). By far the biggest contributor to fresh litter DOM and nutrient leaching in the catchment (> 60 %) was the understory species *V. myrtillus*, high-

lighting the importance of the understory vegetation composition for leaching processes and soil biogeochemistry. Previous research has argued for the importance of the understory composition in nutrient and carbon cycling as certain species can be either a promoter or suppressor of litter decay (Snyder, 1961; De Long et al., 2016). Advancing climate change is thought to affect understory species composition as moss cover is expected to decrease and shrub cover (*e.g. V. myrtillus*) increase (De Long et al., 2016). My results, however, suggest that litter DOM fluxes might increase as low leaching moss species make room for high leaching *V. myrtillus* shrubs. This might have important consequences for soil biogeochemical processes such as carbon sequestration.

The high bioavailability of high reactive litter (*e.g. V. myrtillus*) leachates suggests that it may be more easily processed by microbes than DOM from spruce, pine or wood litter. Long term carbon sequestration is linked to microbial processing of carbon (Cotrufo et al., 2013, 2015) and microbial products have been shown to be a very stable SOM component (Marschner and Kalbitz, 2003; Miltner et al., 2012). In soils an accumulation of aliphatic components can be seen that can persist for millennia (Lorenz et al., 2007). Thus, the production of stable aliphatic compounds by the decay of high reactive litter leachates might be an important process in soil carbon sequestration. Moreover, because *V. myrtillus* is such a prominent species in both the production of DOM as well as its chemistry, future increases in shrub density might possibly lead to higher soil carbon sequestration rates.

In situ litter mass loss and thus leaching is depended on the litter water content (Don and Kalbitz, 2005). The amount of water needed to achieve litter mass loss is smaller than the amount of water needed to transport leachates from litter to soils. While completely dry litter might preserve its potential for DOM leaching, if mass loss progresses the DOM potential of the reactive litter species such as *V. myrtillus* drops exponentially. It can be argued that the DOM in moist litter will be transported after the next rain event. However, large parts of the DOM can be degraded before reaching the soil matrix, which might have otherwise stabilized the carbon (Kalbitz et al., 2005; Hagedorn et al., 2015). As such, the effects of alterations in vegetation composition should be looked at in parallel with changes in climate, especially autumn precipitation patterns.

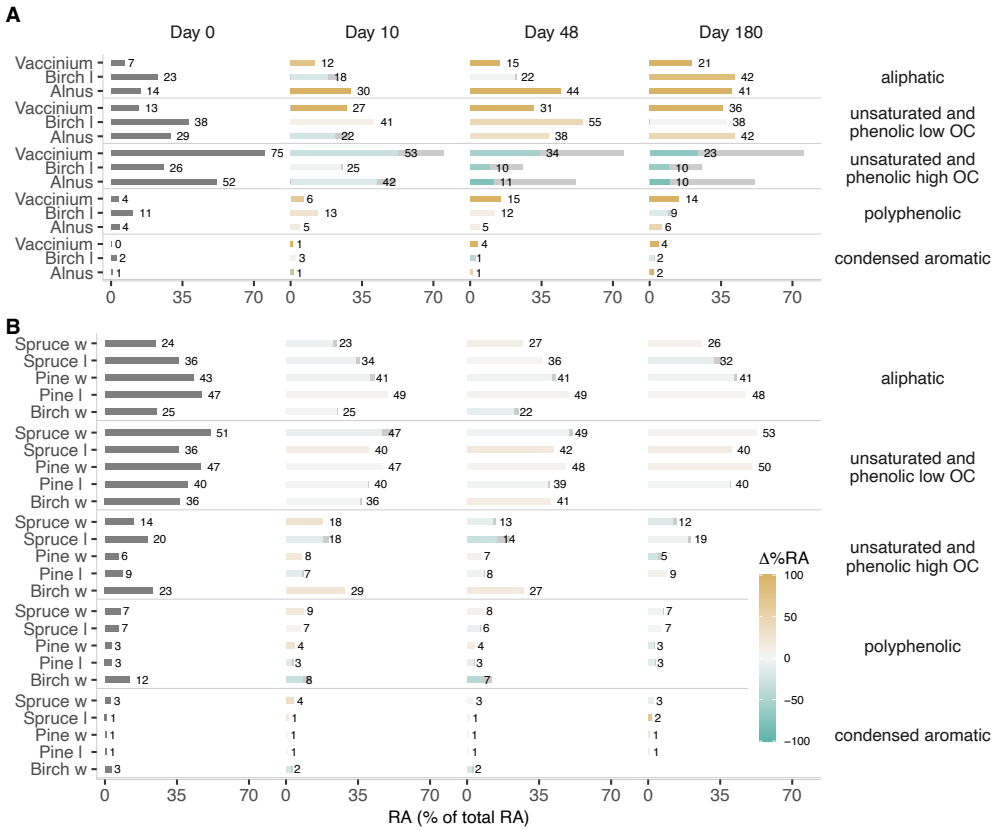

Figure 5: Leachate DOM composition of HR (A) and LR (B) litter species at day 0 to day 180 of litter decomposition. Changes in relative abundance (RA) are shown as relative difference from Day 0 in color scheme with a max change of 100%) (paper II)

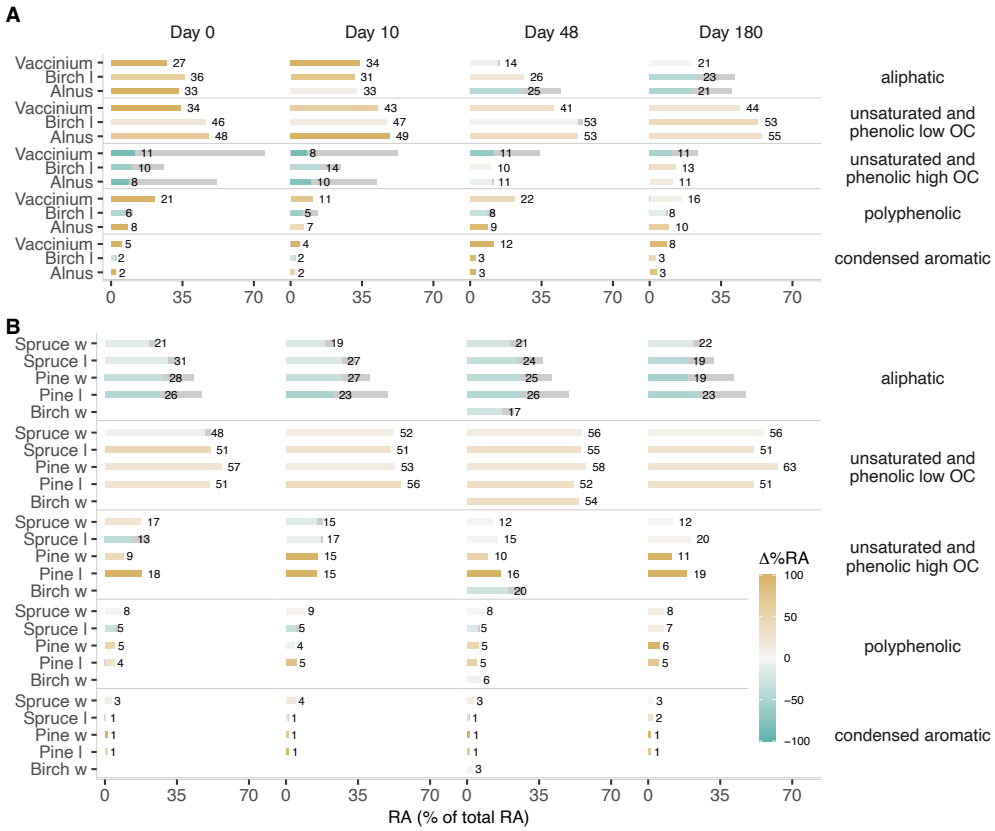

Figure 6: DOM composition after incubation. Composition is shown for (A) HR and (B) LR litter at day 0 to 180 of litter decomposition. Changes in relative abundance (RA) are shown as a difference with pre-incubation DOM in color scheme with a max change of 100%. Grey bars show the pre-incubation RAs) (paper II)

The loss of aged carbon from soils (paper III)

The DOM extracted from sub soil horizons showed modern ^{14}C signatures, even if ^{14}C of the corresponding SOC was depleted (**paper III**). Although these values were rather high (Figure 7) indicating a large influence of highly enriched ^{14}C found during the 1960s to 80s, similarly high values have been found previously in lysimeter water of the same area (Campeau et al., 2019). In addition, elevated ^{14}C signals are found in DOC as compared to SOM (Butman et al., 2007) or POC (Raymond and Bauer, 2001a). This shows that there is a discriminatory release of DOM in soils favoring modern carbon. This is in line with expectations, as younger material is likely more available for leaching than material that has already been preserved for a long time and thus has proven its stability. For example, aged

soil carbon has previously been linked to small molecules (Gleixner et al., 2002; Sickman et al., 2010), microbial material (Miltner et al., 2012; Kallenbach et al., 2016) or carbon aggregates (Six et al., 2002; Ewing et al., 2006) tightly connected with the soil matrix.

Subsequent degradation experiments showed that the labile fraction of the extracted DOM from sub soil layers had depleted ^{14}C values, relating to an age of roughly 1000 years (Figure 7). Although the age of the labile DOM has a relatively high uncertainty, there is a less than 5 % likelihood that the labile DOM was fixed under current ^{14}C values (Graven et al., 2017). This is in accordance with a growing body of literature suggesting that aged soil carbon consists, at least partially, of labile compounds (Gleixner et al., 2002; Ewing et al., 2006; Sickman et al., 2010) as well as the observation that aged carbon exported to rivers is readily bioavailable (McCallister and Del Giorgio, 2012; Berggren and Giorgio, 2015). Furthermore, the selective preservation and sorption of DOM are known to result in the soil retention of recalcitrant carbon (Kaiser and Guggenberger, 2000). However, laboratory experiments suggest a mean residence time of roughly 40 to 90 years (Kalbitz et al., 2005) or shorter if considering the saturation of the sorption complex (Guggenberger and Kaiser, 2003). This is within range of the average age found for the recalcitrant DOM (**paper III**) and shows that recalcitrant sorbed DOM produced during peak ^{14}C atmospheric conditions can still be found in the subsoils of the boreal forest.

On average, roughly 35 % of the water extractable DOM from sub soils consisted of the aged labile fraction (**paper III**). However, due to the presence of enriched ^{14}C recalcitrant DOM, the release of the aged fraction cannot be deferred from its bulk ^{14}C signal. To my knowledge, this is the first evidence and quantification for the masking of aged labile DOM extracted from boreal mineral soils. Previous studies have provided evidence for the release of old labile terrestrial carbon as a result of permafrost thawing, urbanization and tropical deforestation (Alin et al., 2008; Fan et al., 2008; Drake et al., 2019). A wide range of studies have demonstrated the modern age of riverine carbon (Sanderman et al., 2009; Trumbore, 2009; Guillemette et al., 2017). This might lead to the believe that little to no aged carbon is exported in these systems. The results presented in **paper III** suggest that this could be a false conclusion. In addition, in the rivers where ancient carbon is detected, the age might be significantly underestimated if enriched ^{14}C carbon is exported at considerable quantities as well. These findings extend previous research providing evidence for the masking of aged carbon by enriched nuclear ^{14}C carbon (Schefuß et al., 2016; Dean et al., 2019) and are in line with the preferential decay of aged carbon find in various ecosystems (Ewing et al., 2006; McCallister and Del Giorgio, 2012; Berggren and Giorgio, 2015; Guillemette et al., 2017). Although it cannot be concluded how much aged labile carbon is exported to the aquatic system with the data presented here, a number of processes are known to disrupt aged soil carbon (Trumbore, 2009). A change in vegetation (Karltun et al., 2005), carbon chemistry (Fontaine et al., 2007) or nutrient supply (Nowinski et al., 2008), an increase in urbanization or agriculture (Raymond and Bauer, 2001a; Ewing et al., 2006; Sickman et al.,

2010; Butman et al., 2015), forest fires (Czimczik et al., 2006) and the draining (Trumbore, 2009) or warming (Hirsch et al., 2002; Neff et al., 2006) of soils have all been linked to the mobilization of aged soil carbon. With increased climate change on the horizon, these processes might become more severe in the coming decades (Myhre et al., 2013; Gauthier et al., 2015; Astrup et al., 2018). The detection of aged carbon is thus imperative for our understanding of the global carbon cycle in the light of climate change, however our results show that conclusions based on bulk ^{14}C signatures might underestimate the export of aged carbon to aquatic systems.

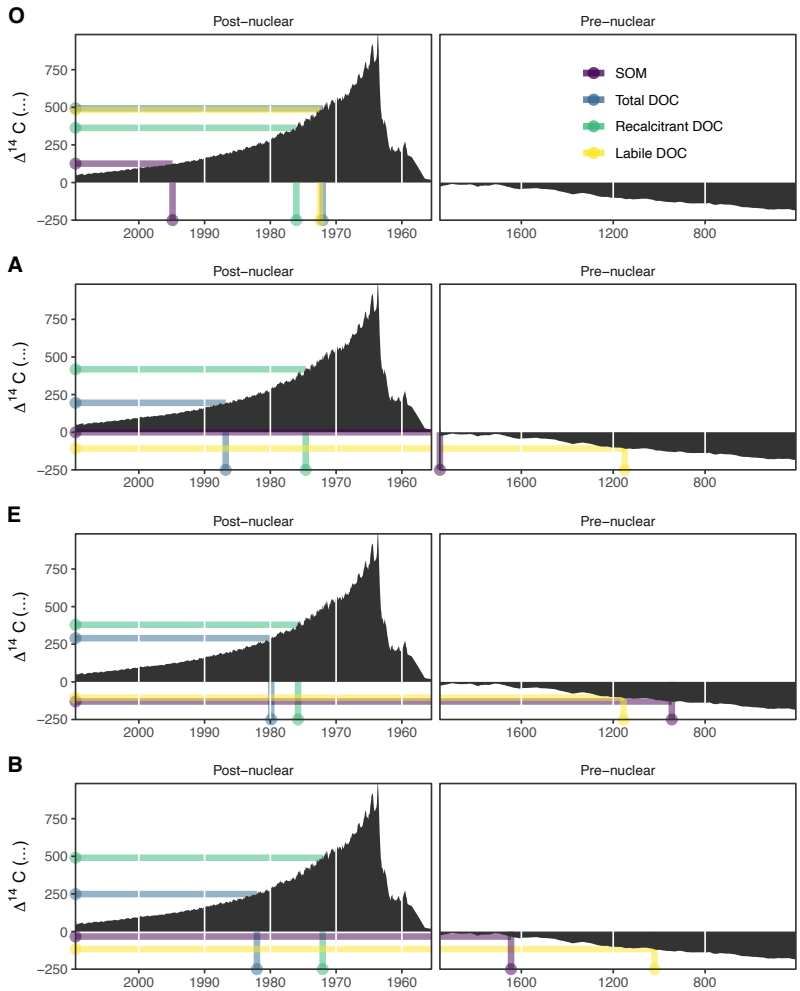

Figure 7: Observed average d^{14}C projected on a timeline of historical atmospheric values for different soil organic matter (SOM) and dissolved organic carbon (DOC) fractions; SOM (purple), total (blue), recalcitrant (green) and labile (yellow) DOC (paper III)

Part II: the regulation of colored DOM in lakes

Background

Many lakes in the northern hemisphere undergo increased DOM export from terrestrial sources as a result of climate and environmental changes. The most profound and noticeable effect of this is the browning of inland waters as a result of an increase of the colored partition of the DOM (CDOM). The CDOM plays an important role in the regulation and health of lake ecosystems as it influences pH, alkalinity, the thermal regulation and the spectral distribution of light (Creed et al., 2015), all of which influence the algal and microbial communities (Brezonik et al., 2015). The majority of CDOM in lakes comes from terrestrial export, although it can also be produced within lakes by the microbial processing of DOM produced by lake autotrophs (Romera-Castillo et al., 2011). Within CDOM there is a fraction called fluorescent DOM (FDOM), which can be measured and characterized through modern fluorescence spectroscopy (see methods).

Roughly speaking, FDOM can be divided into protein-like and humic-like DOM. Protein-like DOM is associated with the autochthonous microbial processing of DOM, while humic-like DOM is often seen as a proxy for terrestrial derived DOM (Stedmon et al., 2007). Although protein-like DOM is mainly a derivative from lake autotrophs, it is exported as a small fraction of the terrestrial CDOM. However, because of the size of the terrestrial CDOM flux, the bulk of the protein-like DOM in lakes might be of terrestrial origin, depending on the total terrestrial DOM export. As such, measurements of CDOM are sometimes taken as synonymous to terrestrial DOM in studies where substantial terrestrial carbon export is expected.

Because of the associations between CDOM, terrestrial export and water browning, measurements of CDOM are important tools in the assessment of terrestrial DOM export and the state of surface waters. Moreover, CDOM is measured as a fraction of light absorption

and can be easily calculated from relatively simple light spectra measurements. This ease of measurement has led to the high frequency (Strohmeier et al., 2013) and remote sensing data collection of CDOM (Kutser et al., 2005), yielding increasingly trustworthy DOM export estimates and resulting in large-scale comparisons between lake DOM concentrations. The remote sensing of CDOM has made it possible to achieve a more generalized understanding of the effects of the catchment environment on lake CDOM regulation. However, while it is known that vegetation, hydrology and climate play a significant role in determining CDOM concentrations in lakes (Brezonik et al., 2015), less is known about how these processes interact with each other. In addition, as large-scale research on CDOM is usually temporally limited, the effect of drought on CDOM regulation is unknown. As climate change is expected to increase both the frequency and severity of droughts this is an important issue that deserves further investigation.

Controls on CDOM in lakes (Paper IV)

In **paper IV** we compared the CDOM regulation of more than 250 lakes from 2016, a normal year, with the extreme drought of 2018. The drought of 2018 was associated with significantly decreased CDOM concentration across the lakes in the region. Moreover, the dryness index negatively affected CDOM concentrations during the dry year, while no relationship was found during the relatively wet year (**paper IV**). This shows that dryness is only a factor in regulating CDOM in lakes during unusually dry periods. During extreme drought, the hydrological connection between catchment and lake can become disconnected (Szkokan-Emilson et al., 2017). With little to no precipitation groundwater levels drop and runoff decreases (Hughes et al., 2012), resulting in the drying of streams and a decrease in the transport of carbon from the catchment (Lake, 2003; Szkokan-Emilson et al., 2017) Groundwater flow, which contains little CDOM, is less affected and as a result the water transported to the lakes is diluted (Tiwari et al., 2017). However, not only the delivery of CDOM to lakes is reduced, also its production in terrestrial ecosystems is affected. During extreme droughts the soil microbial community is less active and thus soil decomposition rates are lower and less DOM is mobilized (Toberman et al., 2008; Wu et al., 2018). Additionally, photosynthetic rates are known to drop during summer droughts, reducing the carbon flow from vegetation to soils (Nemergut et al., 2005; Breeuwer et al., 2009; Kritzberg et al., 2020).

The concentrations of CDOM in lakes is regulated by an interaction between climate, catchment morphology and land cover, of which catchment morphology has the biggest influence under normal conditions (**paper IV**). During the dry year, overall less of the variation in CDOM could be explained due to a reduction of the explanatory power of all combined variables (Figure 8). Further analysis showed that temperature had a systematic positive effect on CDOM concentrations in 2016 and to a lesser degree 2018 (**paper IV**).

High temperatures have been linked to an increase in soil DOM concentrations (O'Donnell et al., 2016) and the export of soil carbon to lakes (Lapierre et al., 2015; Berggren et al., 2018) as a result of increased soil microbial activity. However, during extreme drought the soil microbes are co-limited by moisture and as such explains the lower regulating strength of temperature in 2018 (**paper IV**). This agrees with previous research in northern Sweden, showing that the combination of increased temperature and precipitation leads to increasing CDOM concentrations in recipient waters (Köhler et al., 2008; Kritzberg et al., 2020). The results are in opposition with the idea that temperature is relatively more important during drought as a result of increased microbial DOM degradation in lakes (Berggren et al., 2010), leading to CDOM losses. This implies that the export of terrestrial CDOM was stimulated more by increased temperatures than the losses due to internal CDOM degradation.

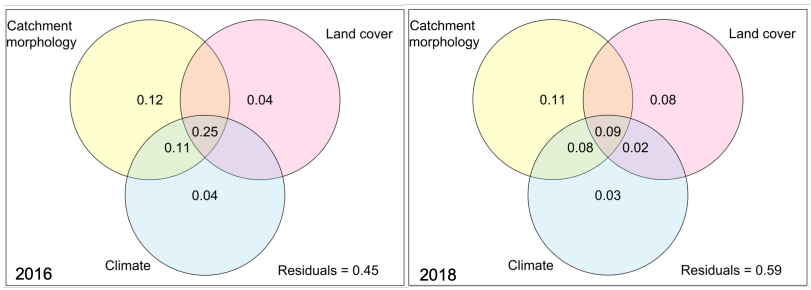

Figure 8: Variations partitioning of CDOM for the categories catchment morphology (variables nr=16), land cover (variables nr=8) and climate (variables nr=3) in 2016 and 2018; (Table 3). The total adjusted is R2 = 0.55 and 0.41 in 2016 and 2018 respectively. Partitioning of adjusted R2 is shown in the graph. Values <0 not shown (paper IV)

Both land cover and catchment morphology had significant effects on the CDOM concentrations (**paper IV**). Lake area had a sustained important negative effect on CDOM during both years. Furthermore, during drought the decrease in CDOM concentrations was biggest in large lakes. These results illustrate the importance of hydrological connectivity within the catchment and indicate that small lakes keep a greater connectivity during drought than big lakes. Small lakes are usually in closer vicinity to terrestrial sources than larger lakes, which are located further down the catchment and fed by a larger proportion of deeper groundwater. Thus, lake area negatively effects CDOM concentrations as previously emphasized in other studies (Mattsson et al., 2005) and higher dilution through groundwater influences are expected in larger lakes. In addition, the proportion of wetlands in the catchment had a positive influence on CDOM which was more pronounced during the dry year (**paper IV**). Because wetlands maintain higher hydrological connectivity during baseflow the area is not likely to be disconnected even during extreme droughts. In fact, low runoff might even increase the concentrations of DOM in the outflow (Laudon et al., 2011).

Thus, future climate change might increase terrestrial CDOM production through positive feedback loops related to temperature, vegetation and soil decay. However, hydrological connectivity plays a key part in whether or not that CDOM will be exported to the lakes in the catchment. Therefore, it is likely that as a result of temperature rise and an increase in the frequency of drought large variations in CDOM concentrations will emerge between and within different years. Rewetting of soils after a dry year might increase DOM production and further the seasonal or annual differences, although increase in export to aquatic systems is thought to be marginal (Tank et al., 2018). This might have unexpected effects on downstream ecosystems. Greater variabilities in DOM concentrations and chemistry might complicate water treatment services, as different protocols might be needed for different situations.

Internal lake DOM processing (Paper V)

Paper V shows that the initial decay values of the DOM decreased as CDOM in the water increased and protein-like DOM decreased. The same pattern is seen in boreal clear- and brown-water lakes, which is linked to a decreasing share of labile autotrophic DOM (Koehler et al., 2012). Compared to other studies of lakes, the initial decay values were relatively high (Koehler et al., 2012; Mostovaya et al., 2016), possibly due to the high frequency measurements of the optical dissolved oxygen sensors used in this study. Another possibility is that the respiratory quotient assumed for this study (RQ = 1) was wrong, leading to slightly higher decay estimates. However, higher temporal resolution of decay measurements do allow for the detection of the most labile DOM fractions present only at the start of the incubations (Guillemette and del Giorgio, 2011; Pollard, 2013). After a few days the decay values decreased to within the range of the expected reactivity in lakes (Mostovaya et al., 2016).

Under dark biodegradation, both CDOM and FDOM were consistently produced as DOM was decomposed (**paper V**). Of the six components found in the study, only one humic-like component was degraded. Furthermore, a trend was seen between ambient CDOM concentrations and the production or degradation of FDOM components. In lakes with low terrestrial influence, FDOM production has been found before (Fox et al., 2017). In temperate lakes, both protein and humic-like FDOM production was seen at low CDOM concentrations, however after CDOM passed the threshold of 2 m^{-1}, the microbial decay shifted and FDOM was net consumed (Guillemette and del Giorgio, 2012). In this study, no such general shift can be seen. The production of the protein-like component decreased as CDOM increased although it never shifted to net consumption. The production of three out of five humic-like components showed increases as ambient CDOM was larger. Of the other two components one didn't show any trend with CDOM and the other was the only component that consistently was degraded. For the latter, the consumption increased with

larger CDOM concentrations. This shows that the FDOM regulation of arctic lakes is considerably different compared to temperate lakes.

Surprisingly, not only the FDOM but also the larger CDOM pool was systematically produced, although no trend was seen with between CDOM production and concentration. As a result, its relative importance was highest in the clearest lakes. Although microbial CDOM production is known to exist (Tranvik, 1993; Shimotori et al., 2009), few observations have been made in laboratory studies (Berggren et al., 2018). Both CDOM and FDOM production were high enough to have a significant effect on its internal regulation, theoretically leading to its renewal within 2 months. As such, it could be possible that CDOM regulations in sub-arctic lakes with a high residence time and low terrestrial influence is done internally through microbial production and subsequent photo-degradation (Cory et al., 2014) of the CDOM. However, whether the microbial community reacts in the same way in situ remains an unanswered question and as such more research is needed in order to translate these laboratory findings to the field. These results show that assuming the terrestrial origin of certain CDOM and FDOM components might not always work as internal production is possible under certain situations.

The sub-arctic lakes in the region are sensitive to climate induced changes (Vincent et al., 2012) and at risk of brownification as a result of increased terrestrial carbon export from the surrounding catchments (Wauthy et al., 2018). The results indicate that as lakes receive more terrestrial CDOM, the internal production of certain FDOM components normally associated with terrestrial DOM increases. Regulation of both CDOM and FDOM components in sub-arctic lakes appears to be governed by different processes than the lakes in the boreal or temperature region. As such, climate induced changes in the carbon cycling of these lakes might lead to unexpected consequences, one of which might be a positive feedback loop on the browning of sub-arctic lakes.

Concluding remarks and outlook

In this thesis the production, chemistry and reactivity of terrestrial sources of DOM were investigated in a systematic way in order to enhance the understanding DOM dynamics in terrestrial and aquatic systems.

The results presented in **paper I** show that the understory vegetation plays a key role in the production of litter leached reactive DOC at the forest stand level. The species *V. myrtillus*, constituting a minority of total litterfall, was responsible for more than half of the initial litter DOC leaching. As DOC leaching decreased exponentially with litter decay for the deciduous species, the influence of these high producing DOC litter species decreases as litter decay furthers. The leaching of DOC from litter is an important process affecting SOM buildup, indicating that the standing biomass and composition of the understory may play a bigger role in long term soil carbon sequestration than previously thought. The exact manner in which future changes in understory composition will affect the carbon sequestration of boreal soils in light of these results is unknown, however an increase can be expected as a result of increased shrub vegetation.

Highly reactive litter, *i.e. V. myrtillus*, produced more bio-available DOM at the start of the litter decay, followed by a decrease in bio-availability as decay progressed (**paper I & II**). Simultaneously, the DOM chemistry of high reactive litter showed greater changes as litter decomposition furthered. High reactive species specifically leached more oxidized phenolic compounds during early litter decay, indicating lignin degradation occurring at greater rates than for the low reactive litter species. These oxidized phenolic compounds proved to be highly biodegradable, leading to increased microbial processing of DOM. In general, throughout the 180 days of DOM incubation, the chemistry of DOM changed significantly and led to a unidirectional change for all litter species leachates, resulting in increased similarities between species. These results might explain why litter leachates, which are known to be major contributors to soil organic matter, loose their chemical characteristics so quickly after being leached into soils resulting in little effect of litter species on soil DOM chemistry. Future research could focus on how leachate chemistry affects soil carbon sequestration and respiration processes in the boreal ecosystem, especially in regard

with high reactive and understory species.

In **paper III** I show that roughly a third of the water extractable (WE-)DOC in subsoils of boreal podzols consists of aged (1000 yr) labile carbon. Podzols are the dominating soil type in the boreal forest and leaching from subsoil layers can lead to lateral transport of DOC to aquatic ecosystems. Moreover, the aged WEDOC fraction cannot be readily detected in bulk ^{14}C measurements as enriched modern carbon following the 1950s and 60s nuclear bomb testing masks its existence. As a result, the masking effect in combination with the high lability of aged soil WEDOC, suggest that the risk for aged carbon mobilization has previously gone undetected. This has important implications for predicting climate carbon feedback and the future carbon balance of the boreal forest. Other methods of separation between aged and nuclear DOM should be sought out in order to more accurately measure and monitor the terrestrial export of aged DOM.

Extreme drought results in a decrease of CDOM concentrations in lakes across the Scandinavian region (**paper IV**). This effect is greater in larger lakes, indicating that hydrological disconnection and subsequent dilution by groundwater flow is the main process explaining this decrease. Regulation patterns of climate and catchment variables differed between a normal and dry year. During normal conditions, climate was the most important factor explaining lake CDOM concentrations, although land cover and catchment morphology were also relevant. Temperature increases CDOM concentrations, likely through higher terrestrial DOM production in the catchment. However, in a dry year temperature had less effect and CDOM concentrations could be explained to a less degree climate and catchment variables overall. These results show the importance of climate change on CDOM export from terrestrial to aquatic ecosystems. As drought becomes more frequent, the variation in CDOM concentrations downstream will increase between years or even seasons. This can have unexpected ecological consequences on downstream ecosystems. In addition, variation in CDOM might complicate water treatment services as treatment plans are usually operating at certain constant and predictable concentrations.

Paper V shows that the internal regulation of mountainous sub-arctic lakes is noticeably different than in temperate lakes. The systematic production of CDOM and FDOM in the lakes show that CDOM concentrations might be regulated by internal CDOM dynamics. This shows that the assumed terrestrial origin of CDOM might not hold in all environments. Moreover, increased CDOM concentrations had different effects on FDOM production and degradation. While increased CDOM concentrations result in a decrease of bacterial CDOM productions, there were FDOM components that showed increasing production. How these results affect in situ regulations remains unknown. Future research could look at whether a shift in FDOM regulation is seen at even higher CDOM concentrations.

Hydrological connectivity, vegetation composition and density, and temperature are all predicted to drastically change across the boreal region in the coming decades. Combined, the results presented here show numerous ways in which DOM dynamics might change as a consequence of these alterations. Changes might cause an intensified DOM cycle, leading to both increased greenhouse gas emissions as aged carbon is lost from soils, and increased carbon sequestration as more the DOM flux from litter to soils increases. Meanwhile, DOM concentrations in recipient waters can be expected to become more variable as both external and internal regulations shift to the new hydrological regimes. There is urgency not just in understanding how all DOM processes interact with each other, but also in developing better tools to track DOM across the terrestrial – aquatic interface in order to accurately predict future changes in DOM regulation.

In summary:

- The understory vegetation plays a key role in the deliverance of litter derived DOM to boreal soils (**paper I**)
- The chemistry of DOM leachates is governed by litter reactivity, high reactive litter leachates are more bioavailable and have a high proportion of lignin derived labile compounds (**paper II**)
- Roughly a third of water extractable DOM from boreal subsoils consists of aged carbon, the detection of which is masked by nuclear DOM (**paper III**).
- Extreme drought decreases CDOM concentrations and its regulation by catchment and climate variables (**paper IV**)
- CDOM is systematically produced in low carbon sub-arctic lakes, showing the importance of internal regulation for a compound thought to be terrestrial (**paper V**)

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