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Reactive dissolved organic carbon dynamics in a changing environment

Experimental evidence from soil and water

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Reactive dissolved organic carbon
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DEPARTMENT OF PHYSICAL GEOGRAPHY AND ECOSYSTEM SCIENCE | LUND UNIVERSITY



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in a changing environment

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Experimental evidence from soil and water

Balathandayuthabani Panneer Selvam



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DOCTORAL DISSERTATION

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Faculty opponent is Professor Nigel Roulet
McGill University, Canada

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<p>Title and subtitle: Reactive dissolved organic carbon dynamics in a changing environment: Experimental evidence from soil and water</p>		
<p>Abstract</p> <p>Dissolved organic carbon (DOC) is the major form of organic carbon in aquatic ecosystems. Biological and photochemical degradation of DOC are major causes of greenhouse gas emissions from aquatic ecosystems. In response to current changes in climate, studies at different northern-hemisphere locations have shown both increases and decreases in total DOC export from land to water. However, there is lack of knowledge on the effect of changing environmental conditions on bio- and photo-degradation potentials. Therefore, this thesis aimed to combine empirical and experimental methods to determine the dynamics of DOC reactivity in response to key environmental parameters related to soil frost conditions and hydrology. I collected samples from the boreal region to carry out laboratory degradation experiments and to analyze the DOC degradation potentials in relation to environmental variables and intrinsic properties of the DOC.</p> <p>In a boreal forest region that has seasonal soil frost, the DOC bio-reactivity decreased with experimental reductions in the extent and duration of soil frost, while photo-reactivity remained constant. However, DOC from experimentally thawed permafrost peat in the subarctic north showed higher bio- and photo-degradation potentials than the DOC from active peat layers above the permafrost. The nature of the soil and intrinsic DOC properties explained these patterns in soil DOC reactivity. In the surface water network, bio-degradation was the dominant DOC degradation mechanism in brow-water lakes, while photo-degradation played a relatively larger role in clearer waters. The surface water photo-reactivity per unit of light absorption was high at both acidic and at alkaline conditions, while lower at intermediate pH, probably due to effects of the protonation state of DOC on photo-reactivity. Therefore, pH change along the aquatic network caused control on the photo-reactivity at the landscape scale.</p> <p>In conclusion the results show that climate warming decreases the export of bio-reactive DOC in a boreal forest, but it likely increases the export of bio- and photo-reactive DOC in a permafrost peatland. In a wetter climate with shorter residence times, clear waters may experience browning and relative shift from photo-degradation to bio-degradation, while already brown lakes will remain brown and dominated by bio-degradation. Furthermore, the loss of photo reactive DOC during transport in aquatic network may be counter balanced by the changes in extrinsic variables such as pH.</p>		
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Experimental evidence from soil and water

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List of papers

- Paper I** Panneer Selvam, B., Laudon, H., Guillemette, F. & Berggren, M. 2016. Influence of soil frost on the character and degradability of dissolved organic carbon in boreal forest soils. *Journal of Geophysical Research: Biogeosciences* 121, 829-840.
- Paper II** Panneer Selvam, B., Lapierre, J. F., Guillemette, F., Voigt, C., Lamprecht, R. E., Biasi, C., Christensen, T. R., Martikainen, P. J. & Berggren, M. Effect of permafrost thawing on degradation potentials of dissolved organic carbon (DOC) from palsas mire. *In review: Scientific Reports*.
- Paper III** Panneer Selvam, B., Lapierre, J. F., Soares, A. R. A., Karlsson, J., Bastviken, D. & Berggren, M. Photo-reactivity of dissolved organic carbon in the freshwater continuum. *Manuscript*.
- Paper IV** Berggren, M., Klaus, M., Panneer Selvam, B., Ström, L., Laudon, H., Jansson, M. & Karlsson, J. Effects of water residence time on color and dissolved organic carbon properties in unproductive lakes. *In review: Limnology and Oceanography*.

List of contributions

Paper I, II, III. The author was involved in planning the study. The author was responsible for data analysis, led the writing of the manuscripts and carried out most of the field and laboratory work.

Paper IV. The author was involved in the data analysis, writing of the manuscript and carried out most of the lab work.

Additional publications

In addition to the above, the author has contributed to the following publications, which are not included in this thesis.

1. Panneer Selvam, B., Natchimuthu, S., Arunachalam, L. & Bastviken, D. 2014. Methane and carbon dioxide emissions from inland waters in India - implications for large scale greenhouse gas balances. *Global Change Biology*, 20, 3397-3407.
2. Natchimuthu, S., Panneer Selvam, B. & Bastviken, D. 2014. Influence of weather variables on methane and carbon dioxide flux from a shallow pond. *Biogeochemistry*, 119, 403-413.

Abstract

Dissolved organic carbon (DOC) is the major form of organic carbon in aquatic ecosystems. Biological and photochemical degradation of DOC are major causes of greenhouse gas emissions from aquatic ecosystems. In response to current changes in climate, studies at different northern-hemisphere locations have shown both increases and decreases in total DOC export from land to water. However, there is lack of knowledge on the effect of changing environmental conditions on bio- and photo-degradation potentials. Therefore, this thesis aimed to combine empirical and experimental methods to determine the dynamics of DOC reactivity in response to key environmental parameters related to soil frost conditions and hydrology. I collected samples from the boreal region to carry out laboratory degradation experiments and to analyze the DOC degradation potentials in relation to environmental variables and intrinsic properties of the DOC.

In a boreal forest region that has seasonal soil frost, the DOC bio-reactivity decreased with experimental reductions in the extent and duration of soil frost, while photo-reactivity remained constant. However, DOC from experimentally thawed permafrost peat in the subarctic north showed higher bio- and photo-degradation potentials than the DOC from active peat layers above the permafrost. The nature of the soil and intrinsic DOC properties explained these patterns in soil DOC reactivity. In the surface water network, bio-degradation was the dominant DOC degradation mechanism in brown-water lakes, while photo-degradation played a relatively larger role in clearer waters. The surface water photo-reactivity per unit of light absorption was high at both acidic and at alkaline conditions, while lower at intermediate pH, probably due to effects of the protonation state of DOC on photo-reactivity. Therefore, pH change along the aquatic network caused extrinsic control on the photo-reactivity at the landscape scale.

In conclusion the results show that climate warming decreases the export of bio-reactive DOC in a boreal forest, but it likely increases the export of bio- and photo-reactive DOC in a permafrost peatland. In a wetter climate with shorter residence times, clear waters may experience browning and relative shift from photo-degradation to bio-degradation, while already brown lakes will remain brown and dominated by bio-degradation. Furthermore, the loss of photo reactive DOC during transport in aquatic network may be counter balanced by the changes in extrinsic variables such as pH.

Keywords: Dissolved organic carbon, photo-degradation, bio-degradation, global warming, intrinsic properties of DOC, extrinsic variables, DOC composition

Sammanfattning

Löst organiskt kol (DOC) är den huvudsakliga formen av organiskt kol i vattenekosystem. Biologisk och fotokemisk nedbrytning av löst organiskt kol (DOC) är viktiga orsaker till utsläpp av växthusgaser från akvatiska ekosystem. Enligt studier vid olika platser på norra halvklotet så kan pågående klimatförändringar orsaka både ökning och minskningar i total DOC-export från mark till vatten. Det finns dock kunskapsbrist om effekterna av förändrade miljöförhållanden på DOC-reaktivitet (bio- och fotonedbrytningspotentialer). Därför syftade avhandlingen till att kombinera empiriska och experimentella metoder för att bestämma dynamiken i DOC-reaktivitet orsakad av förändringar i viktiga miljöparametrar kopplade till markfrostförhållanden och hydrologi. Jag samlade prover från olika delar av den boreala regionen för att utföra laboratorienedbrytningsexperiment och analysera DOC-nedbrytningspotentialer i förhållande till miljövariabler och intrinsiska (inneboende) egenskaper hos DOC.

I en boreal region med säsongstjäle så minskade DOC-bioreaktivitet med reduktioner av tjälens utbredning och varaktighet, medan fotoreaktiviteten var oförändrad. Dock så uppvisade DOC från experimentellt upptinat permafrosttorv i subarktiska områden högre bio- och fotoreaktivitet än DOC från aktiva torvlager ovanför permafrosten. Marktyp och skillnader i intrinsiska DOC-egenskaper kunde förklara dessa skillnader i DOC-reaktivitet. I ytvattens så var biologisk nedbrytning den dominerande mekanismen för DOC-nedbrytning i bruna sjöar, medan fotonedbrytning spelade en relativt större roll i klara vatten. Fotoreaktivitet per enhet ljusabsorption var hög både vid både sura och alkaliska förhållanden, medan lägre fotoreaktivitet uppvisades vid intermediärt pH, troligen på grund av effekterna av DOC-protoneringstillstånd på fotoreaktivitet. Således orsakade pH-förändring längs sötvattenskontinuet en extrinsisk kontroll av fotoreaktivitet på landskapsnivå.

Sammanfattningsvis visar resultaten att klimatuppvärmning minskar exporten av bio-reaktivt DOC i en boreal skog, men det ökar sannolikt exporten av bio- och fotoreaktivt DOC i torvmark med tinande permafrost. I ett fuktigare klimat med kortare vattenuppehållstider så kan vattnet bli brunare och en förskjutning ske i den relativa betydelsen av fotonedbrytning respektive biologisk nedbrytning, medan redan bruna sjöar förblir bruna och dominerade av biologisk nedbrytning. Vidare så kan förlusten av fotoreaktivt DOC under transport i sötvattensnätverket uppvägas av förändringar i extrinsiska variabler såsom pH.

1. Introduction

Inland waters occupy ca 3% of the global land area [Likens, 2009] but they emit as much as 1.2–2.1 Pg C yr⁻¹ (1 Pg = 10¹⁵ g) of carbon dioxide (CO₂) [Aufdenkampe *et al.*, 2011; Raymond *et al.*, 2013] and 0.65 Pg of C (CO₂ equivalent) yr⁻¹ in the form of methane (CH₄) [Bastviken *et al.*, 2011] to the atmosphere. Inland waters are often supersaturated with CO₂ [Cole *et al.*, 1994; Raymond *et al.*, 2013] due to inflow of CO₂ saturated water from groundwater and bacterial as well as photochemical degradation of dissolved organic carbon (DOC) in the aquatic ecosystems.

Organic carbon which passes through 0.45 µm filter is called DOC and represents a complex mixture of organic compounds ranging from simple molecules such as amino acids to highly complex humic acids [Stubbins *et al.*, 2014]. Measured with classical ultrafiltration techniques, DOC molecules and molecular aggregates typically have a weight that varies from 100 to 100,000 dalton (Da) [Aitkenhead-Peterson *et al.*, 2003], although new ultra-high resolution mass spectroscopy suggests that the single DOC molecules are not larger than 1000 Da [Stubbins *et al.*, 2014]. DOC is the major form of organic carbon in aquatic ecosystems [Findlay and Sinsabaugh, 2003], mediating the availability of nutrients for aquatic food webs [Findlay and Sinsabaugh, 2003; Karlsson *et al.*, 2012]. The DOC has effects on optical properties in freshwaters [Creed *et al.*, 2015], alters the acidity [Valinia *et al.*, 2014] and transports metals and organic pollutants [Shafer *et al.*, 1997; Dawson *et al.*, 2009]. Therefore, DOC plays an important role in the biogeochemistry of aquatic ecosystems.

In northern latitudes, several studies have found increased DOC concentrations in the surface waters over the last decades. This is likely due to changes in land use [Garnett *et al.*, 2000] and to a decrease in anthropogenic sulphur deposition which makes the soils release more DOC to the aquatic ecosystems [Roulet and Moore, 2006; Monteith *et al.*, 2007]. Furthermore, the increase in surface air temperature triggers permafrost thawing which generally leads to increase in the DOC concentration of the surface waters [Frey and Smith, 2005], although there are exceptions [Walvoord and Striegl, 2007; Olefeldt and Roulet, 2012]. Since DOC plays a substantial role in the biogeochemistry of aquatic ecosystems, any change in the DOC export to aquatic ecosystems could have large effects on the food web structure and on the carbon cycle of aquatic ecosystems.

1.1 Reactivity of DOC in the aquatic ecosystems

The fate of DOC that reaches the aquatic ecosystems is sedimentation, downstream transport or bio- and photo-degradation. Reactivity is an operational concept defined as the amount of DOC degraded by microbes [*del Giorgio and Davis, 2003*] or ultraviolet (UV) light [*Amon and Benner, 1996*] usually during one week of a bioassay (laboratory incubation trial) or in response to a certain experimental light dose. Different types of DOC sources are known to represent systematically different patterns in reactivity. For example, freshwater DOC of low molecular weight is often bio-reactive whereas high molecular weight DOC generally has high photo-reactivity [*Benner and Kaiser, 2011*]. In addition to the intrinsic chemical properties of the DOC, extrinsic variables such as temperature, pH, Fe (Iron) and NO₃ (Nitrate) have also been found to influence both bio- and photo-reactivity in various ways [*Pace et al., 2011; Kreyling et al., 2013; Porcal et al., 2014*]. DOC reactivity is strongly affecting the turnover rate of DOC and the carbon emissions from aquatic ecosystems to the air [*Vonk et al., 2013; Cory et al., 2014*].

1.2 Bacterial metabolism

Bio-degradation is the process of DOC degradation by microbes, mainly bacteria. The degraded DOC can be utilized for microbial cell growth (bacterial production) or be transformed into CO₂ through bacterial respiration. From these processes, bacterial growth efficiency is calculated as the ratio between bacterial production and the total carbon assimilation (bacterial production plus respiration). The term ‘bio-reactivity’ is operational, but typically used to denote DOC which has a potential to be degraded into CO₂ under certain conditions.

Macrophytes and algae are major contributors of bio-reactive DOC to aquatic ecosystems, often of low molecular weight [*Baines and Pace, 1991; Münster, 1993; Bertilsson and Jones Jr, 2003*]. Furthermore, terrestrial export of allochthonous DOC of variable molecular weight has also been found to contribute substantially to the bio-reactive DOC [*Vonk et al., 2013; Mann et al., 2015*]. Nonetheless, freshwater bacteria tend to preferentially assimilate low molecular weight fractions of the DOC pool in a given sample [*Benner and Kaiser, 2011*]. Interestingly, *Guillemette and del Giorgio* [2012] found that when bacteria consume low-molecular weight DOC they simultaneously produce high molecular weight DOC which could undergo photo-degradation later in the aquatic

continuum process. In addition to the influence of DOC source and composition on bio-reactivity, extrinsic factors such as temperature and nutrients are known to be of importance for the bacterial metabolism. In general, higher shares of the DOC are bio-reactive at a higher temperature. Moreover, *Berggren et al.* [2010] found high bacterial growth efficiency at low incubation temperature combined with high inorganic nutrient concentrations.

The bio-degradation plays a major role in carbon mineralization and CO₂ emissions from aquatic ecosystems. *Berggren et al.* [2012] found that bacterial respiration in epilimnion (surface of the lakes) alone could amount to approximately 70% of the CO₂ emission from lakes. Boreal and arctic regions are rich in surface waters and global warming could potentially increase the export of bio-degradable DOC from terrestrial to aquatic ecosystems [*Vonk et al.*, 2013], leading to increased CO₂ emission from aquatic ecosystems in northern latitudes.

1.3 Photochemical degradation

The process of DOC degradation by sunlight is called photochemical degradation. The DOC photo-degradation produces carbon monoxide, low molecular weight substances, partially oxidized DOC and CO₂ [*Zafiriou et al.*, 1984; *Cory et al.*, 2010a; *Cory et al.*, 2014]. High molecular weight DOC such as humic substances is generally more susceptible to photo-degradation than the low molecular weight DOC [*Benner and Kaiser*, 2011]. Photo-reactivity is an operational term describing the potential of DOC to be degraded into CO₂ during given experimental conditions.

Humic substances represent fraction of colored DOC (CDOM) which absorbs UV irradiation more effectively than non-colored DOC. However, also the non-colored DOC absorbs UV irradiation but at a shorter wavelength (<250 nm) [*Mopper et al.*, 1991; *Dahlén et al.*, 1996; *Mostofa et al.*, 2013]. The CDOM effectively limits the penetration of UV irradiation in the water column. For example, in brown-water lakes the light penetration is limited to the water surface, hence the photo-degradation occurs pre-dominantly in the epilimnion. However, in clear water lakes the sunlight penetrates deep in the water column and the photo-degradation occurs in the whole water column [*Koehler et al.*, 2014].

Koehler et al. [2014] estimated that up to 10% of the greenhouse gas emission from lakes comes from the photo-oxidation, globally. However, the DOC photo-degradation rate depends substantially upon the geographical location, season, intrinsic properties of DOC and other extrinsic factors. Therefore, the relative importance of photo-degradation is very variable. For example, sunlight degradation represented less than 3% of the DOC in the water column of a subtropical lagoon during May and July [*Ziegler and Benner*, 2000], but 70-95%

of the DOC in arctic lakes and rivers during summer [Cory *et al.*, 2014]. In arctic and boreal regions, global warming increases the formation of thermokarst lakes and it also increases the export of DOC to the aquatic ecosystems [Frey and Smith, 2005; Jorgenson and Osterkamp, 2005; Frey and McClelland, 2009]. Further, the duration of sunlight is longer during summer in arctic compared to in tropical countries. Hence, there is a high potential for the DOC which has been stored in permafrost soil for millennia to get photodegraded and emitted as CO₂ to the atmosphere in arctic conditions.

In addition to the source and composition of DOC, extrinsic variables such as pH and Fe influence DOC photo-degradation [Porcal *et al.*, 2014]. Pace *et al.* [2011] showed that at alkaline conditions the DOC photo bleaching increases due to the physical expansion of DOC polymers and colloids in 3D space in response to deprotonation of carboxylic groups which expose the chromophores to UV irradiation. Furthermore, also at the low-end of the pH scale the photo-degradation of DOC increases due to an increase in the efficiency of low wavelength light absorption by the DOC in its compact protonated state [Bloom and Leenheer, 1989; Porcal *et al.*, 2014].

Most of the studies that have analyzed the photo-reactivity of DOC in freshwaters have looked at the quantity of DOC degraded by the UV irradiation and not the DOC degradation rate per unit irradiation energy absorbed (PD-E_w). The PD-E_w shows the quantity of DOC degraded per unit of irradiation energy absorbed. Given that the total cumulative UV light absorption in the water column is similar in lakes with different DOC and CDOM concentrations, the absorption specific photo-reactivity is key to explaining differences in total photo-mineralization between natural freshwater sites [Koehler *et al.*, 2014].

1.4 Environmental change impact on bio- and photo-degradation

It is increasingly recognized that riparian soils play an important role in the quantity, quality and origin of DOC delivered to aquatic ecosystems [Seibert *et al.*, 2009; Haei *et al.*, 2012; Dick *et al.*, 2014]. Campbell *et al.* [2010] found that duration of soil frost will likely decrease in the future due to increase in surface temperature, and therefore it could be hypothesized that processes that regulate the quantity and composition of the exported DOC will be affected in a warmer climate. However, there is a lack of knowledge whether or not the soil frost in riparian zone may affect the export of bio- and photo-reactive DOC.

Similarly, there is a large knowledge gap with regard to the overall effect of peat permafrost thawing on DOC reactivity in recipient waters. Peatlands act as a

sink of carbon since Holocene and containing presently ca 277 Pg of organic carbon in their deposits [Post *et al.*, 1982; Harden *et al.*, 1992; Tarnocai *et al.*, 2009]. There is a substantial loss of carbon from peatlands due to increased decomposition [Tarnocai *et al.*, 2009] and change in soil carbon accumulation [Jorgenson *et al.*, 2013]. To my knowledge there is no study that concurrently analyzed the effect of environmental change on bio- and photo-degradation of DOC from permafrost peatlands.

Koehler *et al.* [2014] estimated the global greenhouse gas emissions from lake photo-oxidation. However, more systematic data along the aquatic network is required to evaluate the assumptions and to improve predictions of the fate of increasing loads of terrestrial DOC to inland waters. Further, most of the studies that have analyzed photo-degradation in freshwaters have addressed the absolute quantity of DOC degraded by UV irradiation. However, it is important to relate the photo-degradation rate to the amount of irradiation energy absorbed.

Water brownness plays important role in the biogeochemistry of aquatic carbon cycling. A recent study noted that the water brownness (absorbance at 440 nm) was proportional to increases in reactive DOC and ambient concentrations as well as CO₂ efflux [Lapierre *et al.*, 2013]. Although color of the water plays an important role in freshwater biogeochemistry, the variation in water color remains poorly understood in response to changes in water residence times.

1.5 Aim and objectives

The aim of this PhD project was to study the dynamics of reactive DOC in a changing environment. In order to conduct this study, I combined empirical and experimental methods. For paper I, an experiment in a boreal riparian zone was conducted to study the effect of winter soil frost on bio- and photo-degradation processes. For paper II, permafrost cores were collected from subarctic peatland and incubated in the laboratory to study the effect of permafrost thawing on bio- and photo-degradation processes. For the purpose of paper III, water samples were collected from different aquatic ecosystems across Sweden to study the spatial and temporal variation of PD-E_w. For paper IV, data was used from boreal lakes collected during 3-7 years per site to analyze photo- and bio-degradation in response to the dynamic (temporally variable) water residence times.

The research questions were:

1. How does seasonal soil frost affect the character and reactivity of DOC in boreal forest soils? (Paper I)
2. How does permafrost thawing affect the degradation potentials of DOC in palsas mire? (Paper II)
3. How does the PD- E_w of DOC vary during the freshwater transit from land to sea? (Paper III)
4. Does water residence time affects the color and the relative importance of different DOC degradation processes in lakes? (Paper IV)

2. Methodology

2.1 The study sites

Parts of the project (Papers I, III and IV) was conducted in the Krycklan catchment (64°14'N, 19°46'E) situated near Umeå, northern Sweden. The catchment is on average snow covered for 167 days/year (1981–2015). The mean winter soil frost depth was 19 cm (1992–2007), the mean maximum snow depth was 76 cm (1981–2015) and the mean annual air temperature was 1.8°C (1981–2010), as measured 1 km away from the study site in a reference climate station. The site is well studied in terms of hydrology [Laudon *et al.*, 2004], influence of soil frost regime on plants [Kreyling *et al.*, 2012], microbial communities [Haei *et al.*, 2011], cellulose degradation [Kreyling *et al.*, 2013] and mobilization of DOC [Haei *et al.*, 2010].

Additional samples were collected from the Skogaryd research catchment (Paper III) and Abisko (Paper III). The Skogaryd research catchment is located in the southwest of Sweden (58°22'N, 12°9'E), where the mean annual temperature was 7°C (1983-2013) and the mean annual precipitation was 910 mm (1983-2013) (SMHI – <http://luftwebb.smhi.se/>). Abisko is located in the northernmost parts of Sweden. The mean annual temperature of Abisko was -1°C (1961-1990) [Åkerman and Johansson, 2008] but Callaghan *et al.* [2010] reported that the mean annual temperature has risen above 0°C in the recent decade. Lakes and streams samples for paper III were collected from the above locations, but for rivers, samples were collected along a 1300 km north-south gradient. For more details of the sampling locations, please see the materials and methods section in paper III.

For paper II, I collected peatland permafrost cores from Peera palsa, which is a palsa mire near Kipisjärvi. Palsas are a characteristic of the discontinuous permafrost zone [Seppälä, 1997]. The age of the palsa mire in northern Finland is <1000 years [Seppälä, 2005], but peatland developed far earlier, ca. 8000-9000 years before present [Oksanen, 2006]. The palsa in this study site is at the starting stage of a collapse and is classified as a dome shaped and peat-cored palsa which rises ca. 3m above the surrounding peat [Seppälä, 1988; Gurney, 2001; Hofgaard, 2003]. For a more complete description of the sampling locations, please see the materials and methods sections of paper II.

2.2 In-situ field studies

2.2.1 Soil frost manipulation facility

The first study was conducted in an existing soil frost manipulation experiment which was initiated in 2002. Soil pore water for laboratory analyses (see section 2.3) was collected from five depths (10, 25, 40, 60 and 80 cm) using lysimeter from three soil frost treatments: deep soil frost, shallow soil frost and control plots. The plots are in triplicate ($3 \times 3 \text{ m}^2$), 3-5 m away from each other, distributed randomly, and the center of each plot was 3 m away from a small first order stream. Deep soil frost treatments were covered with a roof to prevent the accumulation of snow during winter which exposes the soil to air temperature. Shallow soil frost treatments were covered with water permeable geo textile bags filled with styrofoam pellets. The bags were placed prior to snowfall in November but removed during early snow melt in May. Control plots were untreated and exposed to ambient weather conditions (Figure 1). In late winter, snow was transferred to the treated plots to ensure the same water balance between all the plots. For more information, please see the materials and methods in Paper I.



Figure 1. Soil frost manipulation experiment in Krycklan catchment.

2.3 Laboratory methods

2.3.1 Photochemical Degradation

The photo-degradation (used in papers I, II, III and IV) was performed in 20 mL quartz vials with filtered water samples (Figure 2): 10 mL of the quartz vial was filled with the sample and the remaining 10 mL of the headspace was flushed with standard synthetic air mixture. Samples were kept on a spinning disc in a climate chamber to ensure a uniform exposure of light to all the samples. They were placed 40 cm below the UV lamps (Figure 2) where the radiation was $3.64\text{--}6.89\text{ Wm}^{-2}$ for UV-A and $0.06\text{--}0.1\text{ Wm}^{-2}$ for UV-B. The total energy received by the samples is roughly equal to the mean daytime radiation during summer in Sweden [Dahlén *et al.*, 1996]. For every sample, I prepared three to four vials, one or two vials as control and two vials for incubation. Samples were incubated under UV irradiation for 24-48 hours.

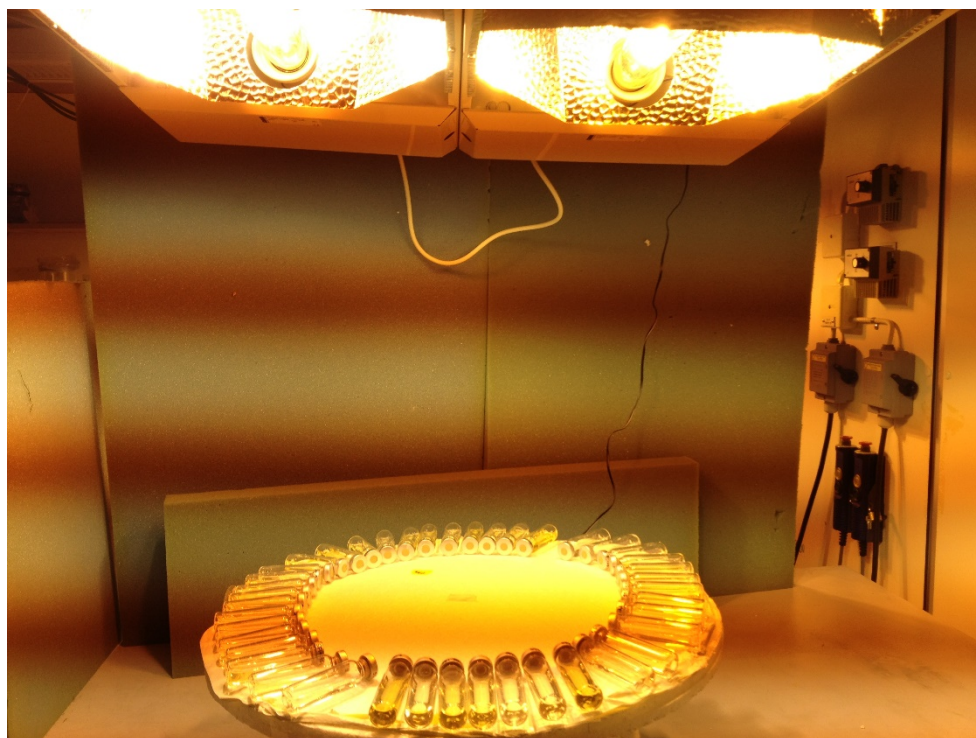


Figure 2. Water samples in quartz vials were incubated under UV lamps

Control vials were acidified immediately but the sample vials were acidified after incubation with light. After acidification samples were shaken for one minute and left 4 to 5 hours for equilibrium. Headspace CO₂ was measured by injecting at least 5 mL of headspace gas into an infrared gas analyzer. The DIC (dissolved inorganic carbon) that was produced during incubation was calculated as the difference between the DIC in UV treated and control samples. Since the photo-degradation rate is several fold (17 to 40) higher than the dark bacterial respiration, I assumed that there was only negligible influence of bacterial respiration on photo-degradation. The PD-E_w (Papers I, II and III) was calculated to quantify the DOC degraded per unit of irradiation energy absorbed. For more details of the calculation, please see methods descriptions in papers I, II and III.

2.3.2 Bacterial metabolism

Aliquots of incubated were used to measure bacterial production and bacterial respiration (Papers I, II and IV). Samples were incubated in dark condition at 20°C and bacterial production was measured at different time intervals using ³H-leucine incorporation method [Smith and Azam, 1992]. Samples for bacterial respiration were incubated at 20°C in dark condition for 7 to 450 days.

Bacterial respiration was assessed from consumption of dissolved oxygen (O₂) measured using non-invasive optical oxygen sensors. The slope of the linear regression lines of oxygen concentration versus time was converted to DOC consumption by assuming a respiratory quotient (RQ) of 1. Although the respiratory quotient has been shown to vary in some systems, for example in lakes [Cimblaris and Kalff, 1998; Berggren *et al.*, 2012], RQ of 1 is a standard and well-supported assumption for soils [Dilly, 2001]. In lakes, high RQs above 1 are mainly caused by recent light exposure [Allesson *et al.*, 2016], but the bioassays in this project were relatively long-term and dark (at least 1 week).

From bacterial production (BP) and bacterial respiration (BR) measurements, bacterial growth efficiency (BGE=BP/ [BP+BR]) and total bacterial carbon consumption (BCC=BP+BR) were calculated. The BGE determines the relative degree to which bio-degradable DOC fractions can sustain BP and is thus of ecological relevance, but in addition BGE tends to indirectly inform about the origin and composition of DOC [Berggren *et al.*, 2007].

2.4 Optical DOC characterization

The UV absorbance was measured from 200 nm to 800 nm using a 1 cm cuvette in a Varian Cary 50 Conc UV visible spectrophotometer (Papers I, II, III and IV). Excitation emission matrices (EEMs) were generated using a Cary Eclipse Fluorescence Spectrophotometer. Excitation was measured from 230 to 450 nm by 5 nm increment and the emission was measured from 260 to 600 nm by 2 nm increments. The EEMs were corrected for inner filter effect, instrument specific biases and further normalized to the Raman water peak using the FDOM correct toolbox developed for MATLAB [Murphy *et al.*, 2010].

From the corrected dataset fluorescence indices such as the fluorescence index (FI) [McKnight *et al.*, 2001; Cory *et al.*, 2010b], the freshness index (FRESH or β/α) [Parlanti *et al.*, 2000], and the humification index [Zsolnay *et al.*, 1999] were calculated (Papers I, II and III). Corrected EEMs were modeled using parallel factor analysis (PARAFAC) following the procedure in Murphy *et al.* [2013]. Core consistency [Bro and Kiers, 2003] and the split half validation method [Harshman, 1984] were used to assess the proper number of components (Papers I and II).

3. Results and Discussion

3.1 Impact of frost on degradation potentials of DOC (Papers I & II)

3.1.1 Seasonal soil frost (Paper I)

The treatments which had the shortest duration of soil frost (shallow soil frost) released significantly lower amount of DOC than the control and deep soil frost treatments, in the top soil layer. The top soil layer (10-40 cm) is referred to as unsaturated zone and the bottom soil layer (60-80 cm) is referred to as saturated zone. In the case of DOC composition, there were less clear difference between the treatments at any layer. However, an explorative redundancy data analysis (RDA) suggested that the deep soil frost treatments had higher loadings of tyrosine like substances (low molecular weight DOC) than the control and shallow soil frost treatments (Figure 3). This is likely due to the impact of soil frost, that causes microbial cell lysis and damage to the fine roots [*Tierney et al.*, 2001; *Austnes and Vestgarden*, 2008]. Further, *Kreyling et al.* [2012] showed that low temperature decreases cellulose degradation in the soil. Hence, the low molecular weight DOC produced in the deep soil frost treatments is subjected to less decomposition due to low temperatures in winter.

The high loadings of tyrosine-like substance in the deep soil frost treatments resulted in higher bacterial metabolic activities than the other two treatments, as indicated by the RDA. Tyrosine-like substances are more quickly bio-degraded than the humic-like substances as indicated by the positive and negative relationship of bacterial metabolism with tyrosine and humic-like substances, respectively. In the case of photo-degradation, there was no significant difference between any treatments at any layers. However, the photo-degradation could be influenced by humic-like substance as indicated by the positive relationship of photo-degradation and different humus indicators. Further, the photo-degradation rate in the soil is approximately 4 times higher than the rate in boreal lakes [*Bertilsson and Tranvik*, 2000]. This is likely due to that the photodegradable DOC in the soils is more protected from sunlight than the DOC in surface waters.

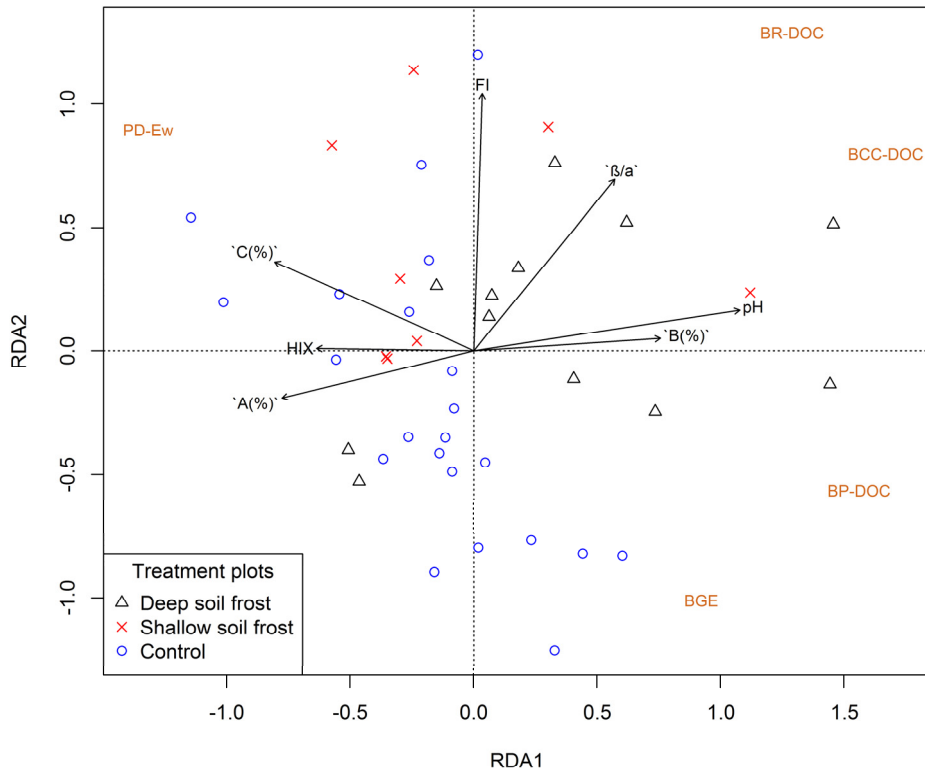


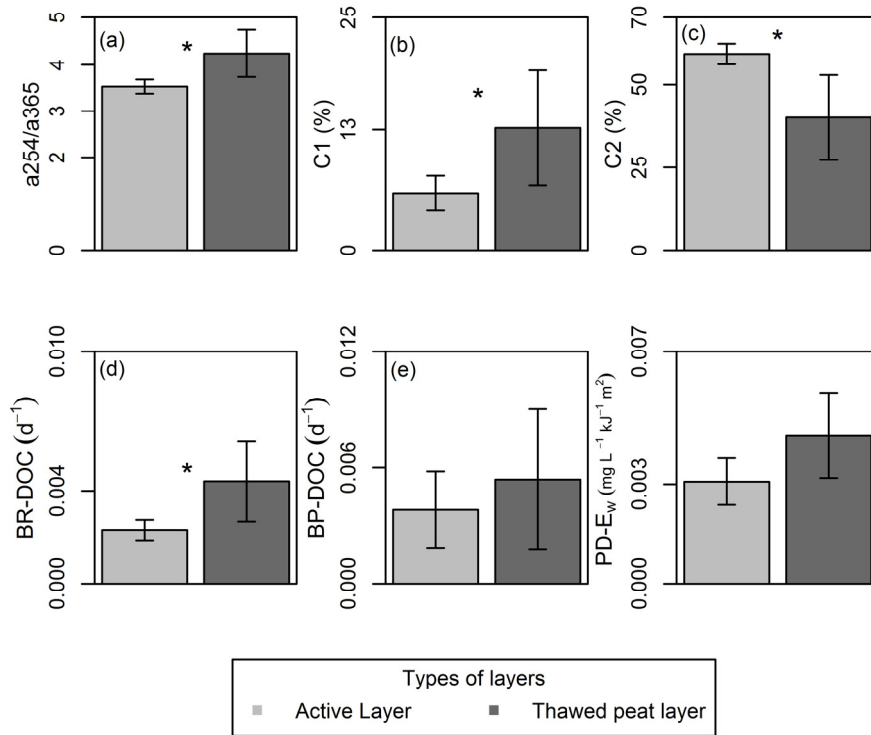
Figure3. Results from redundancy analysis (RDA) for the effects of DOC composition and pH on aspects of the biodegradability and photodegradability of DOC. Explanatory variable loadings are shown as arrows, while dependent variable scores are indicated by the center of the red text labels (BP-DOC, BR-DOC, BCC-DOC, BGE and PD-Ew). Note that most of these explanatory variables are normalized to (divided by) DOC. The BP-DOC has been log transformed prior to analysis to attain normality. Site scores for different types of treatments are shown by symbols: open triangle for deep soil frost, cross for shallow soil frost and open circle for control soil frost. Site scores and dependent variable scores are scaled by a factor of 3 for clarity purposes.

3.1.2 Permafrost (Paper II)

The peat-permafrost and active layer showed significant differences in the key optical properties and in the degradability of DOC. Similar to in the riparian zone (Paper I), the observed DOC concentrations were high compared to the DOC concentrations in lakes (Paper IV). The peat-permafrost had significantly higher low-molecular weight DOC than the active layer, as indicated by high values on the absorption ratio (a_{254}/a_{365}) (Figure 4). This is likely due to the fact that the peat characteristics are different in the different layers of the soil. The peat on the surface of the soil originated from different plant species than the peat from the permafrost [Seppälä, 1988]. Further, the fermentation process that occurs in the permafrost soils could release high quantity of low molecular weight substance such as acetate [Ewing *et al.*, 2015].

These differences in DOC composition were reflected in a higher bio-degradability in peat permafrost than in the active layer. Bacterial respiration was significantly higher in the peat-permafrost derived DOC than in DOC from the active layer (Figure 4). However, bacterial production and bacterial growth efficiency showed no significant difference between active layer and peat-permafrost, suggesting that DOC released from the thawed peat layer may not affect aquatic food webs in a qualitatively different way compared to DOC from the active layer. Nonetheless, compared to bio-degradation rate of DOC from yedoma soils, the bio-degradation rate in peat soil is lower [Vonk *et al.*, 2013; Spencer *et al.*, 2015]. This is likely due to the differences in the nature of the soil and DOM composition.

The active layer showed significantly higher values on humic-like fluorescence component C2 than the peat-permafrost and humic substances are susceptible to photo-degradation [Benner and Kaiser, 2011]. Nonetheless, the peat permafrost DOC showed significantly higher photo-degradation than DOC from the active layer (Figure 4). This is likely due to the presence of significantly higher values on the humic-like fluorescence component C1 in peat permafrost compared to the active layer. The fluorescence component C1 has previously been found to correlate with chemical compounds which has higher aromaticity [Stubbins *et al.*, 2014]. Therefore, the peat-permafrost showed significantly higher photo-degradation than the active layer. Overall, the DOC from peat-permafrost showed higher bio- and photo-degradability than the DOC from active layer.



*significantly different (p<0.05)

Figure 4. DOC composition and degradation in peat-permafrost (n=8) and active layer (n=8). The plots a) absorption ratio, b) humic-like fluorescence component (C1), c) humic-like fluorescence component (C2), d) bacterial respiration (BR-DOC), e) bacterial production (BP-DOC) and f) DOC degradation rate per unit of irradiation energy absorbed (PD-E_w). Error bars indicate standard deviation of the mean.

3.2 PD-E_w variation in aquatic network (Paper III)

Large rivers, which represent the extreme end members of the land-water continuum had significantly higher DOC degradation rates per unit of irradiation absorbed (PD-E_w) compared to most of the other aquatic ecosystems (Figure 5). This stands in contrast to the previous studies that showed that DOC photo-degradation is reduced from headwater streams to rivers due to an increase in the cumulative exposure history of the DOC to sunlight and hence a reduction in the aromaticity of DOC. It is often believed that aromatic DOC effectively absorbs UV irradiation and hence has a higher photo-degradation. However, *Cory et al.* [2013] showed that the photo-bleaching of DOC is not correlated to SUVA₂₅₄ (specific ultraviolet absorbance at 254 nm). SUVA₂₅₄ is proportional to the aromaticity of DOC i.e. high molecular weight substances. Therefore, it is evident that the photo-degradation of DOC is not only influenced by the high molecular weight DOC.

Moreover I found a positive correlation between PD-E_w and absorption ratio (proportional low molecular weight DOC) which indicates that not only high molecular weight DOC but also low-molecular weight DOC influences the photo-degradation under certain environmental conditions. This explains the high PD-E_w in the rivers. Rivers had a significantly higher absorption ratio than other aquatic ecosystems; hence, higher PD-E_w than most of the other aquatic ecosystems.

A core result of this study is that extrinsic factors exert a control on the broad scale patterns in the photo-degradation of DOC. *Anesio and Granéli* [2003] noted high photo-degradation at low pH due to increase in the efficiency of UV absorption, but *Pace et al.* [2011] found high photo-bleaching at high pH also due to increase in the size of DOC and hence more exposure to UV irradiation. In this study pH varied from 3.7 to 7.6 and hence I captured both the effects resulting in a U-shaped relationship between pH and PD-E_w. River mouths had higher pH than other aquatic ecosystems hence the colored DOC was effectively removed from the river mouths. The absence of colored DOC and change in pH made low molecular weight DOC more photo-reactive.

In the case of samples that were incubated in the laboratory for 365 days, I noted no significant change in PD-E_w but significant decreases in the absorption ratio between the start to the end of the incubation. It is likely due to the bacterial mineralization of DOC. *Guillemette and del Giorgio* [2012] found that bacteria consume low molecular weight DOC but simultaneously produces high molecular weight DOC, which is also photo-labile. In both the *in situ* and *ex situ* samples I observed no continuous significant decrease in photo-reactivity with increase in water residence time.

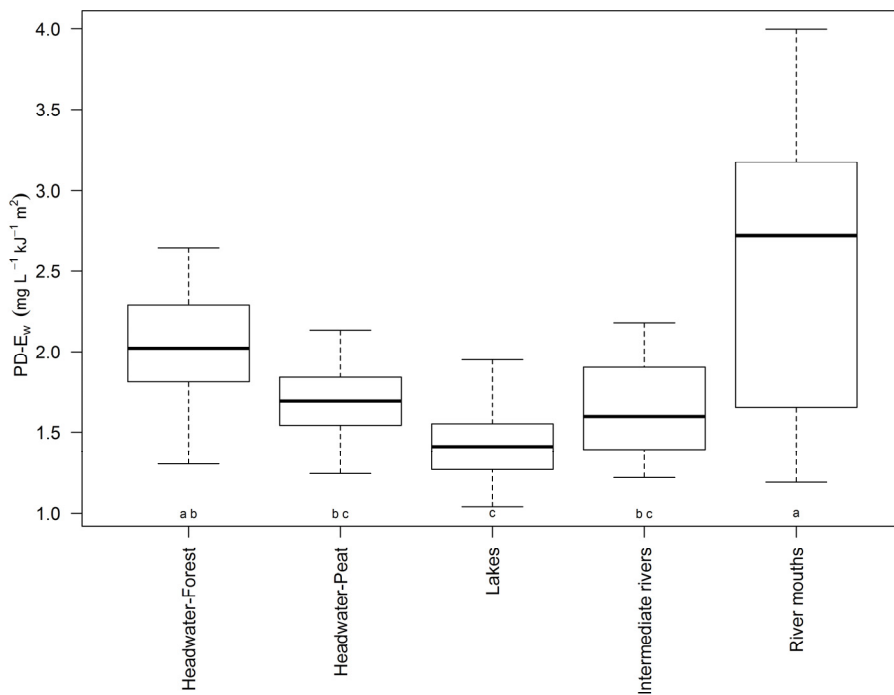


Figure 5. DOC degradation rate per unit of irradiation energy absorbed (PD-E_w) variation in different aquatic ecosystems. Outliers were removed for clarity of the plot. Each different letter indicates significant difference between the different aquatic ecosystems.

3.3 Impact of runoff and water residence time on lake brownness and DOC composition (Paper IV)

The mechanistic underpinnings of the changes in optical properties and concentration of DOC along freshwater continuum are incompletely understood. *Weyhenmeyer et al.* [2012] reported a decrease in brownness along the freshwater continuum due to selective removal of colored DOC, but *Creed et al.* [2015] argue that shifting color of the DOC may largely be caused by new DOC that is added downstream. From the robust data of Björntjärnarna brown-water catchment ($n = 277$), I found that the absorption coefficient at 420 nm (a_{420}), which is a measure of the brownness of the water, showed no significant change with increase in the water residence time (WRT). Furthermore, there was no selective removal of colored DOC with increase in WRT. This was further tested in other brown lakes and I noted no significant relationship between the change in brownness of the water and WRT in brownish lakes.

Nonetheless, in the epilimnion of clear water lakes I observed a significant decrease in the brownness with increase in the WRT. This is likely due to the photo-degradation of DOC, because colored DOC absorbs UV irradiation effectively from sunlight and breaks it down into low molecular weight DOC. Hence, the absorption ratio (a_{254}/a_{365}) which is proportional to low molecular weight DOC increased with increase in WRT. However, in most of the brown water lakes the a_{254}/a_{365} was decreasing with increase in WRT. Brown water lakes limit the penetration of sunlight into water column hence making the bacterial metabolism the dominant degradation mechanism. Since the sunlight could penetrate relatively deep in the clear water lakes, photo-degradation was the dominant mechanism in the clear water lakes.

Partly the same pattern was found in experimental samples which were incubated biologically in the dark for 450 days. After incubation at dark conditions, a_{254}/a_{365} significantly decreased but brownness per unit DOC actually increased similar to the field results in brown water lakes. In the samples which were incubated under UV irradiation, I found an opposite pattern; a_{254}/a_{365} was significantly increased but brownness per unit DOC decreased as in the clear water lakes *in situ*. This shows that the colored DOC in the brownish lakes was not selectively removed, but rather the low molecular weight non-colored DOC was selectively removed by bacterial metabolic activities. Since the photo-degradation dominates the degradation mechanism in clear water lakes, I noticed an opposite pattern to the brownish lakes, i.e. the brownness was reduced with increases in WRT.

3.4 Further research

Peatlands has since the Holocene acted as a sink of carbon and they export generally more DOC than forests [Post *et al.*, 1982; Harden *et al.*, 1992; Mattsson *et al.*, 2005; Creed *et al.*, 2008]. However, most of the studies that have analyzed the effect of permafrost thawing on DOC degradation potentials have been performed in mineral soils [Vonk *et al.*, 2013; Spencer *et al.*, 2015], in spite of the fact that peatlands are vulnerable to global warming and therefore important. Hence, more studies are recommended to be conducted in peat permafrost catchments to analyze the effect of peat permafrost thawing on DOC degradation potentials. Furthermore, most of the available literature has focused only on bio- or photo-degradation. Therefore, future studies should concurrently analyze bio- and photo-degradation to more clearly understand their relative roles in the carbon cycling of aquatic ecosystems.

Freshwaters studies have often investigated the influence of intrinsic properties of DOC on photo-degradation. However, there are not many studies that address the influence of extrinsic variables on DOC photo-degradation. Nonetheless, results from this thesis show that extrinsic variables have substantial influence on the DOC photo-degradation. Further, most of the studies that have analysed the effect of extrinsic variables are under laboratory conditions, but this thesis illustrates how important it is to study the effect of changing extrinsic variables on photo-degradation in the *in situ* aquatic network.

Rising brownness (a₄₄₀ nm) of the water has been found to cause increases in reactive DOC, total DOC concentration and in the efflux of CO₂ [Lapierre *et al.*, 2013]. However, the mechanistic underpinning of the interaction between brownness and biogeochemical processes, specifically bio- and photo-degradation, are not clearly understood. These interactions are important to understand in order to know the present and predict the future role of inland waters in a changing climate.

4. Conclusion

- The decrease in extent and duration of seasonal soil frost results in reductions of both the amount and biodegradability of the DOC which can be exported from soils.
- There was no clear evidence for the effect of seasonal soil frost on the export of photo-reactive DOC from soils.
- The concurrent analysis of bio- and photo-reactivity in a palsamire showed that the DOC from peat-permafrost is more bio- and photo-degradable than the DOC from active peat layers.
- DOC from peat-permafrost is highly reactive immediately upon thawing suggesting an efficient loss on its way to the nearby aquatic ecosystems.
- Large rivers, which represent the extreme end members of the land-water continuum had significantly higher PD- E_w than most of the other aquatic ecosystems. Hence, rivers act as a potential contributor of photo-reactive non-humic recently produced DOC to coastal areas.
- The theoretical (potential) loss of photo-reactive DOC during freshwater transit is offset by the changes in extrinsic variables such as pH and the downstream addition of new sources of photo reactive DOC.
- Brown-water lakes may not get browner due to temporal increases in discharge during wetter climatic condition, although relatively clear lakes could get browner. Further, bio-degradation was the dominant DOC degradation mechanism in brown-water lakes, while photo-degradation played a relatively larger role in clearer waters.

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