Changing land cover as a driver of surface water browning

Skerlep, Martin

2021

Document Version:
Publisher's PDF, also known as Version of record

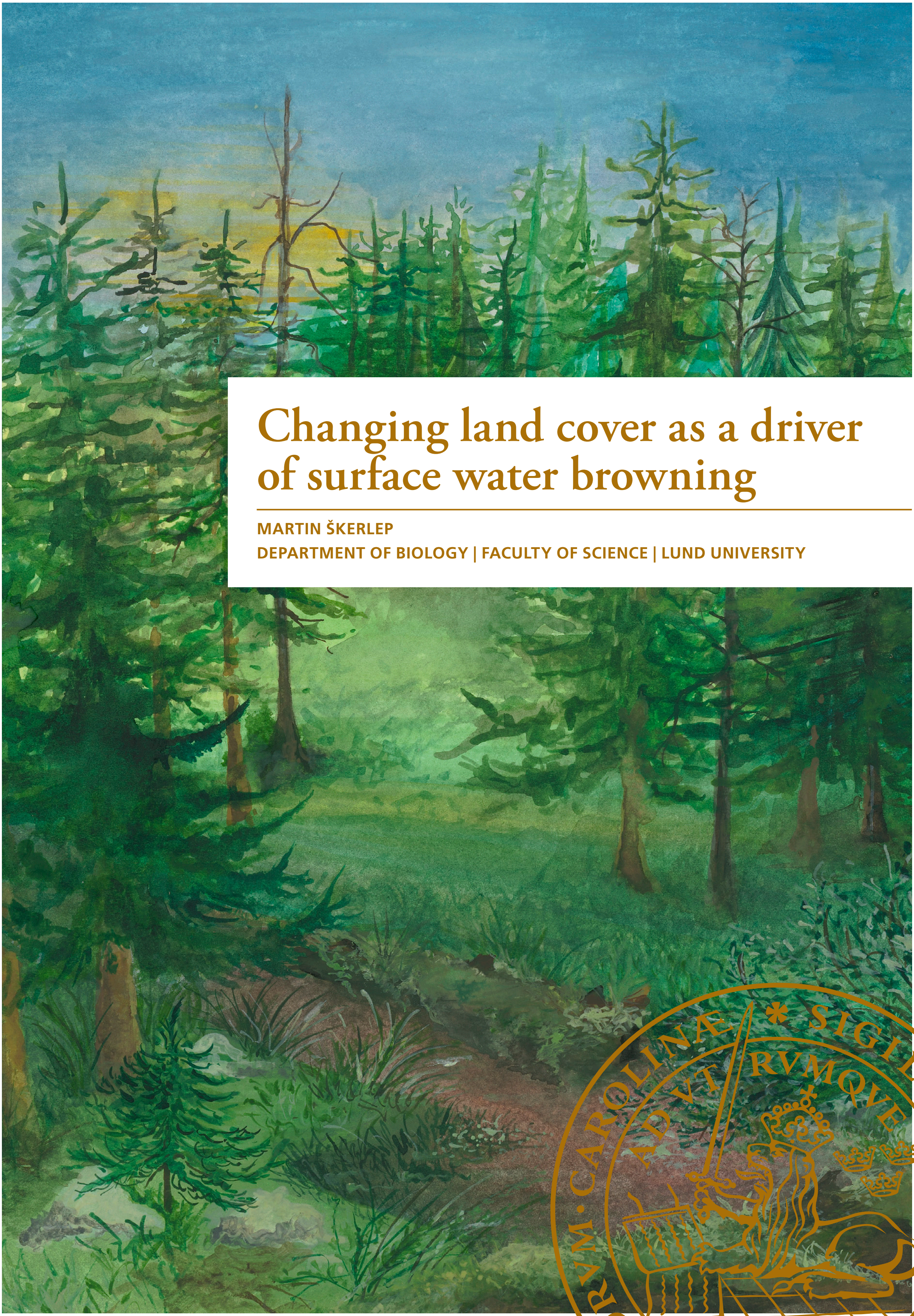
Link to publication

Citation for published version (APA):
Skerlep, M. (2021). *Changing land cover as a driver of surface water browning*. [Doctoral Thesis (compilation), Department of Biology]. Lund University.

Total number of authors:
1

LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00



Changing land cover as a driver of surface water browning

MARTIN ŠKERLEP

DEPARTMENT OF BIOLOGY | FACULTY OF SCIENCE | LUND UNIVERSITY

List of Papers

I. Škerlep, M., Steiner, E., Axelsson, A. L., & Kritzberg, E. S. (2020). Afforestation driving long-term surface water browning. Global change biology, 26(3), 1390-1399.

II. Škerlep, M., Nehzati, S., Johansson, U., Kleja, D. B., Persson, P., & Kritzberg, E. S. (2021). Spruce forest afforestation leading to increased Fe mobilization from soils. *Manuscript (submitted)*

III. Škerlep, M., Nehzati, S., Persson, P., Laudon, H., & Kritzberg, E. S. Differential trends in iron concentrations of small boreal streams linked to catchment characteristics. *Manuscript*

IV. Škerlep, M., Nilsson, B., Axelsson, A. L., Weyhenmeyer, G., & Kritzberg, E. S. Connecting long-term water color changes in three Swedish lakes to land cover history based on aerial photographs. *Manuscript*

Printed by Media-Tryck, Lund 2021 NORDIC SWAN ECOLABEL 3041 0903

LUND UNIVERSITY

Lund University
Faculty of Science
Department of Biology

ISBN 978-91-7895-950-1

Changing land cover as a driver of surface water browning

Changing land cover as a driver of surface water browning

Martin Škerlep

DOCTORAL DISSERTATION

by due permission of the Faculty of Science, Lund University, Sweden.
To be defended at the Blue Hall, Ecology Building, Sölvegatan 37, Lund, Sweden
on the 17th of September at 9:30.

Faculty opponent
Dag O. Hessen

University of Oslo

Organization
LUND UNIVERSITY

Department of Biology
Sölvegatan 37, 22362 Lund, Sweden

Author: Martin Škerlep

Document name: Doctoral dissertation

Date of issue: 2021-08-24

Sponsoring organization

Title and subtitle: Changing land cover as a driver of surface water browning

Abstract

Streams, rivers and lakes across wide areas of the Northern hemisphere have been subject to an increase in water color over the last decades. This increase, also known as browning, is a result of rising dissolved organic matter (DOM) and iron (Fe) concentrations in the water. Over the years, browning has received ample attention due to its impact on the structure and function of freshwater ecosystems, biogeochemical cycles and drinking water production. Several hypotheses have been proposed to explain what causes browning, with climate change and recovery from atmospheric S deposition receiving the most attention as potential drivers. Recently, it has been suggested that land cover changes, specifically increases in coniferous forest cover which promote accumulation of organic soils, is an important and overlooked factor behind browning.

The main aim of this thesis was to evaluate the contribution of changing land cover on long-term water color trends. Since afforestation represents a major shift in land cover in the last century, my aim was to explore how this may have affected processes in the catchment that could contribute to the observed increase in Fe and DOM exports to surface waters.

By combining uniquely long water color time series, with parallel records of climate variables, S deposition, and land cover, it was clear that all drivers significantly influence water color, but that including afforestation was integral to explain long-term browning. Low water color in the decades before peak S deposition, showed that observed browning is not representing a return to pre-industrial conditions. Rather, an earlier water color increase may have been suppressed by the reduced mobility of OM during peak acidification and has led to an accelerated water color increase in recent decades.

The importance of spruce forest to the mobilization of Fe and DOM from soils was also supported by results from a field study based on a forest chronosequence. Both Fe and DOM concentrations were considerably higher in soil solution under old spruce forest stands than under young spruce forest and arable land. This supports a previously suggested notion that impacts of afforestation on soil processes that influence Fe and DOM mobilization can only be seen after several decades, and explain why changes in land cover and water color are temporarily mismatched. Characterization of Fe speciation by X-ray absorption spectroscopy (XAS) supported that mononuclear Fe(III)-OM complexes were the dominant Fe phase in soil solution, a finding that highlights the strong link between Fe and OM mobilization and the importance of organic soils in providing Fe to surface waters.

The role of spruce forests was further indicated by the fact that increasing trends in stream Fe concentrations were observed in catchments with high proportion of old spruce forest, but not in catchments with more mire, open land, and deciduous forest cover. Long-term increase of Fe concentrations in soil solution of a riparian forest soil, and the lack of a trend in soil solution of a mire, also point to spruce forest soils as an important source to support positive Fe trends in streams.

Collectively, these findings show that land cover sets the baseline for the amount of DOM and Fe that is available, and that changes in land cover, S deposition and climate drivers contribute to observed browning trends.

Key words: browning, land cover, iron, organic matter, afforestation, spruce, biogeochemistry

Classification system and/or index terms (if any)

Supplementary bibliographical information	**Language: English**
ISSN and key title	**ISBN:** 978-91-7895-950-1 (print) 978-91-7895-949-5 (pdf)

Recipient's notes	**Number of pages** 174	Price
	Security classification	

Signature

Date 2021-08-09

Changing land cover as a driver of surface water browning

Martin Škerlep

LUND UNIVERSITY

Cover by Saga Lucija Škerlep

Faculty of Science
Department of Biology

ISBN 978-91-7895-950-1 (print)
978-91-7895-949-5 (pdf)

Printed in Sweden by Media-Tryck, Lund University
Lund 2021

NORDIC SWAN ECOLABEL
Printed matter
3041 0903

Media-Tryck is a Nordic Swan Ecolabel certified provider of printed material. Read more about our environmental work at www.mediatryck.lu.se

MADE IN SWEDEN

To Lou, my family and friends

Table of Contents

List of Papers

I. Škerlep, M., Steiner, E., Axelsson, A. L., & Kritzberg, E. S. (2020). Afforestation driving long-term surface water browning. Global change biology, 26(3), 1390-1399.

II. Škerlep, M., Nehzati, S., Johansson, U., Kleja, D. B., Persson, P., & Kritzberg, E. S. (2021). Spruce forest afforestation leading to increased Fe mobilization from soils. *Manuscript (submitted)*

III. Škerlep, M., Nehzati, S., Persson, P., Laudon, H., & Kritzberg, E. S. Differential trends in iron concentrations of small boreal streams linked to catchment characteristics. *Manuscript*

IV. Škerlep, M., Nilsson, B., Axelsson, A. L., Weyhenmeyer, G., & Kritzberg, E. S. Connecting long-term water color changes in three Swedish lakes to land cover history based on aerial photographs. *Manuscript*

Author Contributions

I. MŠ and ESK developed the idea and designed the study. ES and ALA provided chemical and environmental data. MŠ analyzed the data and the results. MŠ wrote the first draft of the manuscript and all the authors provided comments on the manuscript.

II. MŠ, ESK developed the idea and designed the study together with PP, DBK and UJ. MŠ set up the field experiment with support from DBK and UJ. MŠ performed the field and lab work. MŠ and PP collected the XAS data. SN analyzed the XAS data. DBK did the geochemical modelling. MŠ analyzed the results. MŠ wrote the first draft of the manuscript and all the authors provided comments on the manuscript.

III. MŠ and ESK developed the idea and designed the study together with HL. HL provided the data and wetland samples. MŠ and ESK collected the soil samples. MŠ performed the lab work and together with PP collected the XAS data. SN analyzed the XAS data. MŠ analyzed the results. MŠ wrote the first draft of the manuscript and all the authors provided comments on the manuscript.

IV. MŠ, ESK developed the idea and designed the study together with ALA and GW. BN did the land use reconstruction from historic aerial photographs and ALA provided critical input on the reconstruction. MŠ analyzed the data and the results. MŠ wrote the first draft of the manuscript and all the authors provided comments on the manuscript.

MŠ – Martin Škerlep
ESK – Emma S. Kritzberg
ES – Eva Steiner
ALA – Anna-Lena Axelsson
PP – Per Persson
DBK – Dan B. Kleja
UJ – Ulf Johansson
SN – Susan Nehzati
HJ – Hjalmar Laudon
GW – Gesa Weyhenmeyer
BN – Björn Nilsson

Abstract

Streams, rivers and lakes across wide areas of the Northern hemisphere have been subject to an increase in water color over the last decades. This increase, also known as browning, is a result of rising dissolved organic matter (DOM) and iron (Fe) concentrations in the water. Over the years, browning has received ample attention due to its impact on the structure and function of freshwater ecosystems, biogeochemical cycles and drinking water production. Several hypotheses have been proposed to explain what causes browning, with climate change and recovery from atmospheric S deposition receiving the most attention as potential drivers. Recently, it has been suggested that land cover changes, specifically increases in coniferous forest cover which promote accumulation of organic soils, is an important and overlooked factor behind browning.

The main aim of this thesis was to evaluate the contribution of changing land cover on long-term water color trends. Since expansion in spruce forest represents a major shift in land cover in the last century, my aim was to explore how this may have affected processes in the catchment that could contribute to the observed increase in Fe and DOC exports to surface waters.

By combining uniquely long water color time series, with parallel records of climate variables, S deposition, and land cover, it was clear that all drivers significantly influence water color, but that including afforestation was integral to explain long-term water color dynamics. Low water color in the decades before peak S deposition, showed that observed browning is not representing a return to pre-industrial conditions. Rather, an earlier water color increase may have been suppressed by the reduced mobility of OM during peak acidification and has led to an accelerated water color increase in recent decades.

The importance of spruce forest to the mobilization of Fe and DOM from soils was also supported by results from a field study based on a forest chronosequence. Both Fe and DOM concentrations were considerably higher in soil solution under old spruce forest stands than under young spruce forest and arable land. This supports a previously suggested notion that impacts of afforestation on soil processes that influence Fe and DOM mobilization can only be seen after several decades, and explain why changes in land cover and water color are temporarily mismatched. Characterization of Fe speciation by X-ray absorption spectroscopy (XAS) supported that mononuclear Fe(III)-OM complexes were the dominant Fe phase in soil solution, a finding that highlights the strong link between Fe and OM mobilization and the importance of organic soils in providing Fe to surface waters.

The role of spruce forests was further indicated by the fact that increasing trends in stream Fe concentrations were observed in catchments with high proportion of old spruce forest, but not in catchments with more mire, open land, and deciduous forest cover. Long-term increase of Fe concentrations in soil solution of a riparian forest

soil, and the lack of a trend in soil solution of a mire, also point to spruce forest soils as an important source to support positive Fe trends in streams.

Collectively, these findings show that land cover sets the baseline for the amount of DOM and Fe that is available, and that changes in land cover, S deposition and climate drivers contribute to observed browning trends.

Popular Summary

In recent years, the water of many lakes, streams and rivers in northern areas have become increasingly browner. The brown color comes from decomposed organic material and iron that originate from surrounding soils. While this so-called browning is not directly dangerous to people swimming in the waters, it does have an impact on organisms that live in browner and darker waters. Freshwater plants for example need light for photosynthesis, while fish rely on vision to catch their prey, and research has shown that both these groups of organisms are negatively impacted by browning. The organic matter and iron also cause problems for drinking water production, which becomes more expensive, requires more chemicals and the quality of drinking water may be impaired. These are all reasons why we need to understand what causes the browning and why much research on the issue has already been done.

Researchers have studied browning intensively, but it is still not entirely clear what causes this phenomenon. Climate change and recovery from acidification have been most widely considered as the main explanations for browning. Acidification was caused by high concentrations of sulfate in rain, which peaked ~1980. It is believed that leakage of organic matter was low due to the acidic conditions, and that as soils have recovered from acidification, more organic matter can move into the water and cause the browner color. A theory that has received much less attention, is that changes in land use have contributed to browning. During the last century many agricultural areas were replaced by forests, which either grew naturally on abandoned farmland, or were intentionally planted for forestry. Spruce forest has become especially widespread, as it is favored for forestry. The litter from spruce forests decomposes very slowly, and for this reason layers of organic soils build-up. These organic soil layers are an important source of dissolved organic matter leaking into freshwaters.

In this thesis, I studied what role expanding spruce forests have had on water color and if their expansion can be responsible for the observed browning. To do this I compared historic records of water color extending back to the 1930s, in a river and three lakes, to changes in spruce forest, precipitation, temperatures and sulfate deposition in rain. The results showed that all the above mentioned factors seem to play an important role to water color changes, and that the expansion of spruce forest is the one that has had the strongest effect on long-term browning. Although many lakes and running waters have become browner, waters in areas that do not have any forests or wetlands, do not respond to changes in climate and sulfate deposition, since the surrounding soils do not contain enough organic matter.

The link between expanding spruce forests and browning was previously not clear - during the last decades when browning has been very pronounced, spruce forest has not expanded notably. However, the results in this thesis show that it takes

several decades for organic layers to build up and become sources of organic matter. Consequently, after forests expanded, there was a delay of several decades before the effect was observed as browner water in streams and lakes. We also saw that the increased amount of organic matter brought more iron, since the two are bound to each other in soils.

In summary, this thesis shows that expanding spruce forest has played a major role in freshwaters becoming browner and that climate change and recovery from acidification further add to this trend. Recognizing that land use is an important factor, means that managing the land cover can be a way to locally counteract browning.

Introduction

Streams, rivers and lakes across wide areas of the Northern Hemisphere have been subject to an increase in water color over the last decades (Driscoll et al. 2003, Hongve et al. 2004, Arvola et al. 2010, de Wit et al. 2016). This phenomenon, commonly referred to as browning or brownification, is a result of increased concentrations of colored dissolved organic matter (DOM) and iron (Fe) in surface waters (Kritzberg and Ekstrom 2012, Sarkkola et al. 2013). The brown water color comes from the optical properties of DOM and ferric iron (Fe(III)), giving water a distinct reddish brown coloring (Fig.1). Although both DOM and Fe separately absorb light, it has been observed that water color increases further when they are associated (Maloney et al. 2005, Xiao et al. 2015).

While there is a general trend in increasing water color, DOM and Fe, the magnitude of these increases vary by a wide range between systems. For example, between 1972 and 2010 the increase in water color, chemical oxygen demand (a proxy for DOM), and Fe across 30 rivers in Sweden was 0 - 279 %, 0 - 122 % and 0 - 468 %, respectively (Kritzberg and Ekstrom 2012). Studies looking at trends in DOM and Fe at wider geographical scales also show that although increases are widespread, they are not ubiquitous and have been most pronounced in Northern Europe and the UK (Monteith et al. 2007, Björnerås et al. 2017). This variation in trends among systems poses the question if changes in water color are affected by very local processes, or whether each catchment responds differently to large-scale changes. Furthermore, in many waters increases in Fe have been higher than increases in DOM, indicating that processes controlling the catchment export of the two might differ (Kritzberg and Ekstrom 2012).

During the last two decades, several hypotheses have been proposed to explain browning, and have been extensively studied with regards to DOM (quantified as dissolved organic carbon; DOC), but to a lesser extent regarding Fe. Most efforts have been directed towards exploring the role of climate change (Laudon et al. 2012, Ekström et al. 2016) and recovery from atmospheric acid deposition (Monteith et al. 2007, Neal et al. 2008), while changing land cover has only recently gained attention as a possible cause for browning (Meyer-Jacob et al. 2015, Kritzberg 2017). Several studies have suggested that it is a combination of these factors, acting on different geographic and temporal scales, which explain observed trends in DOM and Fe (Clark et al. 2010, Bragee et al. 2015).

The overarching aim of this thesis is to increase our understanding on how browning is influenced by changes in land on a centennial timescale. Before further specifying the research questions, I here give a brief overview of the consequences of browning, a general description of the principal controls on DOM and Fe loading from the catchment to surface waters, and a general account over how the proposed drivers may affect DOM and Fe concentrations.

Figure 1 Brown water in a small stream in northern Sweden. (Photo: Martin Škerlep)

What are the consequences of browning?

The multiple and far-reaching consequences of browning are one of the reasons it has received considerable attention (Solomon et al. 2015, Creed et al. 2018). The impaired light climate it brings, fundamentally affects the structure and function of the aquatic ecosystem, and the increased loading of DOM and Fe influences biogeochemical cycling. Finally, browning may reduce the societal value of water bodies. The following section briefly reviews these three consequences of browning.

Biodiversity and ecosystem function

Browning of surface waters leads to increased light attenuation in the water column, which has widespread effects on freshwater ecology. Reduced light penetration lead to a decrease in lake primary production (Karlsson et al. 2009, Seekell et al. 2015), and disproportionally affects primary producers, that are dependent on clear water columns, such as submersed macrophytes (Squires et al. 2002). Species better adapted to low light conditions or less reliant on primary production may consequently benefitted (Rengefors et al. 2008, Mormul et al. 2012), and browning can therefore lead to changes in species composition, and potentially lower biodiversity and productivity in freshwater (Jones 1992, Thrane et al. 2014). Changes in primary productivity also have effects on organisms higher in the food-chain, as they determine the food sources available (Grubisic et al. 2012, Hansson et al. 2013b). Predatory species that rely on vision for foraging are further negatively affected (Ranåker et al. 2012). Although small increases in DOM may have positive effects by offering protection from UV light and bringing organic nutrients to the system, larger increases have been shown to negatively impact e.g. phytoplankton and predatory fish (Finstad et al. 2014, Seekell et al. 2015, van Dorst et al. 2019).

Heterotrophic bacterioplankton could benefit from additional allochthones DOM that can serve as a food source (Jansson et al. 2007). Higher input of DOM can increase the importance of allochthonous carbon as an energy resource, favoring bacterial biomass production in aquatic ecosystems (Carpenter et al. 2005, Kritzberg et al. 2005), and thus potentially lead to more lakes becoming net heterotrophic.

Considerably less is known about direct effects of Fe on aquatic biota. Studies show that precipitation of Fe-(oxy)hydroxides on biological surfaces leads to oxidative stress and that high Fe concentrations cause fish gill damage, reduce fish hatching success, induce mortality, physical and behavioral changes in invertebrates, and lead to displacement of periphyton (Peuranen et al. 1994, Vuori 1995).

Biogeochemical cycles

In the last decade, the role of freshwaters in the global carbon cycle has been revised, and it is now recognized that freshwaters receive (5.1 Pg yr^{-1}) process, emit and store (4.5 Pg yr^{-1}) vast amounts of terrestrially derived carbon (Cole et al. 2007, Tranvik et al. 2009, Stocker et al. 2013, Drake et al. 2018). Understanding the potential effects of browning on the fate of carbon in freshwaters is therefore highly important due to the potential implications for climate change. Surface waters are comparable sources of DOC-derived CO_2 as peatlands and soils, and CO_2 emissions from surface waters are positively correlated to DOC (Sobek et al. 2003, Moody et al. 2013). At the same time, burial of C in lake sediments is an important long-term sink of C, which may increase in response to browning (Heathcote et al. 2015). Increasing concentrations of Fe may promote loss of C to sediments, since interactions Fe protects OM from decomposition and enhances C preservation in soils and sediments (Kaiser et al. 1996, Lalonde et al. 2012).

Societal use of freshwaters

Surface waters are an important societal resource, partly by serving as source of drinking water in many countries. Sweden, for example, relies on surface water for 50% of its total drinking water production (http://svensktvatten.se). Although DOM can to a large extent be removed by chemical precipitation, the increase in DOM requires increased chemical use, which increases drinking water cost and reduces quality (Kohler et al. 2016). As chemical precipitation never completely removes DOM, this poses risks in the form of potentially carcinogenic chlorinated OM, microbial growth in pipes and reduced efficiency of pharmaceutical and pollutant removal (Lavonen et al. 2013). Another concern with increasing DOM and Fe in freshwaters is their ability to form complexes with potentially toxic metals (Nason et al. 2012, Okkenhaug et al. 2018) and organic pollutants (Fukushima et al. 2006), concentration of which have been increasing along with DOC and Fe loadings in recent years (Wallstedt et al. 2010).

Surface waters also provide recreational value. Browner waters have been found to be less appealing for tourism and bring fewer opportunities for angling (Ranåker et al. 2012, Keeler et al. 2015).

What determines the amount of DOM and Fe exported from soil to surface waters?

Catchment soils are the main source of both DOM and Fe for surface waters. The amount of DOM and Fe that reaches surface waters is determined both by processes regulating their mobilization from the solid phase into suspension, and by the processes that control their subsequent transport form soils to surface waters.

Mobilization of DOM and Fe from soil to soil solution

The total amount of OM in soils represents the initial constraint for how much DOM can be transported from soils. Soil OM pools are determined by the rates of primary production by terrestrial vegetation and the decomposition rates. High rates of production and lower decomposition rates lead to accumulation of OM in soils and increase the OM pool. Only a fraction of the accumulated soil OM will however be mobilized into solution and made available for transport to surface waters. The mobility of soil OM is determined by mineral binding sites, redox conditions, pH and ionic strength in solution (Kaiser et al. 1996, Hagedorn et al. 2000). In general, DOM concentrations are higher in organic rich layers and decrease sharply in mineral soils where DOM sorbs to Fe and Al on mineral surfaces (McLaughlin et al. 1994). Reducing conditions promote reduction of Fe(III), which releases associated OM from mineral surfaces, allowing an increase in DOM in solution (Hagedorn et al. 2000). At low pH (<5.5) high concentrations of H^+ ions protonate functional groups of OM, decreasing its surface charge and solubility, and thereby OM mobility is suppressed as pH decreases (Tipping and Hurley 1988, Ekström et al. 2011).

Although Fe is abundant in most soils, a majority of it is present in minerals of low solubility (Lindsay and Schwab 1982). Fe is present in several different phases, sometimes also referred to as Fe species, which can vary considerably between different soils and soil profiles (Blume and Schwertmann 1969). Phyllosilicates and Fe-(oxy)hydroxides (FeOOH) represent the majority of Fe in mineral soils (Schwertmann and Taylor 1989), while Fe complexed with OM (Fe-OM) can represent a major component especially in OM rich soils (Sundman et al. 2014). Also, Fe can form minerals with other elements, such as phosphorus (vivianite), sulfur (pyrite) or carbonates (siderite), which are less common but can represent major Fe components in certain environments (Howarth and Merkel 1984, McMillan and Schwertmann 1998, Rothe et al. 2016). The occurrence of different Fe species in soils can vary considerably and their formation dependents on pH, redox and the OM available in soils (Cornell and Schwertmann 1979, Schwertmann and Murad 1983, Thompson et al. 2006). Complexation with OM for example can suppress formation of crystalline FeOOH and thereby increases the reactive Fe pool in soils (Schwertmann 1966, Jansen et al. 2003).

Mobilization of Fe is determined by dissolution rates of soil Fe phases and the solubility of Fe in solution, which are controlled by pH, redox potential and OM (Schwertmann 1991). In general, solubility of Fe minerals increases with decreasing pH, leading to higher mobilization rates at lower pH (Tyler and Olsson 2001, Björnerås et al. 2019). Reductive dissolution in low oxygen environments also leads to reduction of Fe(III) to Fe(II), which is more stable in solution and therefore more mobile (Schwab and Lindsay 1983). Finally, organic molecules, such as organic acids, can promote dissolution of mineral Fe phases. Organic acids can either be a byproduct of OM decomposition or can be excreted by plants or microorganisms to mobilize Fe (Jones et al. 1996, Schmidt 1999). Complexation with OM supports higher Fe concentrations in solution as it suppresses hydrolysis of Fe(III) and thereby prevents it from precipitating (Karlsson and Persson 2012).

Transport of DOM and Fe from soil solution to surface waters

Once Fe and DOM are mobilized into soil solution, they are available for transport. However, this does not necessarily mean that they will end up in surface waters. The transport from soils to surface waters is highly dependent on hydrology and the biogeochemical processing along the hydrological pathway (Tiwari et al. 2017). Loss of Fe and DOM from solution often occur during downward transport in the soil profile, as OM is mineralized and adsorption to mineral surfaces and precipitation of Fe are promoted by the increasing pH (Jansen et al. 2003). Redox barriers, such as at the interface between anoxic riparian soils and oxygenated surface waters, can lead to oxidation and precipitation of Fe (Duckworth et al. 2009). As Fe-OM complexes are more stable in oxygenated surface waters, they are seen as important sources of Fe coming into surface waters (Sjöstedt et al. 2013).

Hydrology exerts a primary control on both DOM and Fe transported into surface waters and their sources can vary depending on hydrological connectivity (Agren et al. 2007, Björkvald et al. 2008). Contribution by terrestrial sources, such as wetlands and forest soils, has been shown to be highly dependent on seasonal hydrology in catchments (Björkvald et al. 2008, Fork et al. 2020). For instance, surface soils rich in OM and associated Fe are only hydrologically connected to streams during high discharge conditions in the catchment (Agren et al. 2007). In addition, certain parts of the terrestrial landscape might contribute disproportionally to DOM and Fe in streams due to their proximity to surface waters or increased hydrological connectivity. Riparian zones, for example, act as biogeochemical hotspots with a strong influence on stream water chemistry (McClain et al. 2003, Ledesma et al. 2018). Soil water in riparian zones has been found to be highly enriched in DOC (9 times) and in Fe (33 times), when compared to upland soils (Lidman et al. 2017). Furthermore, topographical depressions in the landscape create hydrological focal points within the riparian zone, also known as discrete riparian inflow points (DRIPs), that can have a disproportionally high influence on stream water chemistry (Ploum et al. 2020).

What are the underlying drivers of surface water browning?

Sulfur (S) deposition, climate change and land cover change are composite drivers that influence the amount, the mobility and the transport of DOM and Fe from catchments, and may thereby act as underlying drivers of browning. Beside these, fertilization by N deposition has also been proposed as a driver of browning, since it increases primary production and thereby the amount OM entering the system (Finstad et al. 2016). Better understanding of the individual contributions by each potential driver is not only important in explaining past trends, but also in order to predict and potentially mitigate future increases in DOM and Fe. In the following section, I layout the processes by which these drivers may influence browning, and also what support exist in the current literature.

Recovery from atmospheric acid deposition

Atmospheric S deposition originates largely from combustion of fossil fuels, and was enhanced ever since ~1880, but increased sharply after World War II to reach its peak in the early 1980s. The elevated S deposition caused acidification with far reaching consequences to forested and aquatic ecosystems (Driscoll, 2001). Following international legislation, both S deposition and SO_4^{2-} concentrations in soil and surface waters decreased dramatically (Fig. 2), and have in several regions returned to background levels (Schopp et al. 2003, Akselsson et al. 2013, Garmo et al. 2014). The large organic compounds that stain water brown, e.g. humic substances, are only soluble in water if negatively charged. At strongly acidic conditions, negative functional groups of OM are to a larger extent protonated, which decreases the net charge and reduces its solubility in water (Tipping and Woof 1991, Ekström et al. 2011). Recovery from acidification has led to increasing in pH and decreasing ionic strength, which should enhance OM solubility and mobility in soils and increases its potential for export (Tipping and Hurley 1988).

Mobility of Fe may also be influenced by S deposition, through its effects on SO_4^{2-} concentration and pH in soils and surface waters. In general, the solubility of Fe minerals increases with decreasing pH (Lindsay 1979). However, as low pH suppresses OM solubility it may reduce the mobility of Fe-OM complexes (Neal et al. 2008, Neubauer et al. 2013). Accordingly, field studies where SO_4^{2-} concentrations were manipulated showed that DOM fluxes rather than pH controlled Fe leaching (Bergkvist 1986). This means that although Fe minerals might be more soluble under low pH, the dependence on DOM suggests it might actually be less mobile. In a recent microcosm study, however, it was found that mobilization of Fe into suspension was enhanced by increased acidity under a high SO_4^{2-} treatment (Björnerås et al. (2019).

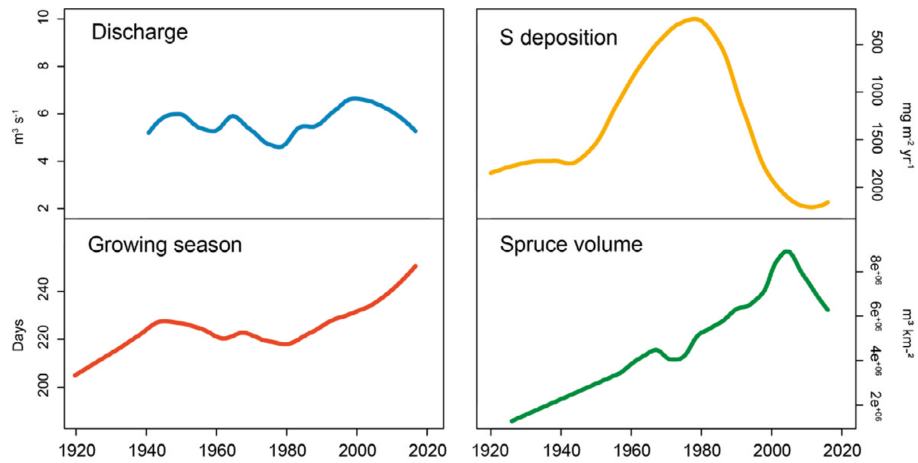


Figure 2 Examples of long-term changes in potential drivers of surface water browning. The data is from the catchment of River Lyckeby (Paper I).

The theory that browning is a result of recovery from acidification has been supported by field studies, demonstrating that less DOM was mobilized in soils that were exposed to high SO_4^{2-} precipitation (Ekström et al. (2011). Moreover, inverse relationships between water color/DOC/Fe and SO_4^{2-} concentrations, observed in surface waters, are in line with such a mechanism and have been widely reported (Monteith et al. 2007, Erlandsson et al. 2008, Arvola et al. 2010, Haaland et al. 2010, Björnerås et al. 2017). Notably however, these data series generally start during or after the period of peak S deposition, and thus can strictly not answer if current browning is a return to a pre-depositional state. The few studies that do provide records extending further back in time show somewhat deviating results. In paleolimnological studies where DOC concentrations were reconstructed, it was suggested that DOC levels were at a minimum during the acidification period (Valinia et al. 2014, Bragee et al. 2015). Historical data records, however, showed no decrease in water color during the period of increasing S deposition, but that water color was consistent and much lower 1930-1980 than during the last couple of decades (Kritzberg 2017).

Climate change

Higher mean annual temperature and changed precipitation patterns are already observed for higher latitude regions (Fig. 2) and expected to change further (Nikulin et al. 2011). Consequences of ongoing warming include longer growing seasons (growing degree days), and greening, i.e. an increase in primary production and expansion of vegetation cover, both of which have been linked to higher DOC concentrations in freshwaters (Larsen et al. 2011, Finstad et al. 2016, Weyhenmeyer et al. 2016a). Moreover, warmer winters lead to shorter soil frost periods, making surface soils hydrologically connected for longer periods of the year and can thereby enhance DOM export (Lepisto et al. 2014).

Higher temperatures in combination with increasing precipitation promote microbial decomposition of OM, and reducing conditions in the catchment. OM decomposition enhance DOM production, and reducing condition favor Fe export as Fe(II) is more mobile than Fe(III) (Andersson et al. 2000, Laudon et al. 2012, Sarkkola et al. 2013, Ekstrom et al. 2016). As soils are the main source of both DOM and Fe to surface waters, hydrology also plays an integral role in connecting soils and surface water, and increasing precipitation thereby enhances export of DOM (Hongve et al. 2004, Sanderman et al. 2009, de Wit et al. 2016).

During dry periods when the water table is low, OM accumulates in the soil, meaning there is more OM available to be flushed out when the water table is raised. With expected increase in the frequency and intensity of dry-wet periods, occurrence of high OM pulses entering surface waters are expected to increase (Fenner and Freeman 2011). Finally, increasing precipitation leads to shorter water residence times, leaving less time for processes resulting in DOM and Fe losses along the water continuum, such as microbial degradation, photo-transformation and aggregation driven sedimentation (Weyhenmeyer et al. 2012, Weyhenmeyer et al. 2014). Although precipitation and discharge are good predictors for within and between year variation in water color, they have likely been less important for observed long-term increases. These factors could however become more important in regulating DOM and Fe concentrations as climate change intensifies (Haaland et al. 2010, de Wit et al. 2016).

Land cover change

Catchment land cover has long been recognized as the best predictor of water color in surface waters across systems (Humborg et al. 2004, Agren et al. 2007). DOM and Fe concentrations in stream waters increase with the proportions of wetlands and coniferous forests in the catchment, as they are major sources of OM and Fe (Björkvald et al. 2008, Mattsson et al. 2009, Palviainen et al. 2015, Weyhenmeyer et al. 2016b). On the other hand, land cover which does not promote accumulation of organic soils to the same extent, such as agricultural or deciduous landscapes, support lower DOC concentrations (Guo and Gifford 2002, Hansson et al. 2013a, Camino-Serrano et al. 2014).

Humans have influenced the landscapes they live in for centuries, and this has shaped surface water chemistry ever since the Iron Age (Renberg et al. 1993). Several paleolimnological studies have connected reconstructed changes in lake water DOM to land-use intensification in the catchments (Cunningham et al. 2011, Meyer-Jacob et al. 2015, Myrstener et al. 2021). While such studies indicate an increase in water color synchronous with intensification of forestry in the catchments in the past century (Meyer-Jacob et al. 2015, Myrstener et al. 2021), the marked browning revealed from monitoring in the last few decades has generally not been connected to land cover change. Some recent studies, however, have proposed that changes in land cover is an important and overlooked factor behind browning (Meyer-Jacob et al. 2015, Kritzberg 2017). These studies suggest that coniferous afforestation in the 20th century has led to a build-up of organic soils, which act as sources of DOM to surface waters. An overview of how land cover has changed is given in **Box 1**.

Due to slow accumulation of organic layers in forested soils, effects of afforestation on soil OM stocks take several decades (Rosenqvist et al. 2010), which could cause a delayed effect on DOM exports (Kritzberg 2017). In spruce forests for example, it takes several decades (~40 years) before increased mobilization of DOM is observed in soil solution (Rosenqvist et al. 2010). This would imply that increases in coniferous forest cover during the earlier parts of the 20st century, and a gradual buildup of organic soils, could be causing a delayed effect on browning (Kritzberg 2017). This would also imply that as forests continue to expand and age the increasing pools of OM will lead to more browning in the future. The mobility of Fe is also influenced by the vegetation cover (Li et al. 2008), although very little is known about how changes in land cover may contribute to long-term Fe trends in surface waters. Across a wide geographical scale in northern Europe and North America, increasing Fe trends were found to be well correlated with the proportion of coniferous forests in the catchments (Björnerås et al. 2019).

Besides increasing forest cover, other land management measures may impact DOM and Fe exports to freshwaters. Changes in water table caused by clear-cutting and forestry soil preparation have been shown to increase DOM leaching in the short-term, although it is less clear how long-term exports are affected (Laudon et al. 2009, Schelker et al. 2012). Effects of ditching, which has been a common practice to promote forest production in Sweden and Finland, include lower exports of DOM directly after ditching, due to a hydrological disconnection with surface soils, but effects vary largely with local conditions (Joensuu et al. 2002, Nieminen et al. 2010). Interestingly, a recent study including 133 peatlands in Sweden and Finland, showed that drainage of peatlands led to higher DOM leaching, and that the increase in DOM leaching was correlated to the tree volume on the drained soils (Nieminen et al. 2021). Higher DOM concentrations after drainage could be the result of increased litter inputs from trees (Straková et al. 2010), or caused by gradual decomposition of peat resulting from lowering of the water table (Sarkkola et al. 2010).

Box 1 How has land cover changed?

Human land use has significantly altered landscapes and the vegetation cover since many centuries. From the 15-16th centuries, human utilization in much of Scandinavia included summer forest grazing, slash and burn, and expanded farming, which resulted in an opening of the landscape and forest loss (Larsson 2012, Meyer-Jacob et al. 2015). From the late 19th century, a major transition has taken place, from a largely open agricultural landscape towards a more closed landscape dominated by coniferous forest, especially Norway spruce (Picea abies; Fig. 3, (Fredh et al. 2012, Lindbladh et al. 2014)). As inferred from sediment pollen records, coniferous forest in Southern Sweden increased in the last 200 years, largely at the expense of grasslands and deciduous forest, with the most dramatic change occurring between 1880 and 1940, after which spruce dominated the landscape (Fredh et al. 2012). A land cover change from extensive agriculture towards industrial forestry, is also supported by an increase in total forest and spruce forest volume by 264 and 333 % respectively, between 1920 and 2008 Lindbladh et al. (2014). In Finland, afforestation has reportedly resulted in a 50 % increase of forest biomass, associated with a 13 % increase in soil and litter C stocks, between 1922 and 2004 (Liski et al. 2006, Hansson et al. 2013a).

Similar large-scale patterns in land cover are seen for other temperate and boreal regions of the world. Records from Massachusetts, Northern USA, show a loss of forest cover after European settlement in the mid 17th century, followed by expanding agriculture, reaching 75 % coverage by 1830 (Foster et al. (1998). This was followed by a period of afforestation, starting in the late 19th century, resulting in 76 % forest cover, and 10 % agricultural cover by 1985. Afforestation, at the expense of grassland and cropland, has been a major and widespread land cover transitions in Europe during the last century, ranging from the Baltic countries and Scandinavia to mountainous regions in Southern Europe with the highest rate of afforestation between 1920 and 1980 (Fuchs et al. (2015).

Figure 3 Planted spruce seedlings around a cottage in Hvitthults Småland, 1912. The photograph was taken by Edvard Wibeck, and was made available by the photo archive of the Swedish University of Agricultural Sciences (SLU).

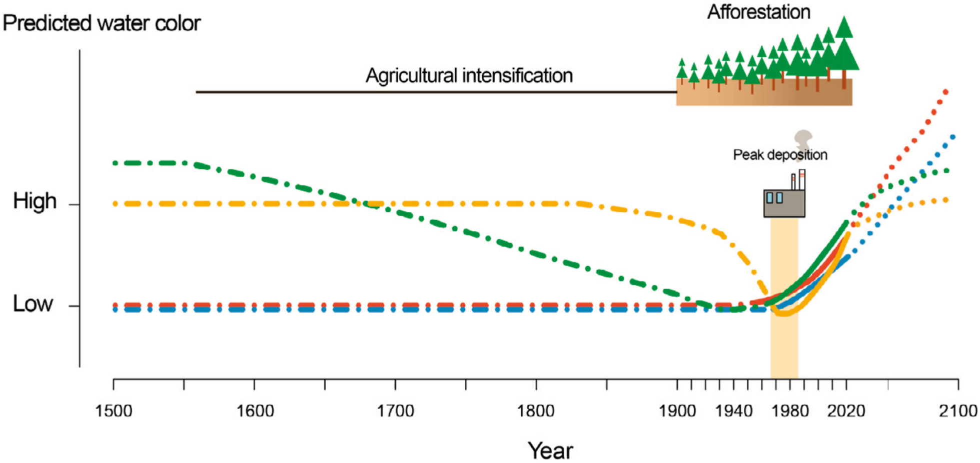


Figure 4 Schematic model over long-term water color assuming it was controlled entirely by atmospheric S deposition (yellow line), land cover (green line), precipitation (blue line) or temperature (red line). Solid lines denote the period for which there is monitoring data, dashed lines represent speculation about the past, and dotted lines represent future predictions of water color, if influenced by each separate driver.

Aims and Research Questions

Monitoring data has been a central resource for the research aiming to reveal the impact of potential drivers of browning. Since large scale environmental monitoring is a relatively modern phenomenon, most data series begin in the 1980s or later. Time series of a few decades, however, are not well suited to study the influence of land cover change, effects of which can only be observed on longer time scales (Meyer-Jacob et al. 2015, Kritzberg 2017). Moreover, since data series generally begin around or after the peak in S deposition, the temporal correlation between water color and S deposition is tested only for the period of strongly declining acid deposition. And the monitoring data cannot tell us if current browning is representing a return to a more natural pre-depositional state (Fig. 3). Most efforts to understand drivers of browning have focused on controls of DOC and water color, and much less on Fe. The shortage of analyses of Fe trends and experimental studies leaves a large gap in our understanding of processes and mechanisms that control Fe mobilization to freshwaters.

The overarching aim of this thesis was to further our understanding of the role that changes in land cover have on surface water browning. Since an expansion in spruce forest represents a major shift in land cover in the last century, my aim was to explore how this may have affected processes in the catchment that could contribute to the observed increase in Fe and DOC exports to surface waters.

More specifically, the research questions I address in this thesis are:

- *What role has land cover change, and particularly spruce afforestation, played to the long-term dynamics of water color, in relation to other environmental drivers on a centennial scale?*
- *How does the growth of spruce and forest stand age affect mobilization of Fe and DOC into soil solution?*
- *Do different catchment sources of Fe, i.e. forest soils and wetlands, contribute equally to the trends in Fe?*
- *Are there aspects of land cover change other than spruce afforestation, which have been significant in relation to browning?*

Research Approaches and Methodology

To answer the questions in this thesis I relied on a suite of complementary scientific approaches, including analyses of temporal and spatial records of Fe, DOM and water color in relation to environmental variables, as well as field experiments examining Fe and DOM mobilization in soils with different land cover. The approaches and the methodology used in each of the papers are presented in the following.

In **Paper I,** temporal records of water color were combined with parallel records of climate variables, S deposition, and land cover in the catchment to evaluate the influence of individual drivers on browning. For this, we made use of a unique data series from Lyckeby River in Southern Sweden, which has been used as a drinking water source since the 17th century and where the water treatment facility has analyzed water chemistry almost daily since 1940 (Fig. 5).

We hypothesized that temperature and discharge control short-term changes (seasonal and periodical) in water color, while S deposition and afforestation (spruce volume) are the dominant drivers of long-term browning.

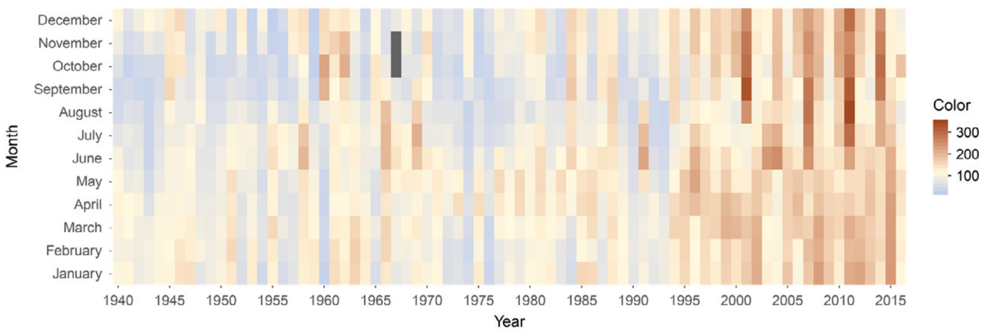


Figure 5 Monthly average water color (mg Pt L^{-1}) for Lyckeby River.

Total tree volume of Norway spruce (*Picea abies*) in the catchment was used as the measure of land cover change and was based on data from the Swedish National Forest Inventory. Total tree volume integrates both aerial extent and growth, which should reflect accumulation of OM in the catchment.

Long-term trends in water color and environmental variables, were assessed by the non-parametric *Mann-Kendall trends test*. Absolute yearly change rates (Δ yr^{-1}) were determined from the Theil slope of the Mann-Kendall test (Theil 1950), to put the changes into perspective.

In the next step, tested how well each variable separately and all variables together predicted the variation in water color. *Partial least square (PLS) regression* was used to determine how well explanatory variables correlated with water color. PLS regression ranks explanatory variables in accordance to how well they can explain the variation in the response variables and are presented as variable importance of projection (VIP) values (Wold et al. 2001). In addition, standard regression coefficients (SRC) were presented to quantify the contribution of each variable in explaining water color variation in the PLS model. To further test how well different combinations of explanatory variables could predict water color, *multiple linear regression (MLR) models* were created. The relative quality of each model was assessed using the Akaike information criterion (Akaike 1974).

For **Paper II,** a field experiment was designed to test the effects of growing Norway spruce forest mobilization of Fe into suspension, as well as effects on the speciation of Fe in soil and soil solution. A chronosequence of first generation spruce, planted onto formerly agricultural land, was used to test how long after plantation effects can be seen. Three plots with spruce stands aged 35, 61 and 90 years, were selected to and three adjacent plots with arable land were used as controls. In these plots, lysimeters were installed to sample soil solution, and soil samples were collected from different depths to determine the amount, crystallinity, and speciation of Fe (Fig. 6).

We hypothesized that thicker organic soil layers and lower pH under older spruce stands would promote Fe dissolution, complexation, and solubility, which would result in higher Fe concentrations in soil solution. With regards to soil Fe, we hypothesized that there would be more extractable Fe in mineral soils under older forest, due to the prolonged weathering and precipitation and adsorption of more amorphous (less crystalline) Fe phases associated with OM.

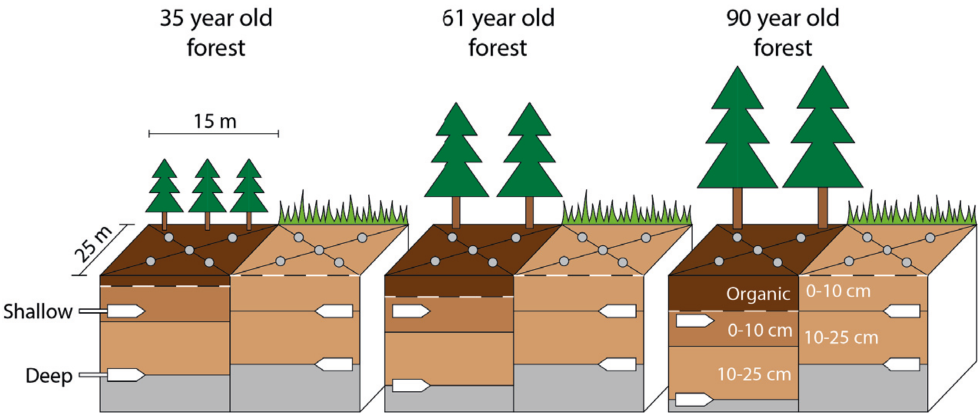


Figure 6 Experimental layout for the forested and accompanying control plots used in Paper II. Grey dots show the position for soil samples and lysimeters. White shapes in soil profile represent lysimeter depth position in each plot. Dashed white lines represent the surface of the mineral layer on each plot.

To compare the chemistry in soil solutions of the different plots, *suction cup lysimeters* were installed at two depths, just below the organic rich O-layer and deeper down in the mineral layer (Fig. 6 and 7). The lysimeters were sampled seven times during 2018-2019 to account for seasonal and between-year variation. Collected soil solution samples were analyzed for Fe, DOC, pH, conductivity, and concentrations of several other ions. In addition, some of the collected soil solution was freeze-dried and the material was used for analysis of Fe speciation by XAS.

To quantify the amount of extractable Fe in soils, three Fe extractions were performed. *Oxalate extractable Fe* (Fe_{ox}), represents more amorphous Fe phases, such as ferrihydrite and to some extent Fe-OM, phases that are most easily mobilized from soil. *Dithionite extractable Fe* (Fe_{dit}) represents both amorphous and crystalline Fe-(oxy)hydroxides, which includes phases such as goethite and hematite. Finally, a *total Fe digestion* (Fe_{tot}) was performed in order to quantify the total Fe pools in the soils.

X-ray absorption spectroscopy (XAS) is a powerful tool that can be used to determine the speciation of elements in their natural state. XAS is element specific, so one can examine one element without interference from other elements in the sample. Here it was used to determine Fe speciation in both soil and soil solution. Understanding Fe speciation in the soil allowed us to identify changes to the Fe pool, resulting from growing spruce forest, and helped us understand what Fe fractions could be mobilized into solution. XAS techniques have previously been successfully used to study Fe speciation and biogeochemical processing in soils and aquatic environments (Karlsson and Persson 2012, Sundman et al. 2014, Bhattacharyya et al. 2018, Herzog et al. 2019).

Figure 7 Spruce forest plot (61-years old; left) and lysimeter sampling bottles with soil solution (right) from Paper II.

XAS data was collected at Stanford Synchrotron Radiation Lightsource (SSRL), beamline 4-1. *Linear Combination Fitting (LCF)* was then used, to determine the relative proportions of different Fe phases in the samples. LCF reconstructs a sample spectrum by using a combination of model spectra, and reports goodness of fit parameters, along with the contribution of each model to the final fit. The accuracy of this method depends on the quality of the obtained sample spectra and the chosen modeled spectra (Datta et al. 2012). In this case sample spectra from the Extended X-ray Absorption Fine Structure (EXAFS) region were fit with reference spectra representing Fe(III)-OM complexes, several Fe-(oxy)hydroxides and biotite. To determine the coordination and oxidation state of Fe in the samples, pre-edge peak integrated intensity and centroid energy position were identified. In addition, *geochemical equilibrium modelling* was performed using Visual MINTEQ ver. 3.1 (Gustaffson 2020), to calculate the theoretical speciation of Fe(III) in solution and the saturation indices of other Fe minerals.

In **Paper III**, we used the infrastructure and monitoring data from the Krycklan Study Catchment (KSC) in Northern Sweden (Laudon et al. 2013). To test if catchment sources, namely forest soils and mires, contribute differently to Fe trends, long-term monitoring data of Fe from boreal streams with varying proportion of forest and mire in the catchment, were examined. Stream water chemistry data, collected during 2003-2020, from 13 nested catchments (Fig. 8) was analyzed and correlated to specific land cover components in each catchment. In addition, we studied temporal dynamics in soil solution of the main catchment sources - a riparian forest soil and a mire – to understand what control Fe mobilization in these source areas (Agren et al. 2007, Björkvald et al. 2008). Finally, to better understand the pools of Fe that are present and can potentially be mobilized from the two sources, both the riparian and mire soils were sampled and analyzed using XAS.

Since forest soils were previously shown to be the important source for increasing DOM trends in these same systems, while wetlands did not contribute to long-term trends (Fork et al. 2020), we hypothesized that a similar pattern, with long-term increases in Fe that would be positively correlated to spruce cover in the catchment. We further hypothesized that wetlands and riparian soils would vary in their contribution to long-term trends and that this would be reflect by trends in streams.

To study Fe dynamics in riparian soils we used monitoring data from lysimeters installed at six different depths and sampled several times per year. For mire solution, data from piezometer installations was used (Fig. 8 & 9). Particular focus was on processes dominant source layer (DSL) of the riparian zone and mire, since this is the layer that provides the greatest contribution of solute and water fluxes from the catchment.

Seasonal Kendall tests were used to test for trends in Fe and other variables in both streams and the soil solutions, for the period 2003-2020. The Seasonal Kendall Test calculates trends for each month separately and then combines the results to identify trends that are not affected by seasonal variability. *Principal component analysis (PCA)* analysis was used to sort the 13 streams in the study based on catchment characteristics. To assess whether Fe trends were correlated with certain catchment characteristics, Theil-Sen slopes from the Seasonal Kendall test were correlated with scores on principal component one (PC1). *XAS analysis* was used to determine Fe speciation of the riparian soils, as described for Paper II. For mire samples XAS measurements were done at Balder beamline at the MAX IV synchrotron light

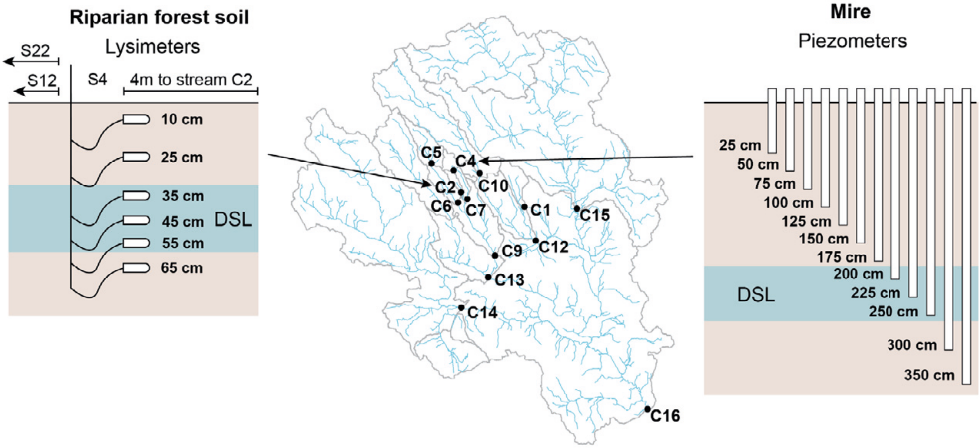


Figure 8 Overview of the sampling sites. Catchments in the Krycklan Study Catchment (middle), lysimeter setup in the riparian forest soil (S4), which drains into stream C2 (left), piezometer setup in the mire draining into stream C4 (right).

Figure 9 Experimental infrastructure on the C4 mire in the Krycklan Study Catchment. Photo: Martin Škerlep

facility in Lund, Sweden. In addition to the EXAFS spectra, LCF fitting was also done on the X-ray Absorption Near Edge Structure (XANES) spectra and was fit with vivianite, siderite and ferrihydrite for the mire.

In **Paper IV**, we compiled long-term records of water color for three lakes (1935-2020), and related them to historic land cover changes in the individual lake catchments. The catchment land cover of the three lakes differed widely (Table 1, Fig. 10). Lake Fiolen is an oligohumic lake with deciduous and mixed forest in the catchment. Lake Skärshultsjön is a polyhumic lake, with a high proportion of coniferous forest in the catchment. Finally, Lake Vombsjön is a eutrophic lake and

Table 1 Catchment characteristics of the three study lakes in Paper IV.

Lake	Lake area	Catchment size	Retention time	Water color 2010-2019	Forest	Open Land	Mire
WGS84	km^2	km^2	yr	mg Pt L^{-1}	%	%	%
Fiolen 57°5'N, 14°32'E	1.6	5.5	3.8	17	64	33	3.5
Skärshultsjön 57°9'N, 14°30'E	0.3	6.8	0.6	112	82	12	4.3
Vombsjön 55°41'N, 13°35'E	12	447	1.0	22	18	81	0.4

the catchment is dominated by open land used for agriculture. The dataset was complemented by data on atmospheric S deposition, and climatic variables, to also consider other factors than land cover change, on long-term water color dynamics.

We hypothesized that a change from a land cover type that does not promote build-up of organic soils, e.g. open land and deciduous forest, to a land cover type that does promote build-up of organic soils, e.g. coniferous forest and/wetland, would result in a significant water color increase in lakes. Furthermore, we expected that the age of the coniferous forest determines how much organic matter has accumulated, and that the effect of afforestation on water color would be delayed by several decades.

Land cover was reconstructed from aerial photographs, which has previously been used in a variety of studies, to assess effects of forest fires on vegetation (Lydersen and Collins 2018), landscape change due to urbanization (López et al. 2001), and afforestation of grasslands (Mast et al. 1997). For the two smaller catchments, reconstruction was done for the complete catchment, by separating distinct land features into polygons and land cover interpretation was done for each polygon (Fig. 10). For the significantly bigger catchment of Lake Vombsjön, reconstruction was done on a point-grid system, since interpretation of the entire catchment would have been too time consuming. This resulted in six catchment maps for each of the lakes from different time-points starting 1947 and ending in 2019.

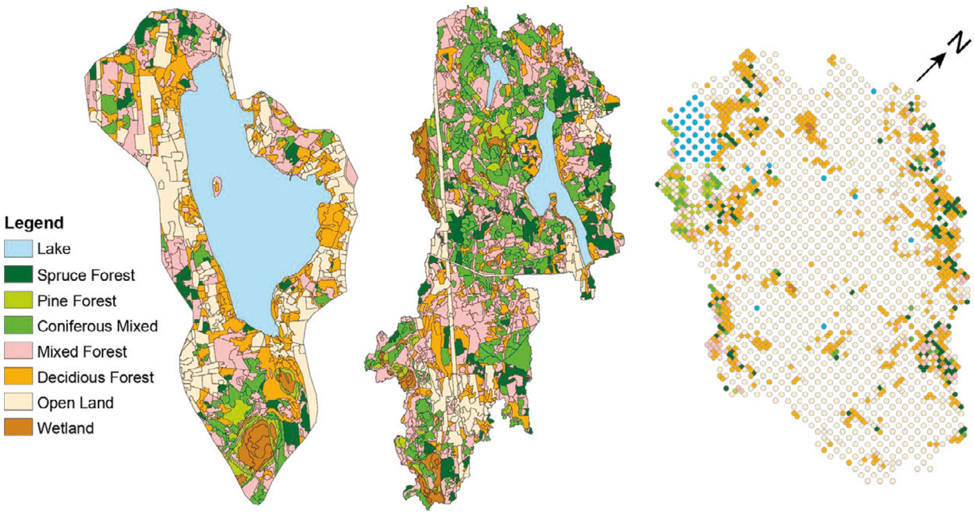


Figure 10 Reconstructed catchment cover of the three lakes in Paper IV for the most recent timepoint (2019/2016). Fiolen (left), Skärshultsjön (middle), Vombsjön (right).

Main Results

Long-term browning cannot be explained without accounting for afforestation (Paper I)

Water color in Lyckeby River increased by 84% between 1940 and 2016. When trying to explain the observed changes in water color, all five predicting variables used in this study (discharge, temperature, GDD, S deposition and spruce volume in the catchment) played a significant role and could together explain 75% of the variation in water color in a MLR model (Fig. 11B). PLS analysis further identified spruce forest, S deposition and discharge as the most important variables explaining variation in water color (Fig. 11A). This highlights the importance of considering multiple variables when evaluating the importance of drivers of browning.

Short-term dynamics were well explained by changes in discharge and to some extent temperature, both of which play an important role in catchment DOC production and its transport to surface waters. S deposition and spruce forest volume on the other hand, were better predictors of long-term water color trends. Spruce volume in the catchment increased by 508% between 1926 and 2016 and could on its own explain 49% of the variation in water color.

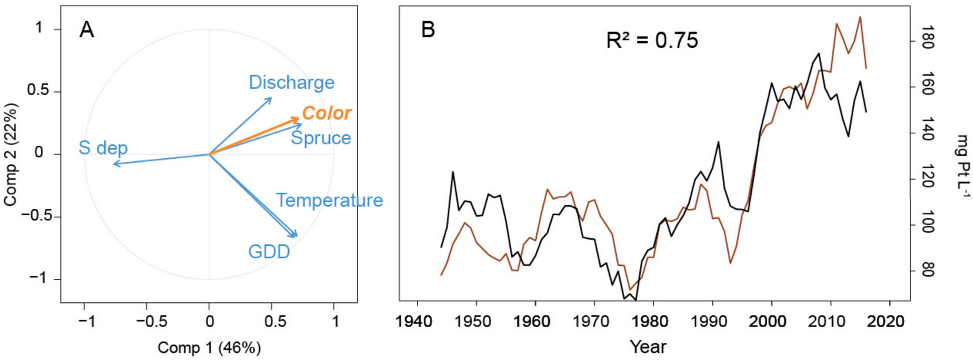


Figure 11 Correlations between water color and explanatory variables from a PLS model (A) and measured water color (brown line) *vs.* fitted water color (black line) from a MLR model using all explanatory variables (B).

By only including S deposition and climatic and variables as predictors, we could explain 45% of the variation in water color, but the model overestimated water color in the beginning and underestimated it in the end of the time series. There was little change in water color in the beginning of the time series when S deposition was increasing. This goes against the atmospheric deposition hypothesis, which predicts that increasing acidity suppressed mobility of DOC in soils. When spruce volume was included in the MLR model, this led to a significant improvement in the predicting power and to a considerably better fit ($R^2 = 0.75$) especially in the initial part of the time series. The mismatch between modelled and measured water color in the end of the time series (Fig. 11 B) can be attributed to windfall caused by storm Gudrun during 2007, which severely reduced spruce volume in the catchment, but may not necessarily have decreased the soil organic C pools.

This and other recent studies, highlight the importance of considering water color dynamics on a longer timescale than monitoring generally support, to be able to distinguish the importance of different drivers of long-term trends (Meyer-Jacob et al. 2015, Kritzberg 2017).

Mobilization of Fe and DOM is enhanced by spruce afforestation (Paper II)

Fe concentrations in soil solution under 61- and 90-year old spruce stands were 5- and 6-times higher than under grass covered control plots and under the 35-year old spruce forest. The higher Fe concentrations were correlated to higher DOC concentrations and lower pH in older spruce stands. In fact, DOC was the best predictor for Fe concentrations across all plots (including control plots), which indicates that complexation with OM is important to stabilize Fe in solution (Fig. 12). XAS analysis, supported by geochemical modelling, showed that mononuclear Fe(III)-OM complexes were the dominant form of Fe in solution, which confirmed the importance of OM complexation and that this is the dominating Fe phase being translocated. Functional groups of OM, such as carboxylic groups, form strong mononuclear Fe complexes (Karlsson and Persson 2012) which have been indicated to be important in facilitating transport of Fe from organic soils to surface waters (Sjöstedt et al. 2013).

While ageing spruce stands had a pronounced effect on Fe concentrations in soil solution, there were no clear differences in Fe speciation and crystallinity in the soil phase between the plots. Fe-(oxy)hydroxides dominated Fe speciation in all soil profiles and the abundance of Fe-OM complexes was highest in organic soil layers. We did however find that more Fe was extractable (Fe_{ox}) from deeper than from upper mineral soils in older forest plots ($p<0.001$), while such a gradient was not observed in control plots. This suggest translocation of Fe from upper to lower mineral soils and could reflect early stages of podsolization under the older spruce stands.

These results show that as spruce forest ages, it can support higher concentrations of Fe in solution, which is highly related to the availability of DOM. This is in line with previous findings showing that increasing trends of Fe in surface waters are more often found in catchments with high percentage of coniferous forest (Björnerås et al. 2017). The similarity between the 35-year old plot and the control plots, further shows that the effects of afforestation are not immediate and it may take several decades before Fe mobilization is enhanced.

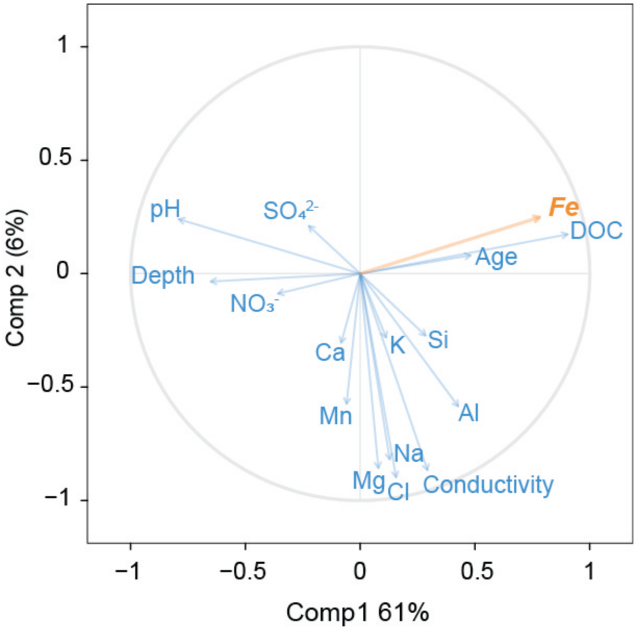


Figure 12 Correlation between Fe and explanatory variables in a PLS analysis for soil solution of forested plots.

Riparian forest soils are the source of increasing Fe trends in small streams (Paper III)

Of the 13 streams investigated, three showed significant increasing trends in Fe (C1, C2, C7), one showed no trend (C4) and the remaining nine showed decreasing trends. Trends in Fe concentrations were well correlated to the catchment characteristics, and all three streams with increasing Fe concentrations had catchments dominated by old spruce forest and high tree volume (Fig. 13). The stream with no trend had a catchment strongly influenced by an upstream mire,

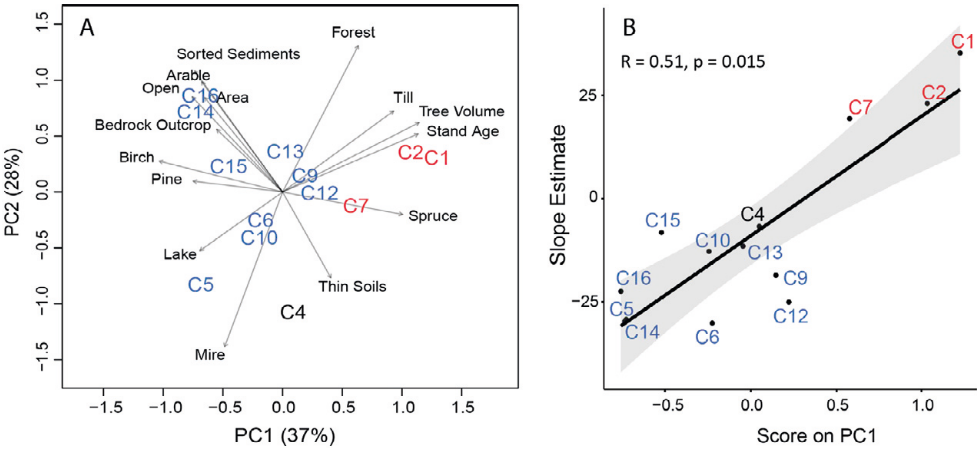


Figure 13 Streams and catchment characteristics sorted by PCA analysis (A). Correlation between the scores on PC1, which represent different catchment characteristics and the slope of the Fe trends in streams (B).

while the streams with negative Fe trends generally had bigger catchments with higher proportions of birch and pine forest in the catchment (Fig. 13). The decreasing trends in the majority of the streams were surprising, especially considering most of those streams exhibited positive trends in DOC.

In the forest riparian zone, Fe concentrations increasing over the study period, particularly in the DSL (~0.25 mg L^{-1} yr^{-1}; Fig. 14B). Concentrations of both Fe and DOC increased after 2007, and showed a strong negative correlation with SO_4^{2-}, which increased by 5-fold between 2006 and 2007 (Fig. 14F). This is believed to have been caused by an extremely dry year in 2006, which promoted mineralization of organic sulfur and a subsequent pulse of SO_4^{2-} once the soils were re-wetted (Ledesma et al. 2016). This drought likely also led to an increase in OM degradation in the riparian soil and may thereby have caused a prolonged increase in Fe and DOC mobilization. These dynamics in the riparian zone were well reflected in the Fe, DOC and SO_4^{2-} in stream C2 that drains the riparian zone in this study. On the other hand, data from the mire solution indicates no long-term change in Fe or DOC mobilization, and again, this was well reflected in the receiving stream (C4), where no long-term trends were observed for either Fe or DOC.

Besides showing differential trends in Fe exports, the riparian soil and the mire were also considerably different in Fe speciation. Riparian soil samples were dominated by Fe-OM complexes in the surface layer and contained a mixture of ferrihydrite, goethite, and biotite deeper down in the profile. In the mire, ferrihydrite, as well as vivianite and siderite, were identified with little variation with respect to depth.

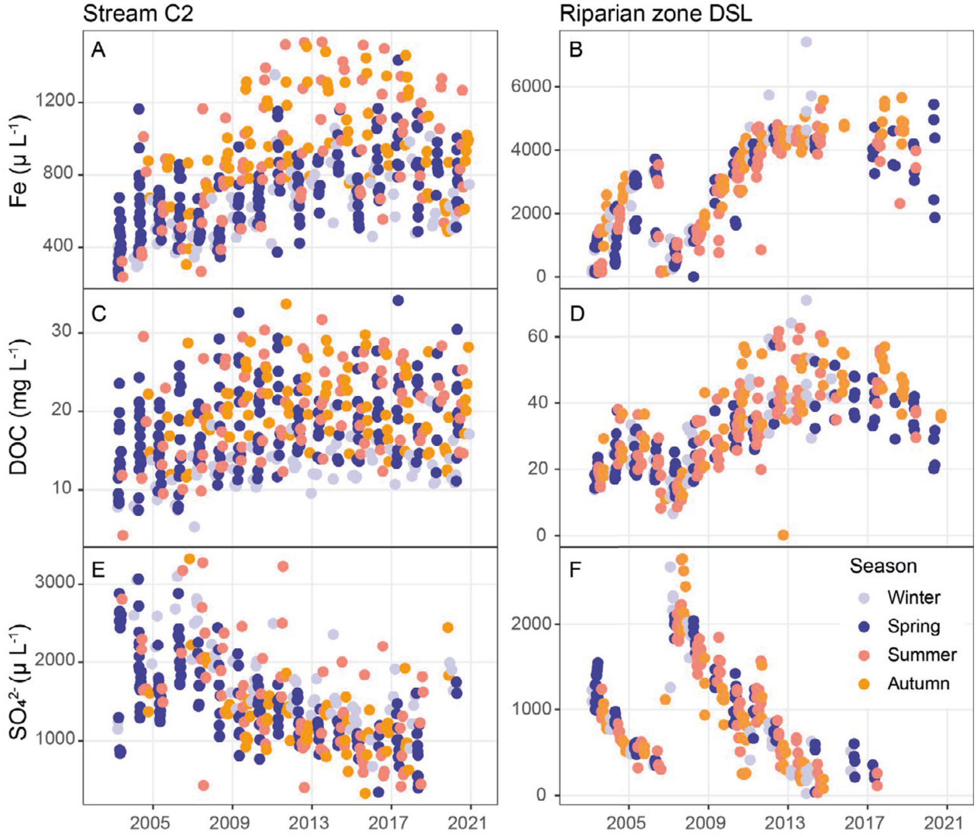


Figure 14 Concentrations of Fe, DOC and SO_4^{2-} in stream C2 (left panels) and the DSL of the riparian zone (right panels). Different colors represent different seasons.

In all, these results show that while both riparian zones and mires are important sources of Fe and DOC to boreal streams, the observed long-term increases can be linked to mobilization from riparian forest soils but not from mires. Finally, while the negative trends in Fe concentrations in the majority of streams could not be explained, these are possibly linked higher inputs from groundwater with lower Fe concentrations. Alternatively, the negative trends could be due to changes in in-stream Fe losses as the majority of these steams had larger catchments with presumably longer water residence times.

Land cover sets the base line for temporal trends in water color (Paper IV)

Water color in lake Fiolen was relatively low (mean 17 mg Pt L^{-1}) and exhibited a significant increase since 1935 (0.4 mg Pt L^{-1} yr^{-1}). Lake Skärshultsjön had considerably higher water color (112 mg Pt L^{-1}) and also showed a strong browning since 1935 (1.4 mg Pt L^{-1} yr^{-1}). In Lake Vombsjön water color remained low throughout the time series (mean 22 mg Pt L^{-1}) and showed a slight decrease since 1937 (-0.2 mg Pt L^{-1} yr^{-1}). The catchments of the two lakes were water color increased, had a considerable proportion of forest in 1947, which increased during the study period (Fig. 15). Forest cover increased at the expense of open land and wetland area. This land cover change is part of a landscape transition in this region that began earlier, where abandonment of open land led to afforestation from the end of the 19th century, and to intensive forestry dominated by spruce in more recent times (Fredh et al. 2012, Lindbladh et al. 2014). Although our results do not specifically show a strong expansion in spruce forest cover, the general expansion of forest in the catchment probably led to an increase in organic soils, which increase the amount of DOM and Fe available for export to surface waters. Wetland area was replaced by pine forest, and in Lake Fiolen where the wetland area was in close connection to the lake, wetland area was negatively correlated to water color. The catchment of Lake Vombsjön was strongly dominated by open land and showed little change in land cover throughout the time series.

Water color in Lake Fiolen and Skärshultsjön was negatively correlated with S deposition, and positively correlated with the length of the growing season and discharge. However, when looking at the period before and after peak S deposition separately, we found that while water color increased during the period of declining deposition, there was no response in water color to increasing deposition. Water color in Lake Vombsjön did neither show an inverse relationship with S deposition nor a positive relationship with GDD or precipitation. This demonstrates, that the influence of climate variables and S-deposition on water color depend on the presence of organic soils, which were abundant and increasing in Lake Fiolen and Skärshultsjön, but lacking in the catchment of Lake Vombsjön.

Overall, these results highlight that climate variables, S deposition, and land cover change in the catchment, all have an influence on lake water color, but that the degree of influence depends on the prevailing conditions surrounding individual lakes.

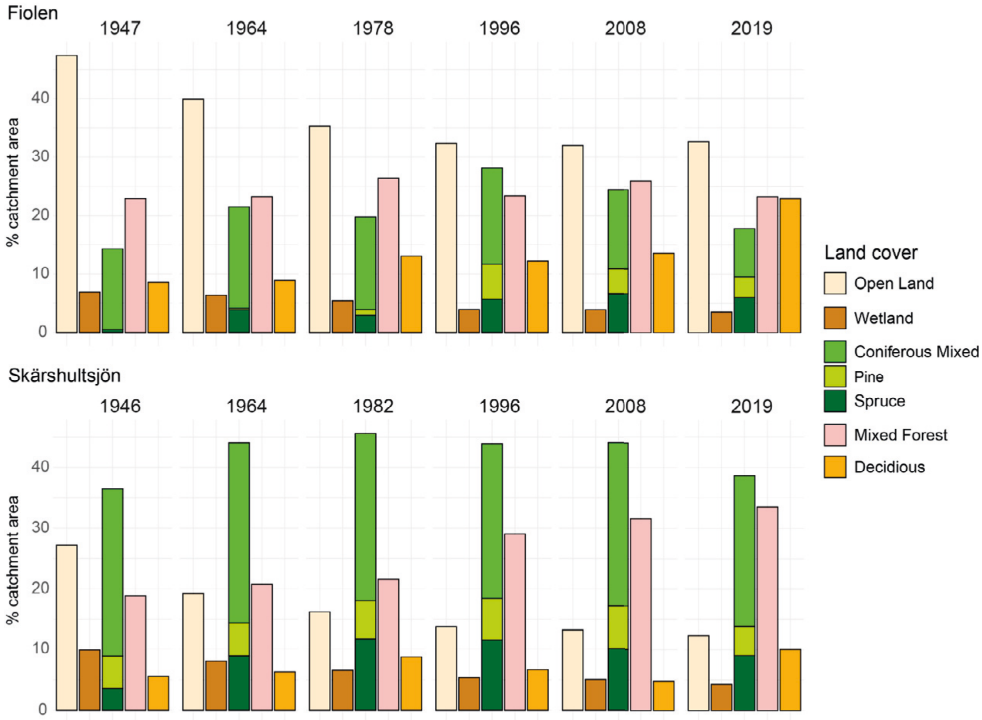


Figure 15 Land cover proportions in different years in the catchments of Lake Fiolen (top) and Lake Skärshultsjön (bottom).

Conclusions and Outlooks

This thesis shows that the three major drivers considered - S deposition, climate change and land cover change – all contribute significantly to long-term trends in water color. Moreover, the pronounced long-term browning since the 1930/1940s cannot be explained without accounting for land cover change. Land cover determines the size of the OM pool in the catchment, and thereby sets the baseline for the amount of DOM and Fe available. Climate drivers and S deposition can then modulate the amount of DOM and Fe that is mobilized and transported to freshwaters.

These conclusions relied on a combination of uniquely long water color time series and the characterization of land cover change (Paper I, IV). Although previous research recognized land cover as decisive to water color on spatial scales, the shorter time perspective in most temporal studies cannot reveal effects of land cover change, which take place on longer temporal scales. The use of spruce volume from forest inventory provided a quantitative and temporally well-resolved measure of land cover change that integrated both the areal extension and tree growth and should thereby reflect the accumulation of OM pools in spruce soils (Paper I). Land cover reconstruction form aerial photographs, provided more spatially resolved information that included several land cover types. The methods are complementary, since the use of spruce volume provided a stronger basis for establishing statistical models, and the use of land cover from aerial photographs allowed the identification of changes in other land cover types that may be of significance, such as wetlands, and knowing where in the catchment changes have happened. There is further potential to use this data to determine the importance of land cover changes depending on their hydrological connectivity with the lake, by including information on hydrology (Bhattacharjee et al. 2021).

The idea that afforestation with spruce may contribute to rising concentrations of Fe and DOM in surface waters, was further supported by experimental efforts, showing considerably higher mobilization of Fe and DOM in soils under older spruce stands in a chronosequence (Paper II). While previous studies have reported similar results for DOM, this enhances our considerably more limited understanding about Fe dynamics and the processes that govern its export form soils. Characterization of Fe speciation by XAS revealed that mononuclear Fe(III)-OM complexes were the predominant phase for Fe mobilization, which in combination with other studies (Sjöstedt et al. 2013, Sundman et al. 2014), suggests that this is also the most likely

Fe phase to be transported to surface waters from organic soils. Mobilization of Fe and DOM under 35-year old forest did not differ from control plots, indicating that effects off afforestation will not be immediate, but can take several decades to materialize. That the slow and gradual build-up of organic moor layers after afforestation will have a delayed effect on browning (Kritzberg 2017) is also in line with the temporal mismatch between changes in land cover and water color in Paper IV.

The role of spruce forests was further highlighted by the fact that increasing trends in stream Fe concentrations were observed in catchments with high proportion of old spruce forest, but not in catchments with more mire, open land, and deciduous forest cover (Paper III). Long-term increase of Fe concentrations in solution of the riparian forest soils, and the lack of a trend in the soil solution of the mire, also point to spruce forest soils as an important source to support increasing Fe trends in streams. Notably, it was only by looking at the dynamics in riparian soil solution that it became clear that the increase in Fe and DOC mobilization was linked to an extreme drought event. This underlines the importance of studying dynamics in source areas, to understand the factors that control mobilization from the catchment, and not relying solely on stream water chemistry.

Besides these main conclusions, research in this thesis led point to several interesting but unresolved questions. For example, the exact mechanism/s involved in the mobilization of Fe into soil solution in organic forest soils remain to identify. The potential role of microorganisms is particularly interesting, since fungal communities differ with the dominant tree species and age of forest, and some species are known to use Fenton chemistry which may enhance Fe mobilization (Reichard et al. 2007, Op De Beeck et al. 2018). Moreover, to what extent and how, mobilized Fe moves through catchment soils, and can provide a source of Fe to surface waters, is poorly understood and warrants further study. That the majority of streams in Paper III showed negative Fe trends is an interesting finding, at odds with other studies that mostly show positive Fe trends in Swedish waters (Ekström et al. 2016, Björnerås et al. 2017), and could thus far not be explained by the associated data.

With continuous build-up of organic soils under coniferous forests and the slow release of historically deposited S from organic soils, one may predict that browning will continue in the upcoming decades. Longer growing seasons, shorter periods with soil frost and increasing precipitation and discharge would further promote such a trend. However, forecasting future water color is not as simple. Increasing deciduous forest cover at the expense of coniferous forest, which is motivated by several positive ecosystem effects and resistance to storm fall and climate change, may reduce export of DOM and Fe to freshwaters, although effects in surface waters could be delayed for decades. Another strongly complicating factor is the increased occurrence of extreme weather events (Stott 2016), and our limited knowledge of the consequences of e.g. drought on DOM and Fe export to surface waters.

References

Agren, A., I. Buffam, M. Jansson, and H. Laudon. 2007. Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. Journal of Geophysical Research-Biogeosciences **112**.

Akaike, H. 1974. New Look at Statistical-Model Identification. Ieee Transactions on Automatic Control **Ac19**:716-723.

Akselsson, C., H. Hultberg, P. E. Karlsson, G. P. Karlsson, and S. Hellsten. 2013. Acidification trends in south Swedish forest soils 1986-2008-Slow recovery and high sensitivity to sea-salt episodes. Science of the Total Environment **444**:271-287.

Andersson, S., S. I. Nilsson, and P. Saetre. 2000. Leaching of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in mor humus as affected by temperature and pH. Soil Biology & Biochemistry **32**:1-10.

Arvola, L., M. Rask, J. Ruuhijarvi, T. Tulonen, J. Vuorenmaa, T. Ruoho-Airola, and J. Tulonen. 2010. Long-term patterns in pH and colour in small acidic boreal lakes of varying hydrological and landscape settings. Biogeochemistry **101**:269-279.

Bergkvist, B. 1986. Leaching of Metals from a Spruce Forest Soil as Influenced by Experimental Acidification. Water Air and Soil Pollution **31**:901-916.

Bhattacharjee, J., H. Marttila, A. T. Haghighi, M. Saarimaa, A. Tolvanen, A. Lepistö, M. N. Futter, and B. Kløve. 2021. Development of Aerial Photos and LIDAR Data Approaches to Map Spatial and Temporal Evolution of Ditch Networks in Peat-Dominated Catchments. Journal of Irrigation and Drainage Engineering **147**:04021006.

Bhattacharyya, A., M. P. Schmidt, E. Stavitski, and C. E. Martínez. 2018. Iron speciation in peats: chemical and spectroscopic evidence for the co-occurrence of ferric and ferrous iron in organic complexes and mineral precipitates. Organic Geochemistry **115**:124-137.

Björkvald, L., I. Buffam, H. Laudon, and C.-M. Mörth. 2008. Hydrogeochemistry of Fe and Mn in small boreal streams: The role of seasonality, landscape type and scale. Geochimica et Cosmochimica Acta **72**:2789-2804.

Björnerås, C., M. Škerlep, D. Floudas, P. Persson, and E. S. Kritzberg. 2019. High sulfate concentration enhances iron mobilization from organic soil to water. Biogeochemistry **144**:245-259.

Björnerås, C., G. A. Weyhenmeyer, C. D. Evans, M. O. Gessner, H. P. Grossart, K. Kangur, I. Kokorite, P. Kortelainen, H. Laudon, J. Lehtoranta, N. Lottig, D. T. Monteith, P. Nõges, T. Nõges, F. Oulehle, G. Riise, J. A. Rusak, A. Räike, J. Sire, S. Sterling, and E. S. Kritzberg. 2017. Widespread Increases in Iron Concentration in European and North American Freshwaters. Global Biogeochemical Cycles **31**:1488-1500.

Blume, H., and U. Schwertmann. 1969. Genetic evaluation of profile distribution of aluminum, iron, and manganese oxides. Soil Science Society of America Journal **33**:438-444.

Bragee, P., F. Mazier, A. B. Nielsen, P. Rosen, D. Fredh, A. Brostrom, W. Graneli, and D. Hammarlund. 2015. Historical TOC concentration minima during peak sulfur deposition in two Swedish lakes. Biogeosciences **12**:307-322.

Camino-Serrano, M., B. Gielen, S. Luyssaert, P. Ciais, S. Vicca, B. Guenet, B. D. Vos, N. Cools, B. Ahrens, M. Altaf Arain, W. Borken, N. Clarke, B. Clarkson, T. Cummins, A. Don, E. G. Pannatier, H. Laudon, T. Moore, T. M. Nieminen, M. B. Nilsson, M. Peichl, L. Schwendenmann, J. Siemens, and I. Janssens. 2014. Linking variability in soil solution dissolved organic carbon to climate, soil type, and vegetation type. Global Biogeochemical Cycles **28**:497-509.

Carpenter, S. R., J. J. Cole, M. L. Pace, M. Van de Bogert, D. L. Bade, D. Bastviken, C. M. Gille, J. R. Hodgson, J. F. Kitchell, and E. S. Kritzberg. 2005. Ecosystem subsidies: Terrestrial support of aquatic food webs from C-13 addition to contrasting lakes. Ecology **86**:2737-2750.

Clark, J. M., S. H. Bottrell, C. D. Evans, D. T. Monteith, R. Bartlett, R. Rose, R. J. Newton, and P. J. Chapman. 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. Sci Total Environ **408**:2768-2775.

Cole, J. J., Y. T. Prairie, N. F. Caraco, W. H. McDowell, L. J. Tranvik, R. G. Striegl, C. M. Duarte, P. Kortelainen, J. A. Downing, J. J. Middelburg, and J. Melack. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems **10**:171-184.

Cornell, R., and U. Schwertmann. 1979. Influence of organic anions on the crystallization of ferrihydrite. Clays and Clay Minerals **27**:402-410.

Creed, I. F., A. K. Bergstrom, C. G. Trick, N. B. Grimm, D. O. Hessen, J. Karlsson, K. A. Kidd, E. Kritzberg, D. M. McKnight, E. C. Freeman, O. E. Senar, A. Andersson, J. Ask, M. Berggren, M. Cherif, R. Giesler, E. R. Hotchkiss, P. Kortelainen, M. M. Palta, T. Vrede, and G. A. Weyhenmeyer. 2018. Global change-driven effects on dissolved organic matter composition: Implications for food webs of northern lakes. Global Change Biology **24**:3692-3714.

Cunningham, L., K. Bishop, E. Mettavainio, and P. Rosen. 2011. Paleoecological evidence of major declines in total organic carbon concentrations since the nineteenth century in four nemoboreal lakes. Journal of Paleolimnology **45**:507-518.

Datta, S., A. M. Rule, J. N. Mihalic, S. N. Chillrud, B. C. Bostick, J. P. Ramos-Bonilla, I. Han, L. M. Polyak, A. S. Geyh, and P. N. Breysse. 2012. Use of X-ray absorption spectroscopy to speciate manganese in airborne particulate matter from five counties across the United States. Environmental science & technology **46**:3101-3109.

de Wit, H. A., S. Valinia, G. A. Weyhenmeyer, M. N. Futter, P. Kortelainen, K. Austnes, D. O. Hessen, A. Räike, H. Laudon, and J. Vuorenmaa. 2016. Current Browning of Surface Waters Will Be Further Promoted by Wetter Climate. Environmental Science & Technology Letters **3**:430-435.

Drake, T. W., P. A. Raymond, and R. G. M. Spencer. 2018. Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty. Limnology and Oceanography Letters **3**:132-142.

Driscoll, C. T., K. M. Driscoll, K. M. Roy, and M. J. Mitchell. 2003. Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. Environmental science & technology **37**:2036-2042.

Duckworth, O. W., S. J. Holmström, J. Peña, and G. Sposito. 2009. Biogeochemistry of iron oxidation in a circumneutral freshwater habitat. Chemical Geology **260**:149-158.

Ekström, S. M., E. S. Kritzberg, D. B. Kleja, N. Larsson, P. A. Nilsson, W. Graneli, and B. Bergkvist. 2011. Effect of acid deposition on quantity and quality of dissolved organic matter in soil–water. Environmental science & technology **45**:4733-4739.

Ekstrom, S. M., O. Regnell, H. E. Reader, P. A. Nilsson, S. Lofgren, and E. S. Kritzberg. 2016. Increasing concentrations of iron in surface waters as a consequence of reducing conditions in the catchment area. Journal of Geophysical Research-Biogeosciences **121**:479-493.

Ekström, S. M., O. Regnell, H. E. Reader, P. A. Nilsson, S. Löfgren, and E. S. Kritzberg. 2016. Increasing concentrations of iron in surface waters as a consequence of reducing conditions in the catchment area. Journal of Geophysical Research: Biogeosciences **121**:479-493.

Erlandsson, M., I. Buffam, J. Folster, H. Laudon, J. Temnerud, G. A. Weyhenmeyer, and K. Bishop. 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. Global Change Biology **14**:1191-1198.

Fenner, N., and C. Freeman. 2011. Drought-induced carbon loss in peatlands. Nature Geoscience **4**:895-900.

Finstad, A. G., T. Andersen, S. Larsen, K. Tominaga, S. Blumentrath, H. A. de Wit, H. Tommervik, and D. O. Hessen. 2016. From greening to browning: Catchment vegetation development and reduced S-deposition promote organic carbon load on decadal time scales in Nordic lakes. Sci Rep **6**:31944.

Finstad, A. G., I. P. Helland, O. Ugedal, T. Hesthagen, and D. O. Hessen. 2014. Unimodal response of fish yield to dissolved organic carbon. Ecology Letters **17**:36-43.

Fork, M. L., R. A. Sponseller, and H. Laudon. 2020. Changing source-transport dynamics drive differential browning trends in a boreal stream network. Water Resources Research **56**:e2019WR026336.

Foster, D. R., G. Motzkin, and B. Slater. 1998. Land-use history as long-term broad-scale disturbance: Regional forest dynamics in central New England. Ecosystems **1**:96-119.

Fredh, D., A. Brostrom, L. Zillen, F. Mazier, M. Rundgren, and P. Lageras. 2012. Floristic diversity in the transition from traditional to modern land-use in southern Sweden AD 1800-2008. Vegetation History and Archaeobotany **21**:439-452.

Fuchs, R., M. Herold, P. H. Verburg, J. G. Clevers, and J. Eberle. 2015. Gross changes in reconstructions of historic land cover/use for Europe between 1900 and 2010. Glob Chang Biol **21**:299-313.

Fukushima, M., Y. Tanabe, H. Yabuta, F. Tanaka, H. Ichikawa, K. Tatsumi, and A. Watanabe. 2006. Water solubility enhancement effects of some polychlorinated organic pollutants by dissolved organic carbon from a soil with a higher organic carbon content. Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering **41**:1483-1494.

Garmo, O. A., B. L. Skjelkvale, H. A. de Wit, L. Colombo, C. Curtis, J. Folster, A. Hoffmann, J. Hruska, T. Hogasen, D. S. Jeffries, W. B. Keller, P. Kram, V. Majer, D. T. Monteith, A. M. Paterson, M. Rogora, D. Rzychon, S. Steingruber, J. L. Stoddard, J. Vuorenmaa, and A. Worsztynowicz. 2014. Trends in Surface Water Chemistry in Acidified Areas in Europe and North America from 1990 to 2008. Water Air and Soil Pollution **225**.

Grubisic, L. M., A. Brutemark, G. A. Weyhenmeyer, J. Wikner, U. Bamstedt, and S. Bertilsson. 2012. Effects of stratification depth and dissolved organic matter on brackish bacterioplankton communities. Marine Ecology Progress Series **453**:37-48.

Guo, L. B., and R. M. Gifford. 2002. Soil carbon stocks and land use change: a meta analysis. Global Change Biology **8**:345-360.

Gustaffson, J. 2020. Visual MINTEQ, version 3.1. KTH, Stockholm, Sweden.

Haaland, S., D. Hongve, H. Laudon, G. Riise, and R. D. Vogt. 2010. Quantifying the Drivers of the Increasing Colored Organic Matter in Boreal Surface Waters. Environmental science & technology **44**:2975-2980.

Hagedorn, F., K. Kaiser, H. Feyen, and P. Schleppi. 2000. Effects of redox conditions and flow processes on the mobility of dissolved organic carbon and nitrogen in a forest soil. 0047-2425, Wiley Online Library.

Hansson, K., M. Froberg, H. S. Helmisaari, D. B. Kleja, B. A. Olsson, M. Olsson, and T. Persson. 2013a. Carbon and nitrogen pools and fluxes above and below ground in spruce, pine and birch stands in southern Sweden. Forest Ecology and Management **309**:28-35.

Hansson, L. A., A. Nicolle, W. Graneli, P. Hallgren, E. Kritzberg, A. Persson, J. Bjork, P. A. Nilsson, and C. Bronmark. 2013b. Food-chain length alters community responses to global change in aquatic systems. Nature Climate Change **3**:228-233.

Heathcote, A. J., N. J. Anderson, Y. T. Prairie, D. R. Engstrom, and P. A. del Giorgio. 2015. Large increases in carbon burial in northern lakes during the Anthropocene. Nature Communications **6**.

Herzog, S. D., S. Conrad, J. Ingri, P. Persson, and E. S. Kritzberg. 2019. Spring flood induced shifts in Fe speciation and fate at increased salinity. Applied Geochemistry **109**:104385.

Hongve, D., G. Riise, and J. F. Kristiansen. 2004. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water - a result of increased precipitation? Aquatic Sciences **66**:231-238.

Howarth, R. W., and S. Merkel. 1984. Pyrite formation and the measurement of sulfate reduction in salt marsh sediments 1. Limnology and Oceanography **29**:598-608.

Humborg, C., E. Smedberg, S. Blomqvist, C. M. Morth, J. Brink, L. Rahm, A. Danielsson, and J. Sahlberg. 2004. Nutrient variations in boreal and subarctic Swedish rivers: Landscape control of land-sea fluxes. Limnology and Oceanography **49**:1871-1883.

Jansen, B., K. G. Nierop, and J. M. Verstraten. 2003. Mobility of Fe (II), Fe (III) and Al in acidic forest soils mediated by dissolved organic matter: influence of solution pH and metal/organic carbon ratios. Geoderma **113**:323-340.

Jansson, M., L. Persson, A. M. De Roos, R. I. Jones, and L. J. Tranvik. 2007. Terrestrial carbon and intraspecific size-variation shape lake ecosystems. Trends in Ecology & Evolution **22**:316-322.

Joensuu, S., E. Ahti, and M. Vuollekoski. 2002. Effects of ditch network maintenance on the chemistry of run-off water from peatland forests. Scandinavian Journal of Forest Research **17**:238-247.

Jones, D. L., P. R. Darah, and L. V. Kochian. 1996. Critical evaluation of organic acid mediated iron dissolution in the rhizosphere and its potential role in root iron uptake. Plant and soil **180**:57-66.

Jones, R. I. 1992. The Influence of Humic Substances on Lacustrine Planktonic Food-Chains. Hydrobiologia **229**:73-91.

Kaiser, K., G. Guggenberger, and W. Zech. 1996. Sorption of DOM and DOM fractions to forest soils. Geoderma **74**:281-303.

Karlsson, J., P. Byström, J. Ask, P. Ask, L. Persson, and M. Jansson. 2009. Light limitation of nutrient-poor lake ecosystems. Nature **460**:506-509.

Karlsson, T., and P. Persson. 2012. Complexes with aquatic organic matter suppress hydrolysis and precipitation of Fe (III). Chemical Geology **322**:19-27.

Keeler, B. L., S. A. Wood, S. Polasky, C. Kling, C. T. Filstrup, and J. A. Downing. 2015. Recreational demand for clean water: evidence from geotagged photographs by visitors to lakes. Frontiers in Ecology and the Environment **13**:76-81.

Kohler, S. J., E. Lavonen, A. Keucken, P. Schmitt-Kopplin, T. Spanjer, and K. Persson. 2016. Upgrading coagulation with hollow-fibre nanofiltration for improved organic matter removal during surface water treatment. Water Research **89**:232-240.

Kritzberg, E. S. 2017. Centennial-long trends of lake browning show major effect of afforestation. Limnology and Oceanography Letters **2**:105-112.

Kritzberg, E. S., J. J. Cole, M. M. Pace, and W. Graneli. 2005. Does autochthonous primary production drive variability in bacterial metabolism and growth efficiency in lakes dominated by terrestrial C inputs? Aquatic Microbial Ecology **38**:103-111.

Kritzberg, E. S., and S. M. Ekstrom. 2012. Increasing iron concentrations in surface waters - a factor behind brownification? Biogeosciences **9**:1465-1478.

Lalonde, K., A. Mucci, A. Ouellet, and Y. Gelinas. 2012. Preservation of organic matter in sediments promoted by iron. Nature **483**:198-200.

Larsen, S., T. Andersen, and D. O. Hessen. 2011. Predicting organic carbon in lakes from climate drivers and catchment properties. Global Biogeochemical Cycles **25**.

Larsson, J. 2012. The Expansion and Decline of a Transhumance System in Sweden, 1550-1920.

Laudon, H., J. Buttle, S. K. Carey, J. McDonnell, K. McGuire, J. Seibert, J. Shanley, C. Soulsby, and D. Tetzlaff. 2012. Cross-regional prediction of long-term trajectory of stream water DOC response to climate change. Geophysical Research Letters **39**.

Laudon, H., J. Hedtjarn, J. Schelker, K. Bishop, R. Sorensen, and A. Agren. 2009. Response of Dissolved Organic Carbon following Forest Harvesting in a Boreal Forest. Ambio **38**:381-386.

Laudon, H., I. Taberman, A. Agren, M. Futter, M. Ottosson-Lofvenius, and K. Bishop. 2013. The Krycklan Catchment Study-A flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape. Water Resources Research **49**:7154-7158.

Lavonen, E. E., M. Gonsior, L. J. Tranvik, P. Schmitt-Kopplin, and S. J. Kohler. 2013. Selective Chlorination of Natural Organic Matter: Identification of Previously Unknown Disinfection Byproducts. Environmental science & technology **47**:2264-2271.

Ledesma, J. L., M. N. Futter, M. Blackburn, F. Lidman, T. Grabs, R. A. Sponseller, H. Laudon, K. H. Bishop, and S. J. Köhler. 2018. Towards an improved conceptualization of riparian zones in boreal forest headwaters. Ecosystems **21**:297-315.

Ledesma, J. L. J., M. N. Futter, H. Laudon, C. D. Evans, and S. J. Kohler. 2016. Boreal forest riparian zones regulate stream sulfate and dissolved organic carbon. Science of the Total Environment **560**:110-122.

Lepisto, A., M. N. Futter, and P. Kortelainen. 2014. Almost 50 years of monitoring shows that climate, not forestry, controls long-term organic carbon fluxes in a large boreal watershed. Glob Chang Biol **20**:1225-1237.

Li, J., D. d. Richter, A. Mendoza, and P. Heine. 2008. Four-decade responses of soil trace elements to an aggrading old-field forest: B, Mn, Zn, Cu, and Fe. Ecology **89**:2911-2923.

Lidman, F., Å. Boily, H. Laudon, and S. J. Köhler. 2017. From soil water to surface water – how the riparian zone controls element transport from a boreal forest to a stream. Biogeosciences **14**:3001-3014.

Lindbladh, M., A.-L. Axelsson, T. Hultberg, J. Brunet, and A. Felton. 2014. From broadleaves to spruce – the borealization of southern Sweden. Scandinavian Journal of Forest Research **29**:686-696.

Lindsay, W., and A. Schwab. 1982. The chemistry of iron in soils and its availability to plants. Journal of Plant Nutrition **5**:821-840.

Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley and Sons Ltd., Chichester, Sussex, UK.

Liski, J., A. Lehtonen, T. Palosuo, M. Peltoniemi, T. Eggers, P. Muukkonen, and R. Makipaa. 2006. Carbon accumulation in Finland's forests 1922-2004 - an estimate obtained by combination of forest inventory data with modelling of biomass, litter and soil. Annals of Forest Science **63**:687-697.

López, E., G. Bocco, M. Mendoza, and E. Duhau. 2001. Predicting land-cover and land-use change in the urban fringe: A case in Morelia city, Mexico. Landscape and urban planning **55**:271-285.

Lydersen, J. M., and B. M. Collins. 2018. Change in vegetation patterns over a large forested landscape based on historical and contemporary aerial photography. Ecosystems **21**:1348-1363.

Maloney, K. O., D. P. Morris, C. O. Moses, and C. L. Osburn. 2005. The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water. Biogeochemistry **75**:393-407.

Mast, J. N., T. T. Veblen, and M. E. Hodgson. 1997. Tree invasion within a pine/grassland ecotone: an approach with historic aerial photography and GIS modeling. Forest Ecology and Management **93**:181-194.

Mattsson, T., P. Kortelainen, A. Laubel, D. Evans, M. Pujo-Pay, A. Raike, and P. Conan. 2009. Export of dissolved organic matter in relation to land use along a European climatic gradient. Sci Total Environ **407**:1967-1976.

McClain, M. E., E. W. Boyer, C. L. Dent, S. E. Gergel, N. B. Grimm, P. M. Groffman, S. C. Hart, J. W. Harvey, C. A. Johnston, and E. Mayorga. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems:301-312.

McLaughlin, J. W., J. C. Lewin, D. D. Reed, C. C. Trettin, M. F. Jurgensen, and M. R. Gale. 1994. Soil factors related to dissolved organic carbon concentrations in a black spruce swamp, Michigan. Soil science **158**:454-464.

McMillan, S., and U. Schwertmann. 1998. Morphological and genetic relations between siderite, calcite and goethite in a Low Moor Peat from southern Germany. European Journal of Soil Science **49**:283-293.

Meyer-Jacob, C., J. Tolu, C. Bigler, H. Yang, and R. Bindler. 2015. Early land use and centennial scale changes in lake-water organic carbon prior to contemporary monitoring. Proc Natl Acad Sci U S A **112**:6579-6584.

Monteith, D. T., J. L. Stoddard, C. D. Evans, H. A. de Wit, M. Forsius, T. Hogasen, A. Wilander, B. L. Skjelkvale, D. S. Jeffries, J. Vuorenmaa, B. Keller, J. Kopacek, and J. Vesely. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature **450**:537-540.

Moody, C. S., F. Worrall, C. D. Evans, and T. G. Jones. 2013. The rate of loss of dissolved organic carbon (DOC) through a catchment. Journal of Hydrology **492**:139-150.

Mormul, R. P., J. Ahlgren, M. K. Ekvall, L. A. Hansson, and C. Bronmark. 2012. Water brownification may increase the invasibility of a submerged non-native macrophyte. Biological Invasions **14**:2091-2099.

Myrstener, E., S. Ninnes, C. Meyer-Jacob, T. Mighall, and R. Bindler. 2021. Long-term development and trajectories of inferred lake-water organic carbon and pH in naturally acidic boreal lakes. Limnology and Oceanography **66**:2408-2422.

Nason, J. A., D. J. Bloomquist, and M. S. Sprick. 2012. Factors Influencing Dissolved Copper Concentrations in Oregon Highway Storm Water Runoff. Journal of Environmental Engineering-Asce **138**:734-742.

Neal, C., S. Lofts, C. Evans, B. Reynolds, E. Tipping, and M. Neal. 2008. Increasing iron concentrations in UK upland waters. Aquatic Geochemistry **14**:263-288.

Neubauer, E., S. J. Köhler, F. von der Kammer, H. Laudon, and T. Hofmann. 2013. Effect of pH and stream order on iron and arsenic speciation in boreal catchments. Environmental science & technology **47**:7120-7128.

Nieminen, M., E. Ahti, H. Koivusalo, T. Mattson, S. Sarkkola, and A. Lauren. 2010. Export of Suspended Solids and Dissolved Elements from Peatland Areas after Ditch Network Maintenance in South-Central Finland. Silva Fennica **44**:39-49.

Nieminen, M., S. Sarkkola, T. Sallantaus, E. M. Hasselquist, and H. Laudon. 2021. Peatland drainage-a missing link behind increasing TOC concentrations in waters from high latitude forest catchments? Science of the Total Environment **774**:145150.

Nikulin, G., E. Kjellstrom, U. Hansson, G. Strandberg, and A. Ullerstig. 2011. Evaluation and future projections of temperature, precipitation and wind extremes over Europe in an ensemble of regional climate simulations. Tellus Series a-Dynamic Meteorology and Oceanography **63**:41-55.

Okkenhaug, G., A. B. Smebye, T. Pabst, C. E. Amundsen, H. Saevarsson, and G. D. Breedveld. 2018. Shooting range contamination: mobility and transport of lead (Pb), copper (Cu) and antimony (Sb) in contaminated peatland. Journal of Soils and Sediments **18**:3310-3323.

Op De Beeck, M., C. Troein, C. Peterson, P. Persson, and A. Tunlid. 2018. Fenton reaction facilitates organic nitrogen acquisition by an ectomycorrhizal fungus. New Phytologist **218**:335-343.

Palviainen, M., J. Lehtoranta, P. Ekholm, T. Ruoho-Airola, and P. Kortelainen. 2015. Land Cover Controls the Export of Terminal Electron Acceptors from Boreal Catchments. Ecosystems **18**:343-358.

Peuranen, S., P. J. Vuorinen, M. Vuorinen, and A. Hollender. 1994. The Effects of Iron, Humic Acids and Low Ph on the Gills and Physiology of Brown Trout (Salmo-Trutta). Annales Zoologici Fennici **31**:389-396.

Ploum, S., H. Laudon, A. P. Tapia, and L. Kuglerová. 2020. Are dissolved organic carbon concentrations in riparian groundwater linked to hydrological pathways in the boreal forest?

Ranåker, L., M. Jönsson, P. A. Nilsson, and C. Brönmark. 2012. Effects of brown and turbid water on piscivore–prey fish interactions along a visibility gradient. Freshwater Biology **57**:1761-1768.

Reichard, P., R. Kretzschmar, and S. M. Kraemer. 2007. Dissolution mechanisms of goethite in the presence of siderophores and organic acids. Geochimica et Cosmochimica Acta **71**:5635-5650.

Renberg, I., T. Korsman, and H. J. B. Birks. 1993. Prehistoric Increases in the Ph of Acid-Sensitive Swedish Lakes Caused by Land-Use Changes. Nature **362**:824-827.

Rengefors, K., C. Pålsson, L.-A. Hansson, and L. Heiberg. 2008. Cell lysis of competitors and osmotrophy enhance growth of the bloom-forming alga Gonyostomum semen. Aquatic Microbial Ecology **51**:87-96.

Rosenqvist, L., D. B. Kleja, and M. B. Johansson. 2010. Concentrations and fluxes of dissolved organic carbon and nitrogen in a Picea abies chronosequence on former arable land in Sweden. Forest Ecology and Management **259**:275-285.

Rothe, M., A. Kleeberg, and M. Hupfer. 2016. The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments. Earth-Science Reviews **158**:51-64.

Sanderman, J., K. A. Lohse, J. A. Baldock, and R. Amundson. 2009. Linking soils and streams: Sources and chemistry of dissolved organic matter in a small coastal watershed. Water Resources Research **45**.

Sarkkola, S., H. Hökkä, H. Koivusalo, M. Nieminen, E. Ahti, J. Päivänen, and J. Laine. 2010. Role of tree stand evapotranspiration in maintaining satisfactory drainage conditions in drained peatlands. Canadian Journal of Forest Research **40**:1485-1496.

Sarkkola, S., M. Nieminen, H. Koivusalo, A. Lauren, P. Kortelainen, T. Mattsson, M. Palviainen, S. Piirainen, M. Starr, and L. Finer. 2013. Iron concentrations are increasing in surface waters from forested headwater catchments in eastern Finland. Sci Total Environ **463-464**:683-689.

Schelker, J., K. Eklof, K. Bishop, and H. Laudon. 2012. Effects of forestry operations on dissolved organic carbon concentrations and export in boreal first-order streams. Journal of Geophysical Research-Biogeosciences **117**.

Schmidt, W. 1999. Mechanisms and regulation of reduction-based iron uptake in plants. New Phytologist **141**:1-26.

Schopp, W., M. Posch, S. Mylona, and M. Johansson. 2003. Long-term development of acid deposition (1880-2030) in sensitive freshwater regions in Europe. Hydrology and Earth System Sciences **7**:436-446.

Schwab, A., and W. Lindsay. 1983. Effect of redox on the solubility and availability of iron. Soil Science Society of America Journal **47**:201-205.

Schwertmann, U. 1966. Inhibitory effect of soil organic matter on the crystallization of amorphous ferric hydroxide. Nature **212**:645-646.

Schwertmann, U. 1991. Solubility and dissolution of iron oxides. Plant and soil **130**:1-25.

Schwertmann, U., and E. Murad. 1983. Effect of pH on the formation of goethite and hematite from ferrihydrite. Clays and Clay Minerals **31**:277-284.

Schwertmann, U., and R. M. Taylor. 1989. Iron oxides. Minerals in soil environments **1**:379-438.

Seekell, D. A., J. F. Lapierre, J. Ask, A. K. Bergstrom, A. Deininger, P. Rodriguez, and J. Karlsson. 2015. The influence of dissolved organic carbon on primary production in northern lakes. Limnology and Oceanography **60**:1276-1285.

Sjöstedt, C., I. Persson, D. Hesterberg, D. B. Kleja, H. Borg, and J. P. Gustafsson. 2013. Iron speciation in soft-water lakes and soils as determined by EXAFS spectroscopy and geochemical modelling. Geochimica et Cosmochimica Acta **105**:172-186.

Sobek, S., G. Algesten, A. K. BERGSTRÖM, M. Jansson, and L. J. Tranvik. 2003. The catchment and climate regulation of pCO2 in boreal lakes. Global Change Biology **9**:630-641.

Solomon, C. T., S. E. Jones, B. C. Weidel, I. Buffam, M. L. Fork, J. Karlsson, S. Larsen, J. T. Lennon, J. S. Read, S. Sadro, and J. E. Saros. 2015. Ecosystem Consequences of Changing Inputs of Terrestrial Dissolved Organic Matter to Lakes: Current Knowledge and Future Challenges. Ecosystems **18**:376-389.

Squires, M. M., L. F. W. Lesack, and D. Huebert. 2002. The influence of water transparency on the distribution and abundance of macrophytes among lakes of the Mackenzie Delta, Western Canadian Arctic. Freshwater Biology **47**:2123-2135.

Stocker, T. F., D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and P. M. Midgley. 2013. Climate change 2013: The physical science basis. Cambridge University Press Cambridge.

Stott, P. 2016. How climate change affects extreme weather events. Science **352**:1517-1518.

Straková, P., J. Anttila, P. Spetz, V. Kitunen, T. Tapanila, and R. Laiho. 2010. Litter quality and its response to water level drawdown in boreal peatlands at plant species and community level. Plant and soil **335**:501-520.

Sundman, A., T. Karlsson, H. Laudon, and P. Persson. 2014. XAS study of iron speciation in soils and waters from a boreal catchment. Chemical Geology **364**:93-102.

Theil, H. 1950. A rank-invariant method of linear and polynomial regression analysis. Indagat Mathematica, New Series **12**:85– 91.

Thompson, A., O. A. Chadwick, D. G. Rancourt, and J. Chorover. 2006. Iron-oxide crystallinity increases during soil redox oscillations. Geochimica et Cosmochimica Acta **70**:1710-1727.

Thrane, J. E., D. O. Hessen, and T. Andersen. 2014. The Absorption of Light in Lakes: Negative Impact of Dissolved Organic Carbon on Primary Productivity. Ecosystems **17**:1040-1052.

Tipping, E., and M. A. Hurley. 1988. A Model of Solid-Solution Interactions in Acid Organic Soils, Based on the Complexation Properties of Humic Substances. Journal of Soil Science **39**:505-519.

Tipping, E., and C. Woof. 1991. The distribution of humic substances between the solid and aqueous phases of acid organic soils; a description based on humic heterogeneity and charge-dependent sorption equilibria. Journal of Soil Science **42**:437-448.

Tiwari, T., F. Lidman, H. Laudon, W. Lidberg, and A. M. Ågren. 2017. GIS-based prediction of stream chemistry using landscape composition, wet areas, and hydrological flow pathways. Journal of Geophysical Research: Biogeosciences **122**:65-79.

Tranvik, L. J., J. A. Downing, J. B. Cotner, S. A. Loiselle, R. G. Striegl, T. J. Ballatore, P. Dillon, K. Finlay, K. Fortino, L. B. Knoll, P. L. Kortelainen, T. Kutser, S. Larsen, I. Laurion, D. M. Leech, S. L. McCallister, D. M. McKnight, J. M. Melack, E. Overholt, J. A. Porter, Y. Prairie, W. H. Renwick, F. Roland, B. S. Sherman, D. W. Schindler, S. Sobek, A. Tremblay, M. J. Vanni, A. M. Verschoor, E. von Wachenfeldt, and G. A. Weyhenmeyer. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnology and Oceanography **54**:2298-2314.

Tyler, G., and T. Olsson. 2001. Concentrations of 60 elements in the soil solution as related to the soil acidity. European Journal of Soil Science **52**:151-165.

Valinia, S., G. Englund, F. Moldan, M. N. Futter, S. J. Kohler, K. Bishop, and J. Folster. 2014. Assessing anthropogenic impact on boreal lakes with historical fish species distribution data and hydrogeochemical modeling. Global Change Biology **20**:2752-2764.

van Dorst, R. M., A. Gardmark, R. Svanback, U. Beier, G. A. Weyhenmeyer, and M. Huss. 2019. Warmer and browner waters decrease fish biomass production. Global Change Biology **25**:1395-1408.

Vuori, K. M. 1995. Direct and Indirect Effects of Iron on River Ecosystems. Annales Zoologici Fennici **32**:317-329.

Wallstedt, T., L. Bjorkvald, and J. P. Gustafsson. 2010. Increasing concentrations of arsenic and vanadium in (southern) Swedish streams. Applied Geochemistry **25**:1162-1175.

Weyhenmeyer, G. A., M. Froberg, E. Karltun, M. Khalili, D. Kothawala, J. Temnerud, and L. J. Tranvik. 2012. Selective decay of terrestrial organic carbon during transport from land to sea. Global Change Biology **18**:349-355.

Weyhenmeyer, G. A., R. A. Muller, M. Norman, and L. J. Tranvik. 2016a. Sensitivity of freshwaters to browning in response to future climate change. Climatic Change **134**:225-239.

Weyhenmeyer, G. A., R. A. Müller, M. Norman, and L. J. Tranvik. 2016b. Sensitivity of freshwaters to browning in response to future climate change. Climatic Change **134**:225-239.

Weyhenmeyer, G. A., Y. T. Prairie, and L. J. Tranvik. 2014. Browning of Boreal Freshwaters Coupled to Carbon-Iron Interactions along the Aquatic Continuum. PLoS One **9**.

Wold, S., J. Trygg, A. Berglund, and H. Antti. 2001. Some recent developments in PLS modeling. Chemometrics and Intelligent Laboratory Systems **58**:131-150.

Xiao, Y.-H., A. Räike, H. Hartikainen, and A. V. Vähätalo. 2015. Iron as a source of color in river waters. Science of the Total Environment **536**:914-923.

Acknowledgements

This PhD has been a great experience and would never have been the same without the people that surround me. I am incredibly grateful to have such amazing people in my life, people that support me, that challenge me, and most of all, people that make me laugh. Writing these acknowledgements will not do all of you justice, but we do what we can!

Emma What a ride this PhD has been! You took me on as a master student and stuck with me all this way. It has been more than six years since I first stepped into your lab. I would like to thank you for all the knowledge you so freely shared and all the long nights you spent helping me out in the end of my PhD. I truly appreciate it! Besides being an absolutely stellar supervisor, you're also an amazing person and how you go about things in life has been an inspiration to me. Hearing your laugh through several layers of wall always brings a smile to my face and talking to you at the coffee table was always a joy. I could not have asked for anyone better to guide me through my PhD.

Per The two trips we've done to Stanford have been some of the best memories from my PhD. Sitting in the constant hum of beamline 4-1 at night is a weirdly fond memory for me and you made sure we always found the best place for a meal during the day. Having a chemist around was of great benefit for my thesis, and has made me realize just how exciting (and complicated) the chemistry of iron truly is.

Dan We have not had much chance to meet, but you were there to help me hammer the first lysimeter into the ground. That first lysimeter never gave any water, but it taught me how to get the next 59 just right.

Susan Thank you so much for all the help with the XAS data, I cannot imagine how that would go without you!

Big thanks to all my other coauthors, **Anna-Lena, Björn, Hjalmar, Gesa, Eva**, without whom this thesis would not have been the same.

Lars-Anders Thank you for being my examiner through this thesis, and for sharing you knowledge with us around the unit and on The Bahamas trip.

Christer, Karin, Anders N Our trip to the Bahamas was one of the highlights of my PhD and I am happy you were there to keep us on the road. Having you around the department always meant that if I needed something I had someone to turn to.

Gustaf and Brian Thank you for helping me come home safely after a Dark and Stormy night on The Bahamas!

Olof R Thank you for all the wonderful discussions at the iron Journal club.

All the wonderful current and past members of Aquatic Ecology, **Olof B, Anders P, Per, Johan, Marie, Mia, Varpu, Jerker, Nan, Kaj, Gorgina, Sandra, Romana, Rosie, Emma J, Huan, Alex, Johanna, Johanna, Mikael, Anna, Arne** and many more, thank you for all the good times at the coffee table, whether it was drinking coffee or eating cray fish.

Caroline You were the one that watched me break bottles and sensors around the lab when I was a master student and your "calm and collected" was the perfect balance to my "fast and chaotic". We have had some really good times and I will always remember how annoyed you were when we missed the conference dinner in Paris. For some reason that memory stands out.

Simon You shared many good tips with me along the way and we shared many good beers on The Bahamas. Maybe one day we'll be back for the Tidal Creeks!

Marcus Thank you for making me discover my badminton talent, and more than that, for going along every time I had something "important" to discuss.

Raphael I could not have wished for a better office mate! Not just that, you are also an amazing friend. The trips to Puerto Rico, The Bahamas, skiing and Edison would not have been the same without you. You tolerated my music, my made up German expressions and all the other crazy stuff that had been going on in our office!

Ainara I am so happy we met early on in my PhD and that I got such an amzing friend in you. Your party organizing skills are exquisite and even just going down town for a beer with you was always fun! Who knows how my PhD would have been if I hadn't met you, but I definitely would had not been as much great!

Margarida Thank you for all the talks, the coffee breaks and for organizing the Best book club there ever was!

Carlos We met all the way back in 2014, two chaps in a Limnology course! The book club you started has made me read some of the worst and best books of my life. We will always have The Life and Times of Michael K.

Dimitri I could barely remember that you were the opponent for my master thesis. And since then you have become a very good friend and spending time with you and **Rodrigo** has been fun every single time!

Franca & Guille I am really happy I met you two during my time in Lund. Just seeing the two of you makes me happy every time, I hope we remain friends for a long, long time and I can't wait to see your little **Guidaí** grow.

Ana and Anais Our time in Cyprus and all the crazy times in Sweden have been a big part of my time in Lund. You both are truly amazing and although we're spread out around the world now I'm sure we'll see each other soon again!

All the wonderful people I have met in Lund, **Milda, Albert, Daniel, Johannes, Katja, Sebas; Mariona, Africa, Alvaro, Chema, Carlota, Pierre, Lokesh, Viktoriia, Pablo.**

The Friday Pub regulars, for whom I've provided beer over the years. **Miguel, Beatriz, Juan-Pablo, Micaela, John, Kat, Maarit, Ann-Kathrin, Linus, Samantha, Maria, David, Violeta, Elsie, Stephen, Utku, Hamid, Rodrigo, Laidys, Charlie, Julian** and all the ones I cannot remember right now. It has brought me much joy sharing beer with you and much pain keeping track of the enterprise that is the Friday Pub. It is on hold now, but I am sure it will be back in someone else's hands!

Chavela We had so many great walks together and I would like to thank you for letting me borrow **Miguel** for a beer every now and again.

And all the other people I've met at the **Biology department** and people who I spent time with in Lund.

Mariana and Matilda We came here together and now I'm the only one still around. You two have been such a big part of my Lund life in the beginning and meeting up with you since then has been so much fun. I hope we get to do it soon again!

Elsa My most wonderful roommate for a very long time!

Blaž, Eva, **Špela, Toš** My best friends from back home. I haven not seen you much in recent years and that has maybe been the hardest part of this PhD. You are the friends I grew up with and I hope that you will be the friends I can keep for life. Hopefully I will get to see you more and hey, maybe we need to learn how to use the phone. I cannot wait to see you and all my other friends very soon!

My family You have been with me this whole way and are the main reason this thesis could ever become. My **Mom**, who always made sure we had everything we need, my **Dad** who has taught me how to walk bike ski and all the practical things in life, my **Little Sister** who I love very much and has painted this amazing cover for me, **Gregor** who has always taken care of us, my **Grandparents** who took care of me when I was little and my **Aunts**, who have taken care of me in Sweden. And to all the other family that I wish I could see more.

Lou Finally I came to you! It has not been that long since I have met you, here in Lund, and you have fast become the most important person in my life. You make everything possible for me. *I love you!*