UPTEC W15029
Examensarbete 30 hp
Juni 2015

Long term organic carbon dynamics in 17 Swedish lakes

The impact of acid deposition and climate change

Jessica Lovell

Abstract

Long term organic carbon dynamics in 17 Swedish lakes – The impact of acid deposition and climate change

Jessica Lovell

During the last three decades, a number of studies based on national environmental monitoring data have found increased concentrations of total organic carbon (TOC) in surface waters in much of the northern hemisphere including Sweden. There are many hypothesis of what has been the main cause of this trend, including changes in land use, decreased atmospheric deposition of acidifying compounds and climate change. Different hypothesis may have different implications for quantifying pre-industrial levels and for future predictions of TOC concentrations, which in turn will have different implications for water classification according to the European Water Framework Directive, water management and drinking water treatment.

To analyse the long term effects of industrialisation and climate change on TOC in surface waters there is a need for long term time series of data. Since environmental monitoring data in Sweden only extends back to the mid-1980s, other techniques must be used in order to reconstruct data. In this study, sediment cores from 17 lakes along a climatic and deposition gradient in Sweden were collected and analysed with visible near infrared spectroscopy (VNIRS), an analytical technique that makes it possible to reconstruct historic surface water concentrations of TOC to pre-industrial conditions. A previous study with VNIRS showed that TOC concentrations declined in response to sulfate deposition until peak sulfur deposition in 1980, and thereafter increased as a result of sharp reductions of sulfate emissions. It was noted that the rate of increase of TOC after 1980 was faster than the rate of decrease due to sulfate deposition before 1980. The purpose of this study was therefore to explore the hypothesis that increasing TOC concentrations have not only been due to recovery from acidification, but also due to changes in climate.

It was possible to analyse the long term effects of industrialisation and climate change on surface water TOC by analysing the reconstructed TOC data together with climate data from the beginning of the 1900s, modelled data of atmospheric sulfate deposition and environmental monitoring data, with uni- and multivariate analysis methods. It was found that the recent increase in TOC concentrations could be explained by both decreases in acidifying atmospheric deposition and increased precipitation, while temperature may have a decreasing effect on TOC. It was also found that the rate of increase of TOC-concentrations has been faster in the colder northern parts of Sweden and slower in the warmer south. The results imply that TOC concentrations will continue to rise to unpreceded levels and should be of concern for drinking water treatment plants that will need to adapt their treatment processes in the future.

Keywords: environmental monitoring, climate change, sulfate deposition, total organic carbon (TOC), VNIRS, trend analysis, multivariate data analysis, PLS.

Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU). Lennart Hjelms väg 9, SE 750-07 Uppsala

Referat

Förändringar i koncentrationer av organiskt kol i 17 Svenska sjöar – påverkan av försurande nedfall och klimatförändringar

Jessica Lovell

Under de senaste tre årtiondena har ett flertal studier baserade på data från nationella miljöövervakningsprogram rapporterat ökande koncentrationer av organiskt kol (TOC) i ytvatten på norra halvklotet inklusive Sverige. Det finns många hypoteser om vad som ligger bakom trenden, till exempel förändringar i markanvändning, minskad atmosfärisk deposition av försurande ämnen och klimatförändringar. Olika förklaringar till vad som ligger bakom den ökande trenden ger konsekvenser vid kvantifiering av förindustriella nivåer och för förutsägelser om framtida koncentrationer, vilket i sin tur ger konsekvenser för vattenklassificering enligt Ramvattendirektivet, vattenförvaltning och dricksvattenberedning.

För att kunna analysera de långsiktiga effekterna av industrialisering och klimatförändringar på TOC i ytvatten behövs långa tidsserier av data. Då den svenska miljöövervakningen endast sträcker sig tillbaka till mitten av 1980-talet måste andra tekniker användas för att rekonstruera data. I den här studien har sedimentproppar från 17 sjöar längs en klimat- och depositionsgradient analyserats med visible near infrared spektroskopi (VNIRS), en analysteknik som gör det möjligt att rekonstruera TOC-koncentrationer i ytvatten till förindustriell tid. En tidigare studie med VNIRS visade att TOC-koncentrationer sjönk till följd av försurande nedfall fram till 1980 då nedfallet kraftigt minskade, varefter koncentrationer av TOC började öka. Det noterades i studien att ökningen av TOC efter 1980 varit snabbare än vad minskningen var före 1980 på grund av försurande nedfall. Syftet med den här studien var därför att undersöka hypotesen att den senaste tidens ökning av TOC inte bara berott på minskat nedfall av försurande ämnen, utan även på grund av klimatförändringar.

Det var möjligt att undersöka de långsiktiga effekterna av industrialisering och klimatförändringar på TOC i ytvatten genom att analysera rekonstruerad TOC data, klimatdata från början av 1900-talet, modellerad sulfatdepositionsdata och miljöövervakningsdata med uni- och multivariata analysmetoder. Resultaten visade att den senaste tidens ökning av TOC kunde förklaras med både en minskande deposition av försurande ämnen och en ökad nederbörd, medan ökande temperaturer kan ha haft en minskande effekt på TOC. Resultaten visade även att förändringshastigheten av TOC-koncentrationer varit snabbare i de norra, kalla delarna av Sverige och långsammare i de varmare södra. Resultaten indikerar att koncentrationer av TOC kommer att öka till nivåer som aldrig tidigare skådats, vilket är något vattenreningsverk kommer att behöva anpassa sina reningsmetoder till i framtiden.

Nyckelord: miljöövervakning, klimatförändringar, sulfat deposition, organiskt kol, TOC, VNIRS, trendanalys, multivariat data analys, PLS.

Institutionen för vatten och miljö, Sveriges lantbruksuniversitet (SLU). Lennart Hjelms väg 9, SE 750-07 Uppsala

Acknowledgement

This master thesis of 30 ECTS was the finishing part of the Master Programme in Environmental and Water Engineering at Uppsala University. It has been carried out on the behalf of the Department of Aquatic Science and Assessment at the Swedish University of Agricultural Sciences, SLU.

Salar Valinia acted as my supervisor and Jens Fölster as my subject reviewer, both at the Department of Aquatic Sciences and Assessment. Fritjof Fagerlund at the Department of Earth Sciences at Uppsala University acted as the final examiner.

First and foremost I would like to thank my supervisor Salar Valinia for initiating this thesis. Thank you for your support, engagement, encouragement and help throughout the project and for always taking the time to answer my questions. I would like to thank Jens Fölster for acting as my subject reviewer and for valuable comments on my report. I would also like to thank Lars Sonnesten for answering questions about PLS. I would like to thank Carsten Meyer-Jacob and Carolina Olid Garcia at the Department of Ecology and Environmental Sciences at Umeå University for helping me with lab work and TOC reconstructions. Finally I would like to thank Anna Landahl and my friends here in Uppsala for supporting me throughout the entire thesis process, and my parents for words of encouragement.

Jessica Lovell
Uppsala 2015

UPTEC W15029, ISSN 1401-5765
Published digitally at the Department of Earth Sciences, Uppsala University
Uppsala, 2015

Populärvetenskaplig sammanfattning

Förändringar i koncentrationer av organiskt kol i 17 Svenska sjöar – påverkan av försurande nedfall och klimatförändringar

Jessica Lovell

De senaste årtiondena har ytvatten i sjöar och vattendrag blivit allt mer brunfärgade av humusämnen på stora delar av det norra halvklotet, också i Sverige. Humusämnen består av organiskt material, som i sin tur består av döda växt- och djurdelar, och sipprar ner till vattnet från mark i närheten. En liten del kommer också ifrån själva sjön. Det pågår mycket forskning om orsakerna till varför brunifieringen håller på att ske och förklaringar som lagts fram är bland annat förändringar i markanvändning, en minskad deposition av försurande nedfall och klimatförändringar. Det är bland annat viktigt att veta vad som ligger bakom brunifieringen för att kunna förutspå hur brunt det kommer att bli i framtiden. Detta är särskilt viktigt att veta för de som producerar vårt dricksvatten då organiskt material är besvärligt att få bort och kan föra med sig giftiga föroreningar.

Ett problem när man vill undersöka orsakerna till den ökande brunifieringen är att det inte finns data som går tillräckligt långt tillbaka i tiden. I Sverige finns ett miljöövervakningsprogram sedan mitten av 1980-talet som kontinuerligt mäter halterna av organiskt material och ett stort antal andra ämnen. För att gå ännu längre tillbaka i tiden kan man analysera sedimentproppar och bestämma hur stor koncentrationen av organiskt material var i ytvattnet före industrialismen. Tillsammans med tidsserier av temperatur och nederbörd från början av 1900-talet, modellerad depositionsdata från industrialismens början och mätdata från övervakningsprogrammet är det möjligt att med olika statistiska metoder undersöka vad som orsakat brunifieringen på lång sikt.

Resultatet av den här studien visade på att att brunifieringen dels berott på både minskat nedfall av försurande ämnen, men också på grund av en ökad nederbörd. Utsläpp av försurande ämnen började i takt med industrialismens framväxt i slutet av 1800-talet och ökade fram till 1980, då det internationella samfundet kom överens om att kraftigt minska utsläppen på grund av den negativa miljöpåverkan den medförde. De försurande utsläppen gjorde att lösligheten hos det organiska materialet minskade vilket gjorde att det stannade kvar i marken, och när utsläppen upphörde började det organiska materialet att sippra ut igen. Nederbörd bidrar till brunifiering genom att vatten rinner igenom mer av markens ytliga lager där det finns mycket organiskt material. Resultaten visade också att ökande temperaturer kan motverka brunifiering, något som skulle kunna bero på att ökade temperaturer leder till mer avdunstning och att mindre vatten rinner igenom de ytliga marklagrena. Ett ytterligare resultat var att brunifieringstakten gått snabbare i de kallare norra delarna av Sverige och långsammare i de varmare södra delarna. Resultaten antyder att sjöar och vattendrag kommer bli ännu brunare i takt med att klimatförändringar ger ökad nederbörd och detta är något som vattenreningsverk kommer att behöva anpassa sina reningsmetoder till i framtiden.

Abbreviations and word list

Acidification: the build-up of hydrogen cations reducing the soil pH. This happens when a proton donor gets added to the soil.

ANC: acid neutralizing capacity. A measure of the buffering capacity against acidification for a solution.

CEDA: Centre for Environmental Data Archival

CRU: Climate Research Unit, the climate research unit at the University of East Anglia

Ionic strength: the concentration of ionic charge in solution. Varies naturally across ecosystems.

Latent variable: variable without itself being observable used to describe observed variables.

Linear regression: a statistical method used to examine the causal relationship between the response variable Y and the predictor variable/variables X.

Loadings: parameter used in multivariate analysis methods used to describe how the latent variables are related to the original variables.

Mann-Kendall test: a method to determine if a trend is statistically significant.

Multicollinearity: also collinearity. A phenomenon where two or more predictor variables are highly correlated.

Multivariate analysis: collective name for statistical methods for description and analysis of multidimensional data sets.

Null hypothesis: a statistical hypothesis that is tested for possible rejection under the assumption that it is true (usually that observations are the result of chance).

PLS: partial least squares projection to latent structures, also known as partial least squares. A multivariate analysis method.

Predictor variable: a variable that is used in regression that explains changes in the response variable. Also referred to as explanatory, experimental or independent variable.

P-value: the probability of observing an effect given that the null hypothesis is true.

Q^2-value: the degree of prediction of a PLS-model.

R^2-value: a measure of the degree of explanation of a regression model.

Reference conditions: a state that is defined as undisturbed by humans by the European Water Framework Directive.

Response variable: also known as dependent variable. The response variable is the variable of focus and may be explained by the predictor variables.

Scores: parameter used in multivariate analysis methods that describes the observations coordinates in the new coordinate system.

Significance level: the probability of rejecting the null hypothesis given that it is true. According to scientific practice the significance level is usually set to 0.05.

Statistically significant: statistical significance is attained when a p-value is less than the significance level.

Theil-slope: the slope (trend) calculated by the Theil-Sen method.

THM: trihalomethanes

TOC: total organic carbon. TOC can be subdivided into the operationally defined fractions dissolved organic carbon (**DOC**) and particulate organic carbon (**POC**). DOC is the fraction of an organic compound that is able to pass through a 0.45 µm filter.

Transformation: the application of a mathematical function to each point in a data set. Transforms are usually applied to normalise the residuals and/or stabilise the variance to meet the requirements of the statistical method.

Trend analysis: the practice of collecting information and attempting to find a pattern, or trend, in the information.

VIF-value: variable inflation factor. A measure of how much of the variable of the estimated regression coefficients are inflated compared to when the predictor variables are not linearly related.

VNIRS: visible-near infrared spectroscopy. An analysis technique making it possible to reconstruct TOC concentrations on a centennial to millennial scale.

Contents

1 Introduction

During the last three decades, a number of studies based on national environmental monitoring data have reported increases in total organic carbon (TOC) concentrations in surface waters in much of the northern hemisphere. These include studies from Sweden (Futter et al., 2014), the United Kingdom (Evans et al., 2005), the Baltic states (Pärn and Mander, 2012), Central Europe (Hruška et al., 2009), the North-eastern United States (US EPA, 2003) and Eastern Canada (Couture et al., 2011). This may have implications for the terrestrial carbon balance and aquatic ecosystem functioning (Tranvik et al., 2009), as well as for water treatment costs and human health (Ledesma et al., 2012). Especially implications for drinking water treatment have drawn much attention since TOC can transport contaminants and toxic compounds which have to be removed before human consumption. Of special concern is trihalomethanes (THM), a group of compounds with potential carcinogenic and mutagenic properties and organic pollutants that can bind to TOC (Alex T. Chow et al., 2003; De Paolis and Kukkonen, 1997). TOC also influences the bioavailability of toxic metals such as mercury, copper and lead as a result of increasing the solubility and mobility of the metals (Ravichandran, 2004; Ashworth and Alloway, 2007; Klaminder et al., 2006).

The causes of increasing surface water TOC concentrations are much debated and hypotheses go widely apart. On a centennial to millennial time scale, paleolimnological studies have linked changes in surface water TOC to land use shifts and early settlement (Meyer-Jabob et al., 2015; Rosén et al., 2011). On a more recent time scale, studies have linked increases in TOC mainly to decreases in atmospheric deposition of SO_4^{2-} and marine Cl^- (Evans et al., 2006; Monteith et al., 2007; Hruška et al., 2009) and to climatic factors such as temperature, precipitation and runoff (Weyhenmeyer and Karlsson, 2009; Hongve et al., 2004). Explanatory factors such as increased atmospheric deposition of nitrogen (Evans et al., 2008), land management (Yallop and Clutterbuck, 2009) and increased CO_2 emissions (Freeman et al., 2004) have also been brought forward as potential explanations. Increasing the complexity is that different mechanisms might be co-factoring, and it is under debate which factor has been the key driver of long term surface water TOC-trends. There have been attempts of reconciliation between different hypothesis, for example Clark et al. (2010) argues that discrepancies between studies can be explained by regional differences in atmospheric deposition, different catchment characteristics and different temporal and spatial scales. Part of the inconsistency may also stem from the general lack of long-term data series of sufficient quality (Larsen et al., 2010).

Different hypothesis of the primary drivers of increasing TOC have different implications for quantifying pre-industrial levels and for future predictions of TOC concentrations, which in turn has different implications for water classification, management and drinking water treatment (Valinia et al., 2014). For example, if climate change is responsible, it implies that TOC-levels will continue to rise to unpreceded levels, while if a decline in acid deposition is responsible it implies that TOC-concentrations are returning towards naturally high pre-industrial levels (Monteith et al., 2007; Erlandsson et al., 2009). To understand what is driving the increase of TOC in surface waters is crucial for assessing different aspects of water quality and human impact on the environment, and for deciding where future efforts should be directed (Valinia et al., 2014).

To analyse the long term effects of industrialisation and climate change on TOC in surface waters, long term time series of data are needed. Since environmental monitoring data in Sweden only extends back to around 1985, other techniques must be used in order to reconstruct data. By analysing sediment cores with visible near infrared spectroscopy (VNIRS) it is possible to reconstruct historic surface water concentrations of TOC on a millennial scale (Rosén, 2005). Lake sediments consists to a large part of compounds derived from organisms formerly living in the catchment and the organic fraction of the lake sediment has a distinctive near-infrared signature that the VNIRS can utilize (Rosén, 2005).

A previous study by Valinia et al. (2014) analysed sediment cores from lakes across Sweden with VNIRS and reconstructed TOC concentrations back to reference conditions in 1860, a state that is defined as undisturbed by humans in accordance with European Water Framework Directive (EC Directive 2000/60/EC). The study demonstrated that lake concentrations of TOC declined until peak sulfate deposition in 1980 and began to increase when acid deposition started to decrease. It was noted that the increase in TOC, which can be seen in Swedish environmental monitoring data that began in 1987, was faster than the decrease due to acid deposition from industrialisation. Furthermore, studies have found that Swedish lakes show slow recovery from historic acidification as many of them are still acidified (Futter et al., 2014). This suggests that recovery from acidification alone may not be responsible for the increase in TOC. The purpose of this study is therefore to explore the hypothesis that increasing TOC has not only been due to recovery from acidification, but also due to changes in climate.

In this study, sediment cores from 17 lakes along a climatic and deposition gradient in Sweden have been collected and analysed with VNIRS. The reconstructed VNIRS-TOC concentrations together with long term climate data, modelled data of atmospheric sulfate deposition and environmental monitoring data makes it possible to analyse the long term effects of industrialisation and climate change on surface water TOC. In this study the following questions were asked:

- How has TOC concentrations in the examined lakes changed before and after peak sulfate deposition in 1980? Has the rate of change of TOC been faster after 1980 than before 1980?
- How has climate (temperature and precipitation) and deposition of acidifying compounds on the examined sites changed since pre-industrialisation up until today?
- How is TOC related to changes in climate, acid deposition and water chemical parameters?
- If the rate of increase of TOC concentrations has been faster than the rate of decrease before 1980, can the discrepancy be explained by increased precipitation and rising temperatures?
- How will TOC concentrations change in the future?

2 Background

The background is the result of the literature review and is mainly based on scientific articles. It covers some of the most common explanations and mechanisms behind changing TOC concentrations in surface waters. The purpose of the background is to give an understanding for the complex processes affecting TOC and to increase the understanding for the reasoning in the discussion and for the conclusions.

2.1 Organic carbon

Organic carbon is an integral component of water chemistry, with importance for carbon budgets, metals, nutrients and organic pollutants, as well as for the speciation, toxicity and bioavailability of different components (Erlandsson et al., 2009). Most of the organic matter in lakes originates from terrestrial sources and a small fraction comes from biological activity within the aquatic ecosystems (Wilkinson et al., 2013). The diversity of TOC molecular composition is vast and depends on factors like climate, hydrology and land use (Kellerman et al., 2014). In general TOC consists of a small proportion of low-molecular weight compounds such as carbohydrates and amino acids, and a larger proportion of complex, high-molecular weight compounds collectively termed humic substances. Humic substances are a complex mixture of aromatic and aliphatic hydrocarbon structures with attached amide, carboxyl, ketone and other functional groups (Leenheer and Croué, 2003).

A way of quantifying the presence of organic matter in aquatic systems is to measure the total amount of organic carbon (TOC). TOC can be subdivided into the operationally defined fractions dissolved organic carbon (DOC) and particulate organic carbon (POC). DOC is the fraction of an organic compound that is able to pass through a 0.45 μm filter (Leenheer and Croué, 2003). In Sweden, POC is generally a very small fraction of TOC (Laudon et al., 2003), therefore all TOC measurements presented in this study are effectively equivalent to DOC.

2.2 Common hypothesis for increasing TOC concentrations in surface waters

2.2.1 Changes in atmospheric deposition

Declining atmospheric deposition of acidifying compounds has been connected to increasing concentrations of surface water TOC in several studies (Evans et al., 2006; Monteith et al., 2007; Hruška et al., 2009). Deposition of acidifying compounds containing sulfur (SO_4^{2-}) began to rise in the mid- to late 1800s as a result of industrialization, accelerated in the 1950s, peaked in the 1970-80:s and declined sharply in the 1980:s due to international cooperation (Mylona, 1996; Sundqvist et al., 2002). Since then reductions in acid deposition has led to a widespread recovery from acidification in Sweden (Laudon and Bishop, 2001). Studies have shown that SO_4^{2-} can inhibit the mobility of TOC by at least two mechanisms – by changing the acidity of soils or changing the ionic strength of soil solutions, or both (Monteith et al., 2007). The theory behind the first mechanism is that the decrease of sulfur and subsequent increase in pH decreases the charge of organic matter which thereby increases its solubility. During low pH the solubility of organic matter is decreased due to protonation, which alters the steric conformation. An increasing pH will therefore facilitate the transport from the terrestrial to the aquatic system (Evans et al., 2012; Tipping and Hurley, 1988). The theory behind the second mechanism is that a decreased ionic strength associated with declining SO_4^{2-} has increased the solubility of TOC (Hruška et al., 2009). Ionic strength is the concentration of ionic charge in solution, and varies naturally across aquatic ecosystems (US EPA, 2015a). Decreased deposition of acidic compounds or sea salt leads to lower concentrations of multivalent ions found in soil solution, such as Ca^{2+}, Mg^{2+} and aluminium, as the acidic compounds no longer compete for adsorption sites (Hruška et al., 2009). A third mechanism has to do with the solubility of aluminium. Soil pH determines the solubility of aluminium, with increasing solubility at lower pH. Aluminium can bind to organic molecules triggering soil organic matter coagulation. Organic matter in soils recovering from acidification is therefore more soluble (Monteith et al., 2007).

A decrease in atmospheric deposition of sea-salt (Cl^-) has also been linked to increasing TOC concentrations in several studies (Monteith et al., 2007; Clark et al., 2011). Sea-salt deposition episodes have been linked to decadal cycles of storm intensities driven by the North Atlantic Oscillation (NAO), causing and/or increasing the effects of acidification (Hindar et al., 2004; Heath et al., 1992). Declining Cl^- deposition could also affect TOC by reducing soil ionic strength and thus increasing the solubility of TOC (Clark et al., 2011).

Studies have found a connection between nitrogen (N) deposition and TOC (Findlay, 2005; Hessen et al., 2009). Human activities have more than doubled the input of nitrogen to terrestrial ecosystems worldwide (Turner et al., 1990). Anthropogenic N can affect ecosystems in many ways, for example altering net primary production, nutrient cycling and degradation. However not all ecosystems respond to additional N in similar ways (Matson et al., 2002), and the connection to TOC is under debate. A field study by (Evans et al., 2008) of 12 N addition experiments in North America and Europe showed inconsistent responses of TOC. They did however find a connection between the form of N added and TOC and linked it to changes in acidity.

2.2.2 Changes in temperature

Some studies have found connections between temperature and TOC (Freeman et al., 2001), (Worall and Burt, 2006), while others have not (Giardina and Ryan, 2000; Hudson et al., 2003). Some of the different responses between studies may be due to differences in the environment where the studies took place, especially differences in climate, vegetation cover, and age of peat and underlying soil type (Hudson et al., 2003). The relationship between temperature and TOC is equivocal as studies have found both positive (Weyhenmeyer and Karlsson, 2009) and negative (Kirschbaum, 1995) relationships to TOC.

There are many temperature dependent mechanisms affecting the global carbon cycle, both physical and biological (Kalbitz et al., 2000). The most dominant predictor of TOC in a study by Larsen et al. (2010) was vegetation, which rose consistently with temperature and precipitation. Counterbalancing this effect could be the positive effect that temperature can have on microbial decomposition, which removes TOC by cellular respiration (Jenkinson et al., 1991). However the effect of temperature on decomposition is not clear. Davidson and Janssens (2006) reviewed studies on the effect of temperature on decomposition and found that a significant fraction of organic carbon was temperature sensitive to decomposition, while another fraction was under different types of environmental constraints that decreased the temperature sensitivity.

Temperature may affect soil drainage conditions, which is an important factor in understanding DOC release. For well drained and moderately drained soils, there is often a negative correlation between average soil temperature and DOC concentrations in surface soil leachates (Kalbitz et al., 2000). Tranvik and Jansson (2002) argue that warming can affect DOC export in different ways, depending strongly on whether it is accompanied by increased or decreased precipitation, and that DOC concentrations cannot be predicted by temperature alone.

Increased temperatures will lead to a shorter winter season in Sweden with less snow cover and frost (Renberg et al., 2001). A study by Lepistö et al. (2014) found that changes in TOC concentrations were controlled by changes in soil frost, seasonal precipitation, drought and runoff, where deeper soil frost led to lower TOC concentrations in the examined river. However other studies have showed that the impacts of soil frost on TOC are complex and highly variable (Austnes and Vestgarden, 2008).

2.2.3 Changes in precipitation and runoff

Studies have found increased DOC export in association with increased precipitation and rising discharge (e.g. Schindler et al., 1997). At the same time other studies have not been able to explain increasing TOC concentrations with increasing TOC precipitation and runoff (Freeman et al., 2004; Monteith et al., 2007). Dosskey and Bertsch (1997) found that rainfall had different effects on DOC depending on soil type, which might explain some of the discrepancies between studies. For example, in sandy soils rainfall had little effect on DOC in soil solution, but seemed to have more effect on DOC release from clayey soils.

Evans et al. (2005) identified three possible mechanisms by which hydrological processes may affect surface water DOC:

(i) A decrease in discharge should lead to increased DOC concentrations, under the assumption that there are no changes in DOC flux entering the stream network.

(ii) Increased flow may increase both DOC flux and concentration by altering water flow path, with more runoff routed through shallow, organic rich soil horizons, relative deeper mineral horizons where DOC adsorption is high.

(iii) Changes in rainfall and runoff distribution within the year may affect both DOC production and transport processes. In the UK drought-rewetting cycles have been identified as a major influence on DOC production, which can explained by enhanced organic matter decomposition due to aeration of saturated peaty soils, and flushing of accumulated DOC in stream waters when rewetted (Freeman et al., 2001).

The effect of precipitation on DOC has been shown to depend on both quantity and season, with a decisive parameter being the contact time between the soil and the soil solution. From this follows that DOC concentrations are lower in spring, when more water passes through the forest floor and the contact time is short (Don and Schulze, 2008). In summer DOC concentrations increase due to low soil water content and longer contact times (Heikkinen, 1994). In the autumn, runoff events can give significant DOC concentration peaks due to leaching from freshly produces organic substrates (Hongve, 1999). During snowmelt after winter, DOC concentrations generally increase in an early stage and rapidly declines as the melting progresses, suggesting a simple flushing mechanism (Boyer et al., 1997; Hornberger et al., 1994).

Both field and laboratory studies have found that concentrations of DOC increase when rewetted after dry periods (Fenner and Freeman, 2011; Tipping et al., 1999). In peat lands normally anoxic conditions prevail, making degradation slow. When peat lands are subjected to drought, oxygen is introduced to the system which stimulates bacterial growth, causing breakdown of organic matter and the release of carbon dioxide and DOC to receiving waters (Fenner and Freeman, 2011).

2.2.4 Changes in climate

Each of the last three decades has been successively warmer than any preceding decade since 1850. The period from 1983 to 2012 was likely the warmest 30-year period of the last 1400 years in the Northern Hemisphere. Average precipitation over the mid-latitude Northern Hemisphere has also increased significantly since 1901, and further climate change is expected (IPCC, 2014). Climate parameters affect vegetation, soils, hydrological conditions and subsequently the organic carbon budget of landscapes and exports into water bodies (Steinberg, 2003).

Many studies have linked increasing TOC concentrations with different climate factors such as temperature (Freeman et al., 2001), precipitation (Tranvik et al., 2009), runoff (Hongve et al., 2004), and drought (Fenner and Freeman, 2011). The fact that DOC concentrations have increased even in remote areas which have never been acidified suggests that climate factors may play a role and become more important in the future (Steinberg, 2003).

2.2.5 Changes in land use and management

Both long and short term studies have shown that land use can have a considerable effect on soil and water TOC. On a centennial to millennial time scale, TOC reconstructions made on sediment cores with VNIRS have shown that land use and early settlement can influence TOC concentrations substantially (Meyer-Jabob et al., 2015; Rosén et al., 2011).

A literature study on the influence of more recent land use and management practices by Chantigny (2002), concluded that land use was the factor with the greatest influence on soil DOC since it determines what type of vegetation is grown on the soil and plant litter is the primary source of terrestrial organic carbon. Another conclusion was that concentrations of DOC in soil water tended to be larger in forest than in agricultural soils. The responsible mechanism was not clearly identified, but a proposed explanation was that there is a greater fungal biomass present in forest floors compared to agricultural soils.

A literature review by K. Kalbitz et al. (2000) found that land use and management practices have been shown to affect soil properties, and thereby the release of DOC, by the following mechanisms:

(i) Changing the input of organic matter
(ii) Changing the substrate quality
(iii) Altering the rates, extent and pathways of microbial degradation

Management practices such as N fertilizing (Chantigny et al., 1998), liming (Chan and Heenan, 1999), addition of organic amendments and mineral fertilization (Zsolnay and Görlitz, 1994), tillage (Angers et al., 1997), crop type and crop rotation (West and Post, 2002) have been shown to have effects on TOC, as well as clear-cutting of forest (Qualls et al., 2000), afforestation (Paul et al., 2001), cultivation of forest soil (Delprat et al., 1997) and cultivation of grassland (Tiessen et al., 1982). It is however difficult to evaluate the effect of DOC of such practices due to different environmental- and soil properties and a lack of studies (Chantigny, 2002). However both liming and organic fertilization have consistently resulted in increased DOC-release from soil (Karlik, 1995; Zsolnay and Görlitz, 1994).

When converting forest to agriculture, the forest is clear-cut and often ploughed. This generally leads to a mobilization of DOC. The mechanisms for the release include an increased water flux (Qualls et al., 2000).

A study by Yallop and Clutterbuck (2009) identified heather burning as the most significant land management predictor of variation in DOC concentration while examining 50 small-scale catchments in the UK. Also draining peat lands making them more favourable for aerobic decomposition can lead to increased carbon losses from such environments.

2.2.6 Increasing CO_2 emissions

Studies have shown that plants respond to increased atmospheric CO_2 content by increasing productivity through increased photosynthesis and more efficient water usage. The increased greenhouse effect also extends the vegetation period and can increase forest production. This may lead to an increased production of organic matter and DOC in some regions (Steinberg, 2003).

Peat-lands are a vast store of global carbon, holding approximately one third of the global soil carbon stock (Gorham, 1991). Freeman et al. (2004) studied the effect of elevated carbon dioxide levels on peat-dominated areas. Their conclusion was that carbon dioxide stimulation of primary production and DOC exudation from plants was the responsible mechanism for rapidly rising DOC-concentrations in rivers draining the examined peat lands in the UK. Their article has been much debated and challenged by for example Evans et al. (2005), who suggested that only a small percentage of total DOC increase could be explained by that specific mechanism.

3 Theory

In order to explain the recent increases in surface water TOC various statistical methods were used. These included trend tests of chemical- and climatic parameters, linear- and multiple linear regression and partial least square regression (PLSR). This section aims to give an understanding for the statistical methods used and for the theory behind the sediment analysis methods.

3.1 Statistical methods

3.1.1 Non-parametric tests of monotonic trends

The Mann-Kendall test is a robust method to determine if a trend is statistically significant or not. It is a non-parametric test based on ranking of observations. Being non-parametric means that it does not need to assume any probability distributions of the data. By using the Theil-Sen method it is possible to calculate an estimate of the slope (trend) known as the Theil-slope (Miljöstatistik, 2015a).

3.1.2 Linear- and multiple linear regression

Linear regression is used to examine the causal relationship between the response variable Y and the predictor variable X. A linear regression model rests on the following assumptions:

1. The relationship between the variables is linear
2. The observations are independent
3. The residuals are normally distributed
4. The variance of the residuals is constant

(Alm and Britton, 2008).

If points 3 or 4 are not fulfilled, there might be a suitable transformation that normalises the residuals and/or stabilises the variance. One of the most common transformations is taking the logarithm of the variable (Miljöstatistik, 2015b).

The regression line is calculated in such a way that it minimises the squared distances between the observations and the regression line. To know if the regression line is good or not, one can look at the correlation coefficient R^2-value. The R^2-value is a measure of the degree of explanation, i.e. how much of the variance in Y that can be explained by X. The coefficient ranges between 0-1, the closer the value is to 1 the higher the degree of explanation (Alm and Britton, 2008). Approximate guidelines to how to interpret an R^2-value can be seen in table 1.

Table 1. Approximate interpretation of an R^2-value

Correlation coefficient R^2	Explanatory strength
0 to 0.19	Very weak
0.2 to 0.39	Weak
0.4 to 0.69	Moderate
0.7 to 0.89	Strong
0.9 to 1	Very strong

Multiple linear regression is an extension of linear regression where several predictor variables X are used to predict Y and rests on the same assumptions as linear regression. An additional pre-condition is that the X-variables do not correlate with each other to much, however if there is a small correlation it is generally not a problem (Miljöstatistik, 2015b). Adding more predictor variables to a regression model often increases the R^2-value and can be treacherous. Adjusted R^2 is a version of R^2 that has been adjusted for the number of predictors in the model and is therefore more reliable (Multiple Regression Analysis, 2015). The variance inflation factor (VIF) is used as an indicator of multicollinearity and is defined as:

$$\frac{1}{1-R^2} \tag{1}$$

The VIF-factor measures how much of the variance of the estimated regression coefficients are inflated as compared to when the predictor variables are not linearly related. The following points are guidelines to interpret the VIF:

- VIF = 0, not correlated
- 1 < VIF < 5, moderately correlated
- VIF > 5 to 10, highly correlated

A common rule of thumb is to discard models where the VIF-value is above 10 (O’Brien, 2007).

3.1.3 Multivariate data analysis

Multivariate analysis is the area of statistics that deals with observations made of many variables. The main purpose of multivariate analysis is to present how the variables are related to each other and how they work in combination (“Multivariate Statistics,” 2015). Multivariate data and models can be represented as points, lines, planes and hyper planes in multidimensional spaces. When analysing two variables, a two-dimensional plot can be made in an x-y coordinate system that is easy to comprehend. When more variables are added to the analysis the number of dimensions increases accordingly, with one variable for each coordinate axis, making it hard to visualise underlying structures. By using projection methods the variables can be transformed into a lower dimensional space, making it possible to produce plots in two or three dimensions that can be easily interpreted and displayed on a paper or screen. Projection methods are widely used in fields such as environmental science, chemometrics, spectroscopy, economics and political science (Eriksson et al., 2006).

3.1.3.1 Partial least squares projections to latent structures

Partial least squares projections to latent structures (PLS), also known as partial least squares, is a multivariate analysis method for relating two data matrices. The task for the data analysis is to relate the positions of the observations in the X and the Y space by a linear multivariate model (Eriksson et al., 2006).

PLS performs well in situations where multiple linear regression will not. These situations are when;

- X-variables are highly correlated
- Predictor variables outnumber the observations
- A large number of X-variables
- Several Y-variables and many X-variables

It also performs well with noisy and incomplete variables in both X and Y and is distribution free (Eriksson et al., 2006).

Before the analysis is performed the data needs to be pre-treated by centring and scaling. This is done by default in the computer program used in this study (SIMCA version 13.0 by Umetrics). Centring is the procedure where the mean of each column is subtracted from each row-value. Scaling divides each column by its standard deviation. This leaves predictor- and response variables with the mean 0 and a standard deviation of 1 (Eriksson et al., 2006). This is done so that variables with a large range and thereby large variance will not be given more importance in the model than variables with small ranges, and also makes different units comparable (Eriksson et al., 2006).

Some variables may need additional transformation in order to make the data more normally distributed which is advantageous for a good PLS model. If there is pre-knowledge about the relative importance of variables in the system it should be used to scale the variables accordingly, giving important variables a slightly higher scaling weight and less important variables a lower weight (Eriksson et al., 2006).

The predictions in PLS are achieved by extracting a set of orthogonal factors called latent variables from the explanatory X-variables. The objective of the analysis is to find the number and combination of factors that will give the best prediction (Hervé., 2007). The factors are constructed in a way that aims to maximise the covariance between the Xs and the Ys and are designed to explain as much variation as possible in both predictor and response variables (Eriksson et al., 2006). The algorithm continues to calculate factors until there is no co variation left, if it has not stopped before due to cross-validation. Cross-validation is performed by default in the program used for this study (SIMCA). This means that for each new factor observations in data are excluded and a partial model is created that is then used to predict the excluded observation Y-values from their X-values. If the prediction error is small the component is accepted, otherwise the algorithm stops.

The PLS model equation is on the form $Y_{predicted} = b_0 - b_{PLS}'\cdot X$, where b_0 is the intercept and b_{PLS} are the model coefficients. The degree of modelling, i.e. how much of Y that is modelled, is specified by the R^2 value:

$$R^2 = 1 - \frac{\text{sum of squares (residuals)}}{\text{sum of squares (Y)}} \tag{2}$$

The degree of prediction, i.e. how much of Y that the model is able to predict, is given by the Q^2-value and is obtained from the cross validation:

$$Q^2 = 1 - \frac{\text{sum of squares (prediction error)}}{\text{sum of squares (Y)}} \tag{3}$$

(Miljöstatistik, 2015d)

A model with a cumulative Q^2 above 0.5 is considered to have good predictive capability.

3.2 Visible-near-infrared spectroscopy (VNIRS)

Sediments are fragmented materials that originate from weathering and erosion of rocks or unconsolidated deposits and are transported and deposited by water (US EPA, 2015b). Organic matter constitutes a minor fraction of lake sediments and consists of a mixture of proteins, lipids, carbohydrates and other biochemicals derived from tissues of organisms formerly living in the catchment (Meyers and Ishiwatari, 1993). By analysing sediments with VNIRS it is possible to reconstruct TOC concentrations in surface water over a decadal to millennial time scale (Rosén, 2005).

To generate a sediment spectrum, radiation containing all relevant frequencies in the particular range is directed to the sample. The radiation will cause individual molecular bonds to vibrate by bending or stretching depending on the constituents present in the soil. The bonds will also adsorb light to various degrees, corresponding to a specific energy quantum between two energy levels. The energy spectrum is directly related to the frequency and the resulting absorption spectrum exhibits a characteristic pattern that can be further analysed. The VNIR region is generally characterized by a broad, superimposed and weak vibrational modes, resulting in a soil NIR spectra with a few, broad adsorption features, making it difficult to determine specific soil constituents. It is however possible to extract useful information regarding the quantity of organic and inorganic material in the soil (Stenberg et al., 2010).

The complex absorption pattern needs to be mathematically extracted from the spectra and correlated with soil properties, which requires the use of multivariate calibrations. A common calibration method is based on partial least square regression (PLSR) which is useful when handling a large number of predictor variables that are highly collinear. When developing multivariate calibrations it is important to select the calibration and validation samples carefully so that they are representative of both the variation in the soil properties and of the variation in the spectra (Stenberg et al., 2010).

3.3 ^{210}Pb γ-spectroscopy

Sediment cores can be dated to a specific time period by using ^{210}Pb γ-spectroscopy. ^{210}Pb is a natural radioactive isotope of lead and can be used to date recent (≤ 150y) environmental samples and is suitable for dating due to its half life of 22.3 years (Appleby, 2001). ^{210}Pb results from the decay of ^{222}Rn in the atmosphere (unsupported ^{210}Pb) and from the decay of ^{226}Ra inherent (supported 210Pb) to the samples. For dating purposes only the unsupported part can be used (Moser, 1992). γ-ray spectroscopy allows direct measurements in various media, including water, rocks, soils and sediments. The method uses an adapted detector that counts the specific γ-rays that are emitted at 46.5 keV by the nuclide during a certain number of hours, for a given amount of sample sealed in a container. The number, N (count s^{-1}) of such photons is directly connected to the activity A (Bq) of ^{210}Pb in the sample. Once the activity is obtained the sample can be related to a specific time period (Pilleyre et al., 2006).

4 Material and methods

4.1 Site descriptions

All lakes in the study, except Gårdsjön, are part of the Swedish national and regional lake monitoring programs and their locations can be seen in figure 1. The lakes are all situated in places consisting mostly of forest with minimal influence from point sources. As a consequence, the water quality is primarily controlled by climatic factors and long-range trans boundary atmospheric deposition and in some places by forestry. More information about the Swedish environmental monitoring programmes can be found elsewhere (Fölster et al., 2014). Table 2 gives more detailed information about the lakes (n=17) and table 3 gives information about the lake parameters included in the study.

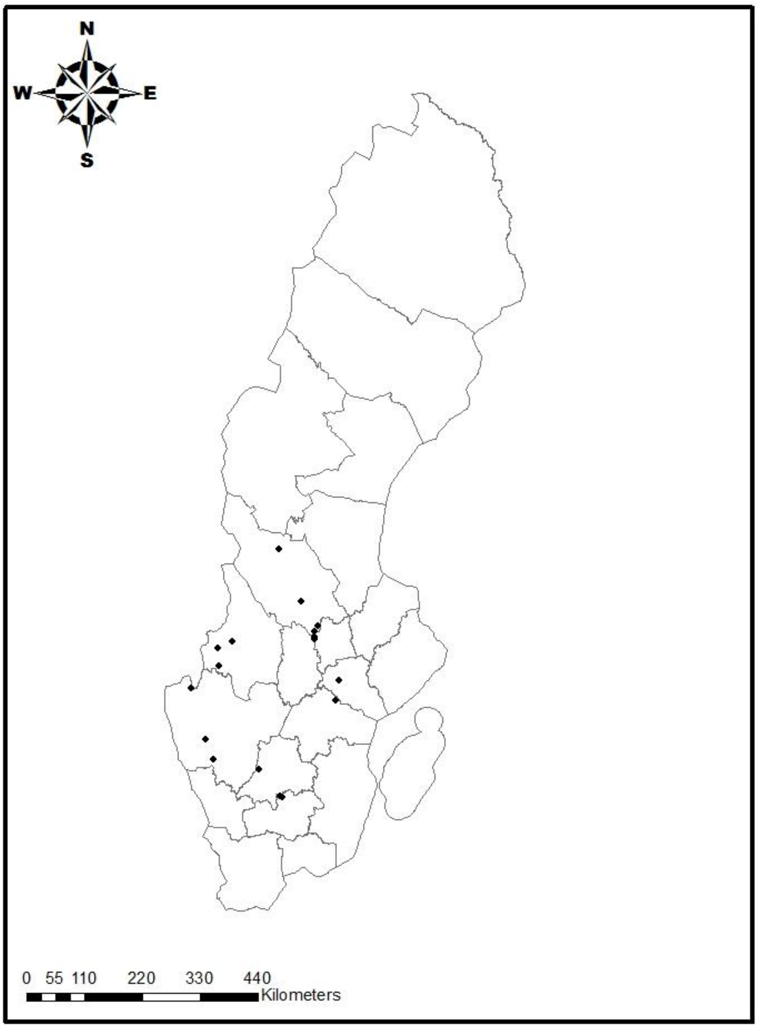


Figure 1. Map of Sweden with lakes included in the study

Table 2. Lakes included the study

Lake	X RT90	Y RT90	County	Sources of impact
Bösjön	6802350	1417990	Dalarna	Forestry, atmospheric deposition
Bysjön	6580860	1302640	Värmland	Atmospheric deposition
Ejgdesjön	6537370	1250170	Västra Götaland	No inf.
Fiolen	6330250	1422670	Kronoberg	Atmospheric deposition
Gyslättasjön	6332090	1419910	Kronoberg	Atmospheric deposition
Gårdsjön	6441344	1277081	Västra Götaland	Atmospheric deposition
Lien	6632160	1484490	Västmanland	Forestry, atmospheric deposition, contaminated soil
Mäsen	6656540	1492060	Dalarna	No inf.
Skärgölen	6515730	1524810	Östergötland	No inf.
Stengårds-hultasjön	6383170	1380100	Jönköping	Forestry, atmospheric deposition
Stora Härsjön	6403640	1292400	Västra Götaland	Forestry, atmospheric deposition
Tryssjön	6702750	1460520	Dalarna	Forestry, atmospheric deposition
Ulvsjön	6615210	1301820	Värmland	No inf.
V. Skälsjön	6646200	1485900	Skinnskatteberg	No inf.
Älgsjön	6552750	1532340	Södermanland	No inf.
Örvattnet	6626820	1328600	Värmland	No inf.
Övre Skärsjön	6635320	1485710	Västmanland	Forestry, atmospheric deposition

Table 3. Information about lake parameters including lake chemistry and climate

Variable	abbreviation	mean ± std dev 1989	mean ± std dev 2013	min 1989	max 1989	min 2013	max 2013
In-lake chemistry							
Total organic carbon (mg l^{-1})	TOC	7.15 ± 3.5	8.99 ± 4.68	3.1	16.7	2.9	25.8
SO_4^{2-} (meq l^{-1})		0.15 ± 0.04	0.08 ± 0.04	0.07	0.23	0.02	0.2
pH		6.36 ± 0.68	6.5 ± 0.5	5	7.81	5.4	7.4
Sum Ca^{2+}, Mg^{+}, K^{+}, Na^{+} (meq l^{-1})	ΣBC	0.42 ± 0.17	0.38 ± 0.17	0.154	0.87	0.117	0.771
Alkalinity (meq/l)	Alk	0.10 ± 0.09	0.13 ± 0.10	0	0.4	0.001	0.42
Acid neutralizing capacity (meq l^{-1})	ANC	0.15 ± 0.13	0.18 ± 0.10	-0.003	0.63	0.015	0.49
Cl (meq l^{-1})		0.10 ± 0.08	0.09 ± 0.08	0.031	0.313	0.012	0.3
Total nitrogen (µg/l)	Tot-N	361.9 ± 145.5	273.8 ± 145	187	770	125	640
Total phosphorus (µg/l)	Tot-P	10.9 ± 5.14	9.6 ± 5.6	2	33	2	25
EMEP sulfate deposition (mg/S04/yr*ha)	EMEP Sulfate	1726.7± 370.3	(2010) 305.6 ± 87.3	969.7	2530.5	161.1	546
Climate variables							
Precipitation (mm month ^{1})	Precip	47.5 ± 21	55.1 + 29.3	2.9	102.6	2.2	123.9
Runoff (m month^{-1})	Q	(1999) 0.04 ± 0.04	0.027 ± 0.03	(1999) 0.0	(1999) 0.22	0.0003	0.14
Temperature °C	Temp	6.7 ± 6.2	5.6 ± 7.6	-9.7	17.5	-9.9	18
Catchment characteristics							
Catchment area (km^{2})		166 ± 512.5	166.3 ± 512.5	5.46	2205	5.5	2205.5

4.2 Sample collection and analysis

The sediment cores were collected using a kayak corer during spring of 2014. Cores were collected from the deepest part of the lake and extruded in the field at either 0.5 or 1 cm resolution. After drying the samples each sample was ground with pestle for 1 minute by hand.

To infer past lake-water TOC, a calibration model between spectra of lake sediments, recently accumulated material and corresponding TOC concentrations in the water column was applied. The calibration set consisted of 140 lakes across Sweden covering a TOC gradient of 0.7 to 24.7 mg l^{-1} (Rosén, 2005; Cunningham and Bishop, 2010). The VNIRS analysis of sediment was carried out in February 2015 at the Department of Ecology and Environmental Sciences, Umeå University. The VNIRS-TOC reconstructions and ^{210}Pb-dating were performed by PhD-students working at the same department.

4.3 Data and software

All data analysis was performed in JMP version 5.0.1.2 (SAS institute Inc. 2002), a statistical program focused on exploratory data analysis and visualisation. The analysis included initial exploratory analysis where series of scatter plots and correlation coefficients were studied to search for patterns in data and connections between variables. PLS analysis was performed in SIMCA version 13.0 by Umetrics, a programme for multivariate analysis and modelling.

4.3.1 Water chemistry

All chemical data were obtained from the Swedish national monitoring database maintained by the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural sciences (http://www.slu.se/vatten-miljo). The chemical analysis was done at the certified laboratory at the same department. Chemical data for Gårdsjön could not be obtained as it is not part of the same monitoring programme. Chemical parameters considered in this study where total organic carbon (TOC mg l^{-1}), pH, alkalinity (alk meq l^{-1}), chloride (Cl meq l^{-1}), sulfate (SO_4 meq l^{-1}), ammonium-nitrogen (NH_4-N µg l^{-1}), nitrate-nitrogen (NO_3-N µg l^{-1}), total nitrogen (Tot-N µg l^{-1}), total phosphorus (Tot-P µg l^{-1}), calcium (Ca meq l^{-1}), magnesium (Mg meq l^{-1}), sodium (Na meq l^{-1}) and potassium (K meq l^{-1}).

The concentration of base cations (BC meq l^{-1}) was calculated by:

$$\Sigma BC = Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} \qquad (4)$$

Acid neutralizing capacity (ANC meq l^{-1}) was calculated by:

$$ANC = (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) - (SO_4^{2-} + Cl^{-} + \frac{NO_2^{+} + NO_3^{-} - N}{14000}) \qquad (5)$$

4.3.2 Sulfate deposition data

Gridded (50 x 50 km) reconstructions of atmospheric sulfate deposition from 1880-2013, calculated by the European Monitoring and Evaluation Programme (EMEP) deposition model, was provided by the Coordination Centre for Effects (CCE). The EMEP model operates on a routine basis at the Norwegian Meteorological Institute (DNMI) and is capable of describing the processes of emission, trans boundary fluxes, chemical transformation and removal with good reliability (Mylona, 1993).

4.3.3 Climate data

Monthly time series data of climatic parameters from 1901-2013 were extracted from the Climatic Research Unit (CRU) at the University of East Anglia and were obtained from the Centre for Environmental Data Archival (CEDA). In this study precipitation- and temperature data were downloaded. The time series are calculated at a resolution of 0.5 x 0.5 degree grids across the world's land areas and are based on an archive of monthly mean values provided by more than 4000 weather stations around the world (Centre for Environmental Data Archival, 2015).

The climate data was provided in netCDF file format. To view the data the geographical information system programme Panoply, developed by NASA (http://www.giss.nasa.gov/tools/panoply/) was used. Lake coordinates were used to identify the appropriate grid from which the climate data was extracted.

4.3.4 Runoff data

Runoff data was obtained from the Swedish Metrological and Hydrological Institute (SMHI) water website http://vattenwebb.smhi.se/. Runoff data is available from 1999 to 2013 and has been modelled by the catchment S-HYPE model (SMHI, 2015a). To take the size of the catchment into account while studying runoff the data was recalculated from [$m^3\,s^{-1}$] to [m $month^{-1}$] by the following equation:

$$\frac{runoff\ [m3]}{s} \cdot \frac{60s \cdot 60[min] \cdot 24[h] \cdot 30.5d}{[min] \cdot [h] \cdot [d] \cdot [month] \cdot catchment\ area\ [m2]} = \frac{m}{month} \qquad (6)$$

4.4 Statistical analysis

4.4.1 Non-parametric tests of monotonic trends

The Mann-Kendall trend test was used to determine trends over time for the variables in table 4. The trend test was divided into the following time periods: 1901-2013, 1901-1980 and 1981-2013. The division was based on previous VNIRS-TOC reconstructions which showed a TOC concentration minima at 1980, coinciding with the time of peak sulfate deposition in Sweden. The division was further based on plots of temperature and precipitation data for the examined sites that showed an increasing trend after 1980. Monitoring data extends back to the beginning of the 1980s, beginning earliest in 1983 and latest in 1987 and currently extends to 2013. The time period for the Mann-Kendall test on monitoring data was therefore between 26 and 30 years depending on the variable and site. The tests were performed in Excel by a macro developed at the Swedish University of Agricultural Sciences (SLU, 2015).

Table 4. Parameters and time periods for which trend tests were performed

Parameter	< 1980	1983-2013	1901-2013
Chemical			
TOC		✓	
pH		✓	
ΣBC		✓	
Alk		✓	
ANC		✓	
Cl		✓	
Tot-N		✓	
Tot-P		✓	
EMEP SO_4^{2-}	✓	✓	
VNIRS TOC	✓		
Climatic			
Precipitation	✓	✓	✓
Temperature	✓	✓	✓

4.4.2 Linear- and multiple regression

Linear and stepwise multiple linear regression was used to see which climatic and chemical parameters that could help explain the spatial variation and/or the rate of change in TOC before and after 1980. The aim was to search for variables that could explain why the rate of change of TOC has been faster after 1980 than the rate of decrease due to sulfate deposition before 1980.

Linear and stepwise multiple linear regression was performed in JMP on two different data sets. The first consisted of annual averages of the examined parameters and was used to predict the annual average values of TOC before (n=9) and after 1980 (n=16), and can be seen in table 5. The second data set consisted of the Theil-slopes and site average values of the parameters in table 6, and was used to predict the Theil-slope and/or site average of TOC before and after 1980. Common transformations were applied when needed to normalise residuals and/or stabilize the variance.

Parameters were kept in the regression model when $p < 0.05$ and gave an improvement of adjusted R^2 of 0.01. When the parameters in the model turned out to be significant but not the intercept, the predictor variables were centred in order to obtain a significant intercept. By centring values the column mean is subtracted from each row value. Nitrogen and phosphorus were not included in the list of predictor values as they were not thought to help explain change over time, although they were strongly correlated to TOC.

Table 5. Summary of candidate predictor variables used in the multiple linear regressions to predict annual average TOC

Parameters	< 1980	1987 -2013 measured
Physical		
Log catchment area	✓	✓
Chemical (1880-1980)		
EMEP sulfate deposition (mg ha^{-1} yr^{-1})	✓	
VNIRS TOC	✓	
Alkalinity (meq l^{-1})		✓
ANC (meq l^{-1})		✓
BC (meq l^{-1})		✓
Cl (meq l^{-1})		✓
pH		✓
SO_4^{2-} (meq l^{-1})		✓
Climatic		
Precipitation (mm)	✓	✓
Temperature °C	✓	✓
Runoff (m/month) (1999-2013)		✓

Table 6. Summary of candidate predictor variables used in the multiple linear regression to predict the site average or Theil-slope of TOC

Parameter	< 1980	1987-2013 measured
Physical		
Log catchment area	✓	✓
Theil-slopes		
Precipitation	✓	✓
Temperature	✓	✓
EMEP SO_4^{2-} deposition	✓	✓
Alkalinity		✓
ANC		✓
BC		✓
Cl		✓
pH		✓
SO_4^{2-}		✓
Chemical parameters		
EMEP sulfate deposition in 1980 (mg ha^{-1} yr^{-1})	✓	✓
EMEP site average/median (mg ha^{-1} yr^{-1})	✓	✓
Alkalinity (meq l^{-1}/l)		✓
ANC (meq l^{-1})		✓
BC (meq l^{-1})		✓
Cl (meq l^{-1})		✓
pH		✓
SO_4^{2-} (meq l^{-1})		✓
Climatic parameters		
Precipitation (mm)	✓	✓

Temperature (°C)	✓	✓
Runoff (m/month) (1999-2013)		✓

4.4.3 Partial least squares projections to latent structures

PLS regression was performed in SIMCA in the same way as for the multiple linear regressions, i.e. with the same predictor variables shown in tables 5 and 6. For annual averages SIMCA auto-transformed the variables according to table 7.

Table 7. Applied transformations

Variable	Transform	Formula
Precipitation	Log	$\log_{10}(x)$
SO_4^{2-}	Log	$\log_{10}(x)$
Cl^-	Log	$\log_{10}(x)$

To show the result of a PLS analysis there are many different diagnostic plots in SIMCA that convey different information. The Variable Importance Plot (VIP) graphs the VIP scores for each X-variable and is a measure of the variables importance in modelling both X and Y. VIP-values larger than 1 indicate important X-variables and lower than 0.5 indicate unimportant X-variables. VIP-values between 0.5 and 1 are a grey area where the importance of the variable depends on the size of the data set (Eriksson et al., 2006).

The regression coefficient plot shows the relationship that the model coefficients have to the Y-variables. The coefficients are analogous, but different from, coefficients obtained from multiple linear regression. By default the coefficients are related to scaled and centred X-variables to make the coefficients comparable, making it possible to assess which coefficients that have more or less importance for the model. The error bars indicate the confidence intervals of the coefficients. The coefficient is significant (above the noise) when the confidence interval does not include zero (Eriksson et al., 2006). Variables that had a small VIP-value and coefficients with large error bars were deleted from the model. The coefficients in the regression expressions are for scaled and centred X-variables and un-scaled and un-centred Y. The coefficients do not express a causal relationship and are usually not independent. This means that one cannot expect Y to actually change by the amount indicated by the coefficient value.

The loadings scatter plot displays the relationship between the X- and the Y-variables for the predictive component. The score scatter plot is a window into the X-space in which it is possible se correlations between observations and thereby also possible to detect groups of observations. Comparing the two plots enables understanding of how the variables relate to the observations (Umetrics MVA FAQ, 2015).

The permutations plot helps to assess the risk that the model only fits the data that has been used to create the model or if it can be used to predict Y for new observations. The validation is done by randomly changing the order (permuting) of Y, while the X-matrix is intact. The horizontal axis shows the correlation between the permuted Y-vector and the original Y-vector. The criteria for validity are:

- All the blue Q^2-values to the left are lower than the original points to the right
- *Or* the regression line for the Q^2 points intersects the vertical axis on the left, or below zero.

5 Results

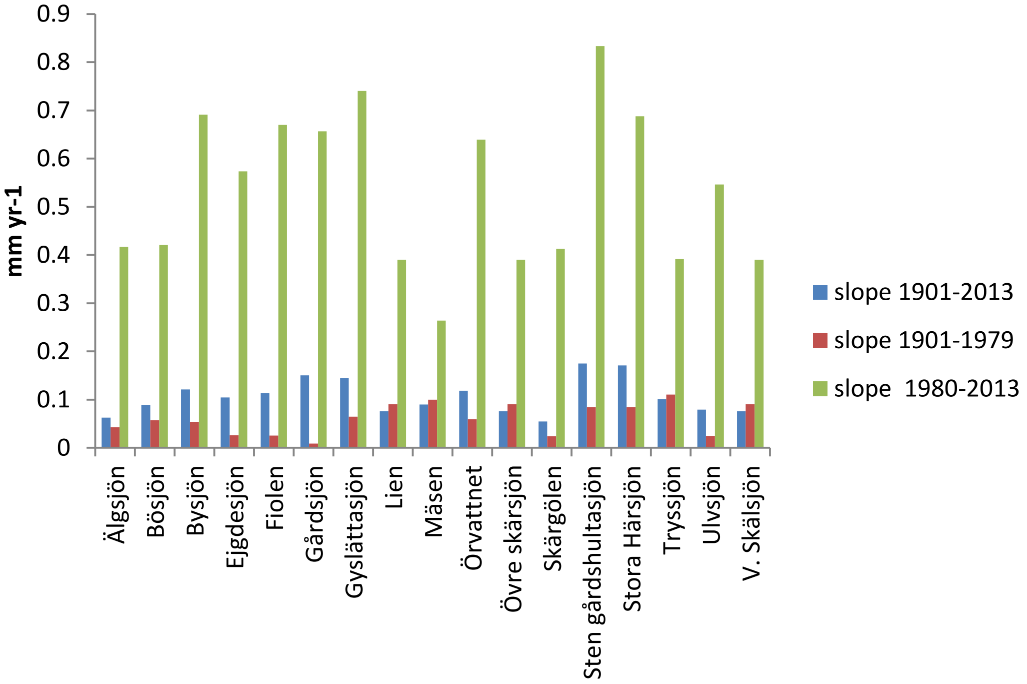
5.1 Trends in precipitation, temperature and runoff

The Mann-Kendall trend test of precipitation from 1901-2013 showed that precipitation has increased significantly ($p \leq 0.05$) in all places except Lien, Skärgölen, Ulvsjön Västra Skälsjön, Älgsjön and Övre Skärsjön (although p-values were close to 0.05). The air temperature during the same time period has increased significantly for all lakes except Stengårdshultasjön ($p = 0.06$). All p-values can be seen in table A1, Appendix A.

Trend tests of precipitation between 1901 and 1979 showed no significant increase in precipitation. Temperature increased significantly only in Stengårdshultasjön during the same time period. P-values can be seen in table A2, Appendix A.

Between 1980 and 2013 precipitation increased significantly in almost half of the lakes; Älgsjön, Bysjön, Fiolen, Gyslättasjön, Örvattnet, Örvattnet, Stengårdshultasjön and Ulvsjön. The remaining lakes all had positive trends and p-values close to 0.05. Temperature increased significantly in the majority of lakes but not in Bysjön, Bösjön, Gårdsjön, Stora Härsjön, Ulvsjön and Örvattnet although p-values were close to 0.05. Runoff data was only available between 1999 and 2013 and has not changed significantly at any site. All p-values can be seen in table A3, Appendix A.

A summary of Theil-slopes for precipitation and temperature for all time periods can be seen in figure 2 and 3. General patterns of precipitation and temperature made on annual averages for all locations between 1901-2013 can be seen in figure 4 and 5.



Figur 2. Theil slopes (mm yr^{-1}) for precipitation during the time periods 1901-2013, 1901-1979, 1980-2013.

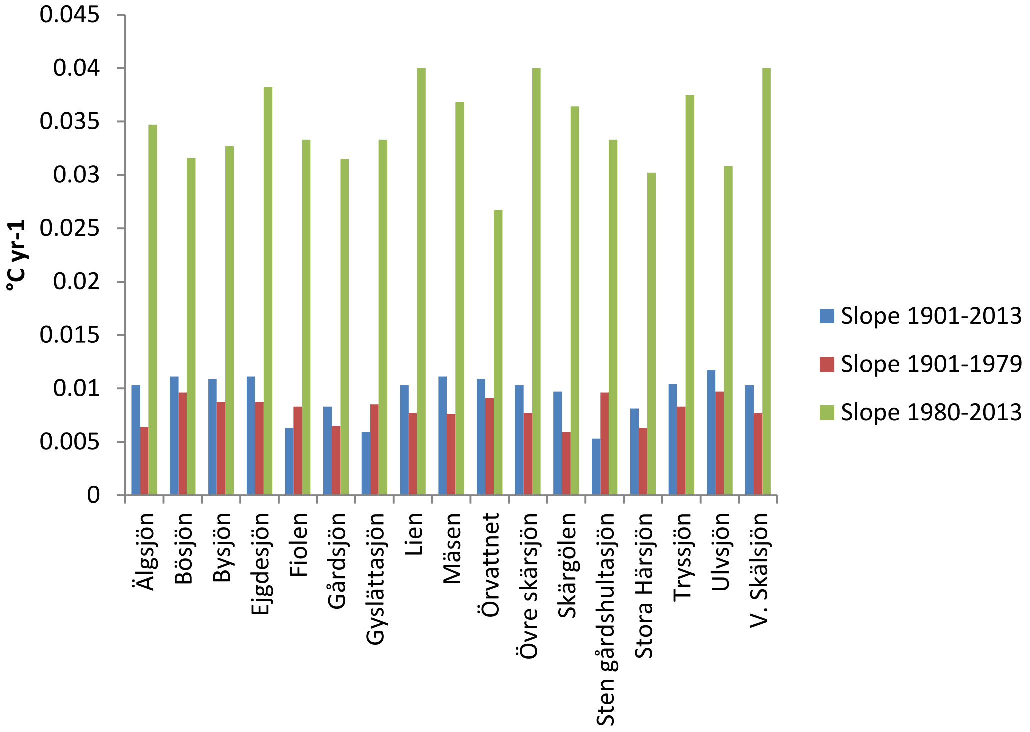


Figure 3. Theil-slopes (°C yr^{-1}) for temperature during the time periods 1901-2013, 1901-1979, 1980-2013.

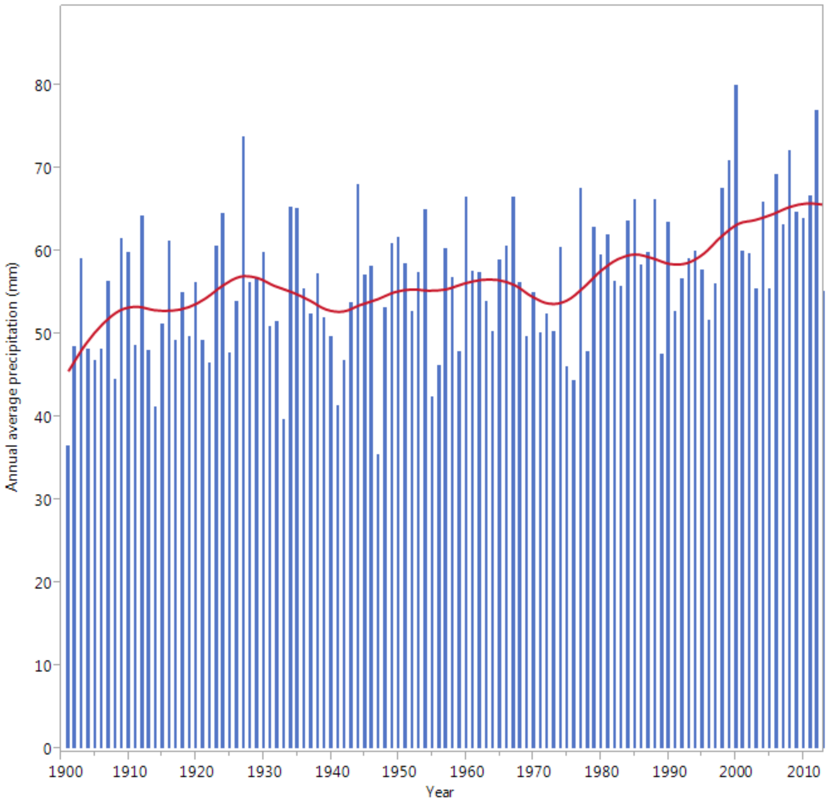


Figure 4. Blue lines show annual average precipitation for all sites between 1901-2013. The red line is a smoother that shows the long term trend. An increasing trend can be seen after 1980.

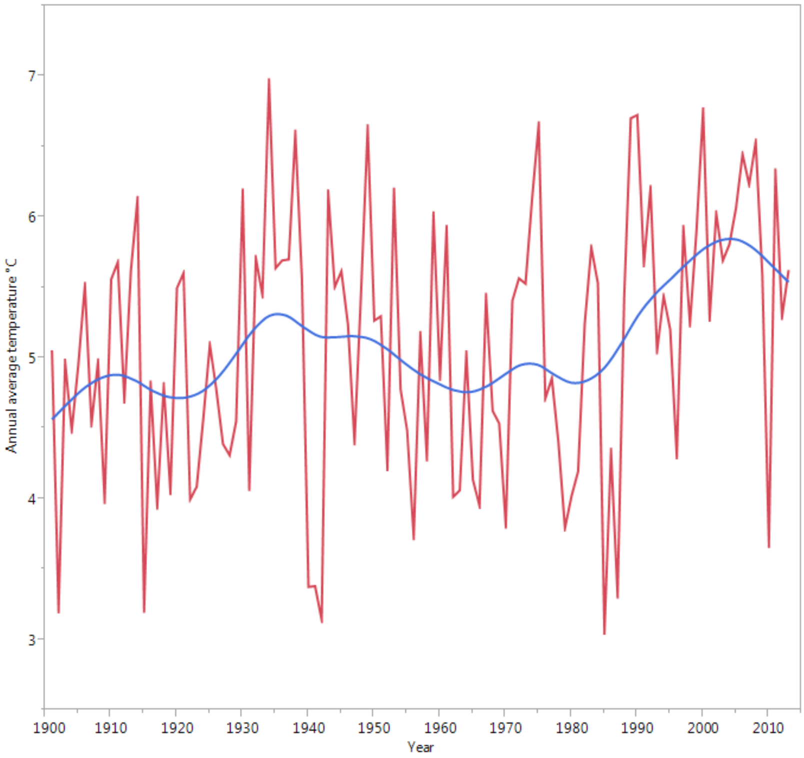
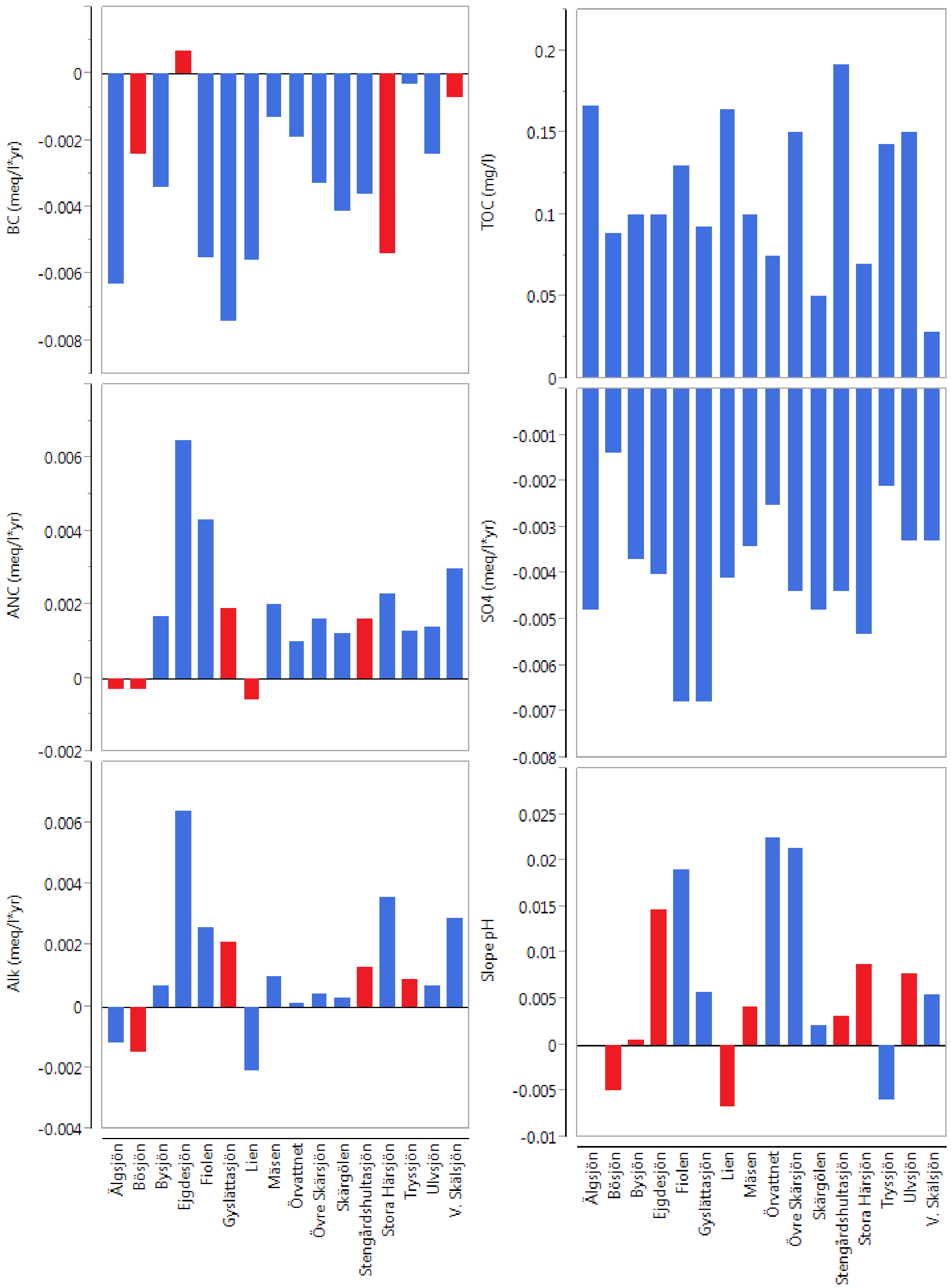


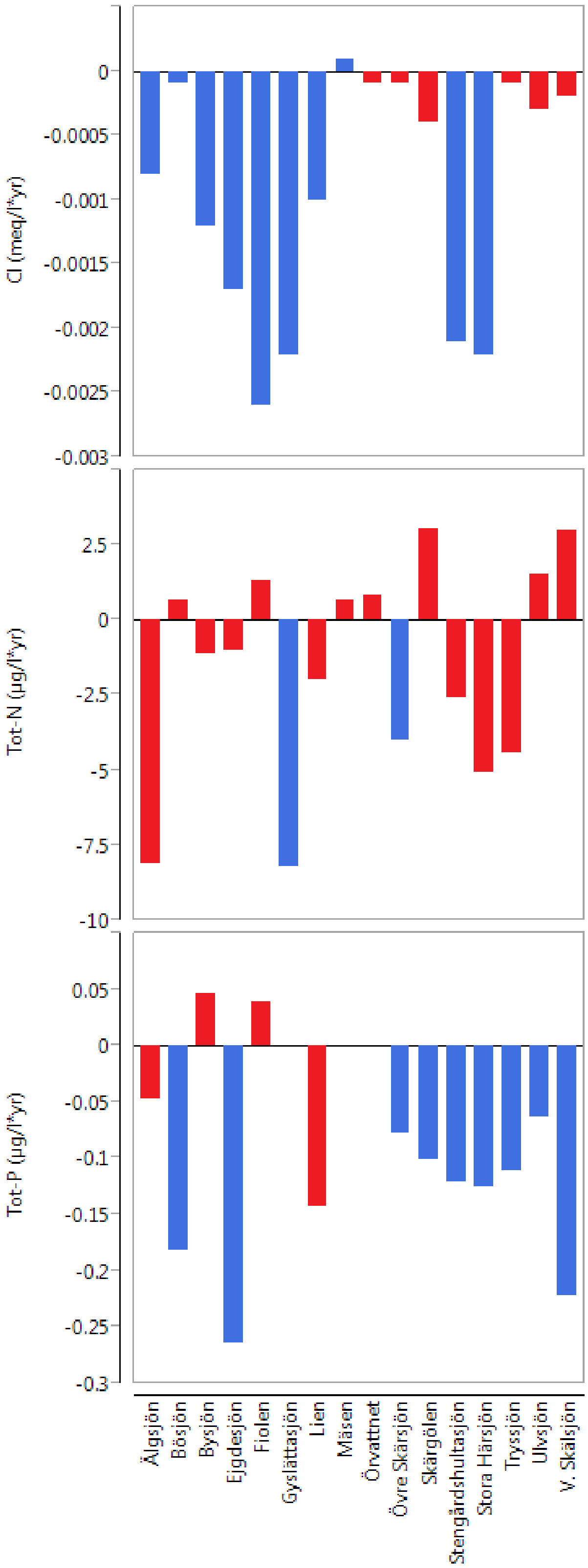
Figure 5. The red line shows the annual average temperature at all sites. The blue line is a smoother that shows the long term trend. An increasing trend can be seen after 1980.

5.2 Trends in water chemistry

The trend analysis of surface water chemistry showed that there has been a substantial increase in TOC and decrease of SO_4^{2-} in all lakes. Alk, ANC and pH have risen in most lakes, BC and atmospheric deposition of Cl^- has decreased in most lakes. Tot-N only changed significantly in two lakes and Tot-P has decreased in the majority of lakes. The average rate of change in Alk, ANC, pH, SO_4^{2-}, BC and Cl^- are in the order of magnitude 10^{-3}. Theil-slopes of Tot-P are in the order of magnitude 10^{-2} and Tot-N 10^{0}. TOC is in the order of magnitude $10^{-}1$. Theil-slopes can be seen in figure 6 and p-values for Theil-slopes can be seen in table A4, Appendix A.

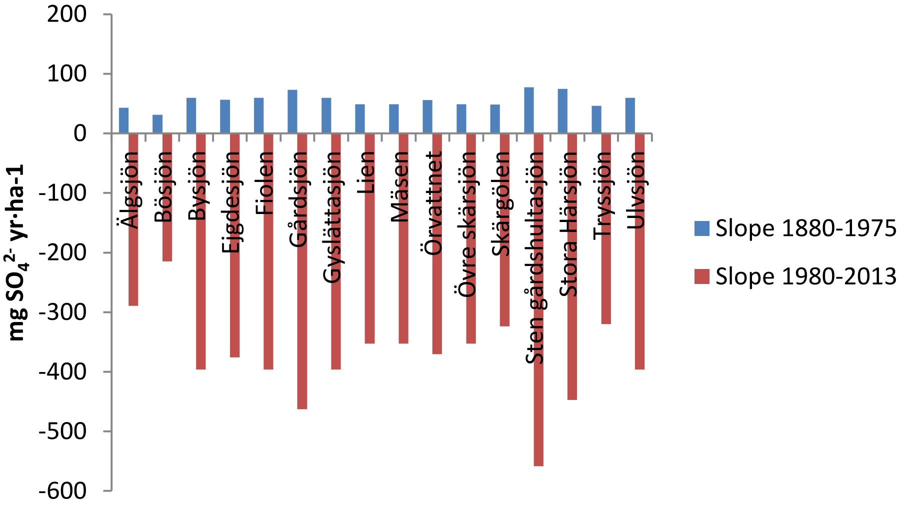
Figure 6. Theil-slopes of lake chemical parameters for each site. Insignificant trends are shown in red.



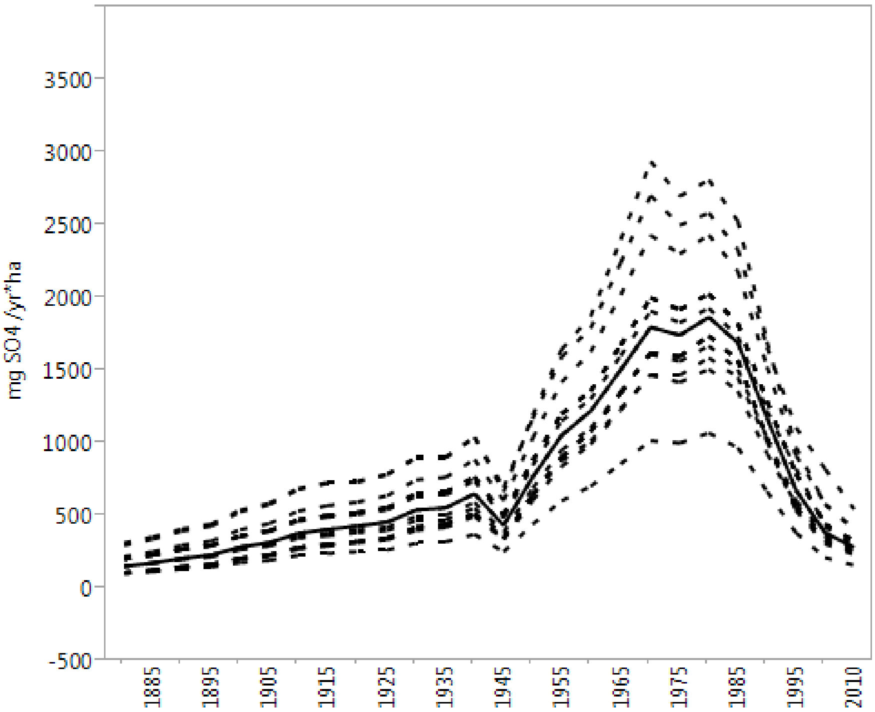

Cl (meq/l*yr)
0
-0.0005
-0.001
-0.0015
-0.002
-0.0025
-0.003
Tot-N (µg/l*yr)
2.5
0
-2.5
-5
-7.5
-10
Tot-P (µg/l*yr)
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
Älgsjön
Bösjön
Bysjön
Ejgdesjön
Fiolen
Gyslättasjön
Lien
Mäsen
Örvattnet
Övre Skärsjön
Skärgölen
Stengårdshultasjön
Stora Härsjön
Tryssjön
Ulvsjön
V. Skälsjön

5.3 Trends in sulfate deposition

The trend test of sulfate deposition showed that deposition increased significantly in all places between 1880-1975. After 1980 sulfate deposition decreased significantly in all places 6-7 times faster than it increased, as can be seen in figure 7. Figure 8 shows the sulfate deposition in all lakes from 1880-2013. It can be seen that deposition increased steadily from 1880, with a decrease in around 1943 due to World War II, peaked in 1980, and thereafter declined sharply. P-values for the trend tests can be seen in table A5, Appendix A.



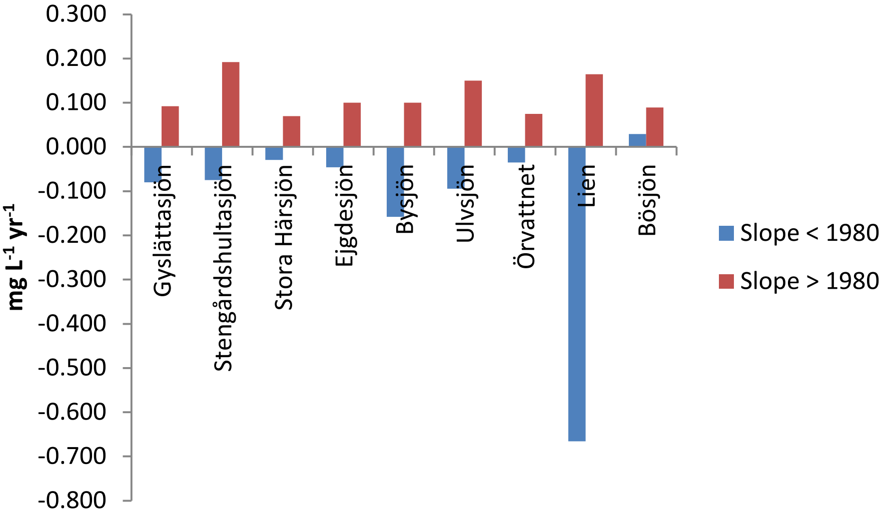
Figur 7. Theil-slopes for sulfur deposition between 1880-1975 and 1980-2013.



Figur 8. EMEP sulphur deposition in all lakes from 1880-2010. The solid line shows the median deposition value.

5.4 Trends in VNIRS-TOC reconstructions

Due to technical problems with the VNIRS-spectrophotometer TOC-reconstructions could only be made for 9 of the initial 17 lakes included in the study. These lakes were: Bysjön, Bösjön, Ejgdesjön, Gyslättasjön, Lien, Stengårdshultasjön, Stora Härsjön, Ulvsjön and Örvattnet. Some reconstructions extended back to the 1100s and others back to the mid-1800s depending on the sedimentation rate in the sediment column. The trend analysis was extended to as far back as the reconstructions reached until 1980, all trends were significant and p-values can be seen in table A6, Appendix A. The trend tests of VNIRS reconstructed TOC and measured TOC after 1980 showed that the rate of increase of TOC after 1980 was 1.15-2.5 times faster than the rate of decrease before 1980 in all lakes except Bysjön, Bösjön and Lien, which can be seen in figure 9. In Bysjön the increase of TOC after 1980 was 1.6 times slower than the decrease from reference conditions, and in Lien 4 times slower. Concentrations of TOC in Bösjön increased between reference conditions and 1980, although the increase after 1980 is 3 times faster than the increase before 1980.

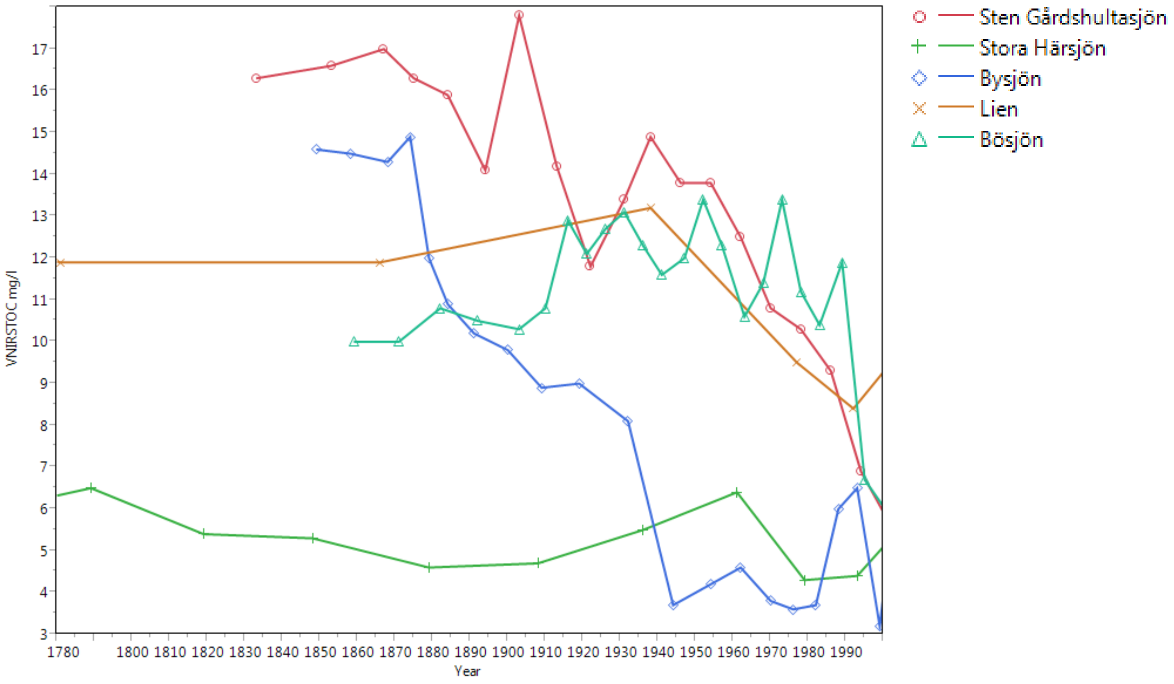


Figur 9. Theil-slopes of VNIRS-TOC before 1980 and slopes of measured TOC after 1980.

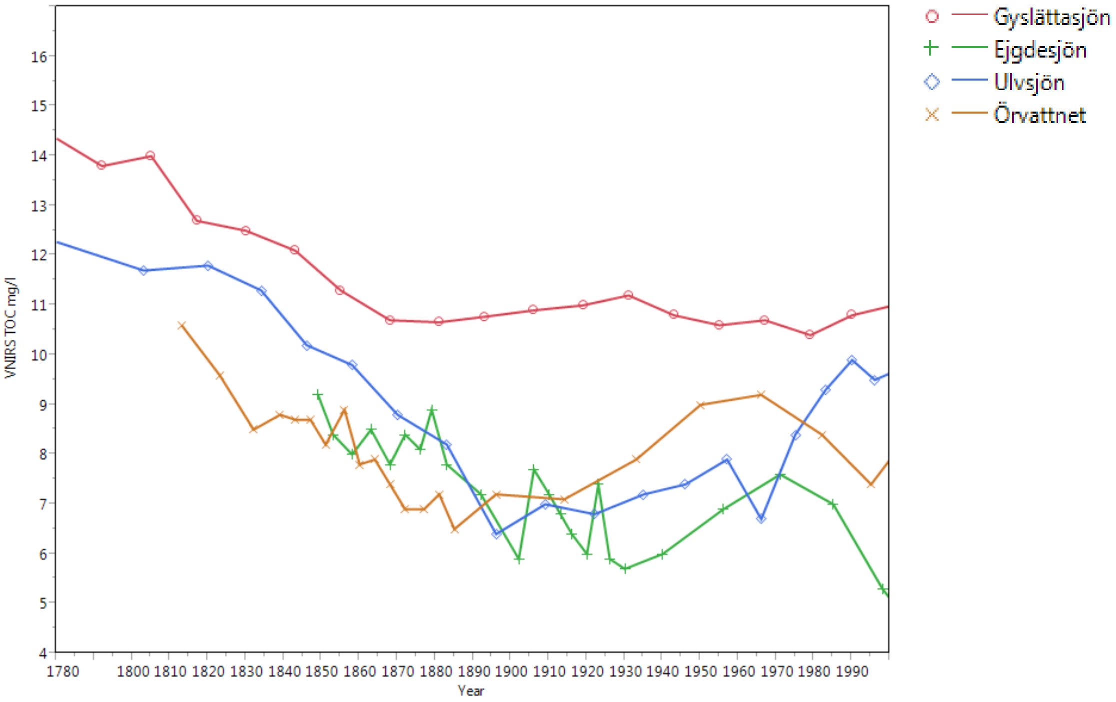
5.5 VNIRS-TOC reconstructions

The TOC-reconstructions in Figure 10 exhibit a similar pattern in response to sulfate deposition, and similar to results of previous studies (Valinia et al., 2014); A decline of TOC begins in the early 1900s, reaches minima around 1980, whereafter TOC concentrations start to increase, even if the increase after 1980 is not evident in the reconstructions. In Stengårdshultasjön TOC began to decline after around 1950 and declined most rapidly after 1980 during peak sulfate deposition. TOC-concentrations in Stora Härsjön exhibited a less clear response to sulfate, but concentrations were lowest at around 1980. In Bysjön TOC decreased sharply from reference conditions, being lowest at around 1980 and thereafter increasing. TOC in Lien decreased steadily from around 1930 and started to increase around 1990. The reconstruction of Bösjön is ambiguous, with TOC-concentrations going up and down from reference conditions, but exhibits a decrease around 1980 whereafter concentrations increase.

TOC-reconstructions in figure 11 shows that TOC-concentrations in all lakes have decreased since as far back as the reconstruction extends, but exhibits increasing TOC-concentrations during peak sulfate deposition.



Figur 10. VNIRS TOC-reconstructions shown from 1780 for a subset of the lakes



Figur 1. VNIRS TOC-reconstructions since 1780 for the second subset

5.6 Linear and multiple linear regression

5.6.1 Slope of TOC after 1980

The candidate parameters in table 5 and 6 were used in order to see which climatic and chemical parameters that could help explain the spatial variation and/or the rate of change in TOC before and after 1980. It was found that site median temperature and site median SO_4^{2-} concentration was related to the rate of change (Theil-slope) of TOC during the time period 1987 and 2013.

Figure 12 shows a plot of actual by predicted Theil-slope of TOC, with an adj. R^2 value of 0.69. An actual by predicted plot is an evaluation of how well the model fits the data. The model and input parameters were significant and the VIF-value was below 10, indicating low collinearity which is a pre-condition for multiple linear regression. Älgsjön and Västra Skälsjön were considered outliers and removed from the analysis.

The prediction expression shows that the rate of change of TOC decreases with higher median site temperature and SO_4^{2-} concentration. The prediction expression can be seen in equation 7 and parameter estimates in table 8.

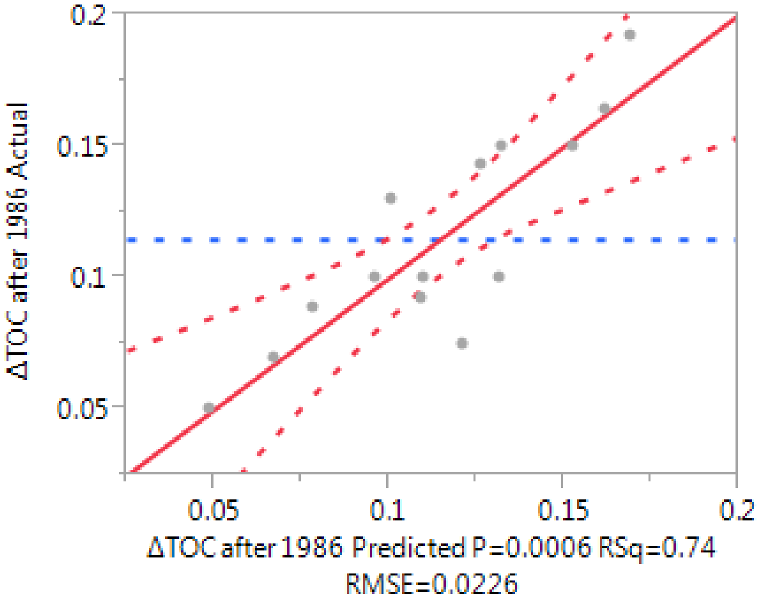


Figure 2. Actual by predicted Theil-slopes of TOC (1987-2013)

$$\Delta TOC = 0.117 - 0.009 \cdot [\text{site median temp}^2] - 0.887 \cdot [\text{site median } SO_4^{2-}] \qquad (7)$$

Table 2. Parameter estimates of the multiple linear regression model

Term	Estimate	Std Error	t Ratio	Prob>|t|	VIF
Intercept	0.1215344	0.006985	17.4	<.0001	.
Centred Median temp^2	-0.008995	0.00201	-4.47	0.0008	1.640147
Centred Median SO_4^{2-}	-0.817155	0.22354	-3.66	0.0033	1.640147

5.6.2 Measured TOC slope / VNIRS-TOC slope

A relationship was found between the ratio measured TOC slope after 1980 and VNIRS TOC slope before 1980 with the Theil-slope of precipitation (1980-2013), with an R^2 of 0.43, seen in figure 13. A relationship was also found between the same ratio and pH with an R^2 of 0.44, seen in figure 14. Regression equations are seen in equation 8 and 9. Parameter estimates are seen in table 8 and 9.

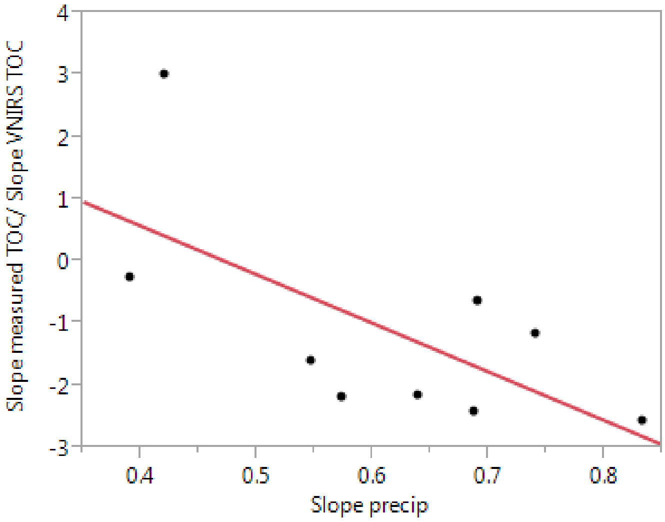


Figure 3. Linear regression of the ration between slope of TOC before and after 1980 against slope of precipitation

Regression equation: Slope measured TOC/ Slope VNIRS TOC = 3.6946783 - 7.8184534*Slope precip (8)

Table 4. Parameter estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	3.694678	2.149077	1.72	0.1293
Slope precip	-7.81845	3.417863	-2.29	0.056

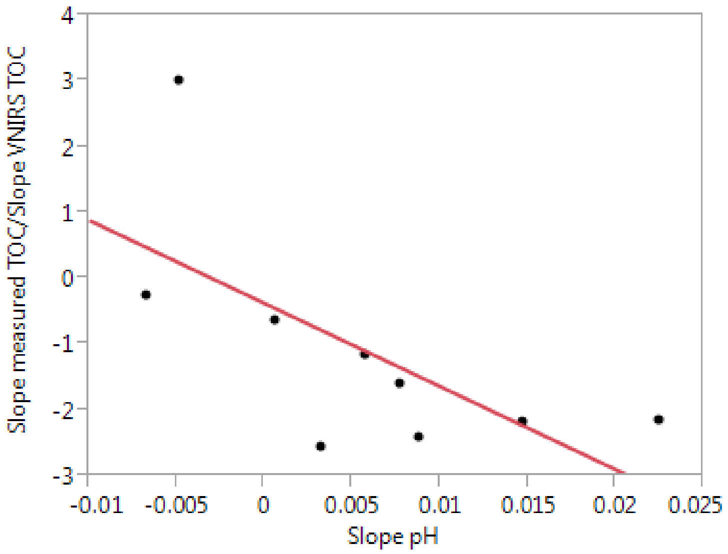


Figure 14. Linear regression of the ration between slope of TOC before and after 1980 against slope of pH

Regression equation: Slope measured TOC/ Slope VNIRS TOC = -0.38 – 126.29*Slope pH (9)

Table 9. Parameter estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-3.3787	0.5544	-0.68	0.5165
Slope pH	-126.297	53.372	-2.37	0.0499

5.7 PLS modelling in SIMCA

5.7.1 Slope of VNIRS-TOC

With PLS regression it was possible so to predict the Theil-slope of VNIRS reconstructed TOC, from as far back as the reconstructions reached until 1980 with the predictor variables in table 6. Lien and Bösjön were considered outliers and removed from the data set. The PLS reduced the predictor variables into two significant components seen in table 10. The cumulative R^2Y was 0.716 and Q^2 0.516. The regression equation can be seen in equation 10.

$$\Delta TOC_{VNIRS} = -0.047 + 0.0271[\Delta precip\ (1901\text{-}1980)] - 0.0186[EMEP\ SO_4^{2-}\ 1980] - 0.0217[\Delta EMEP\ SO_4^{2-}] \quad (10)$$

Table 3. Summary of the PLS components

Component	R2X	R2X(cum)	R2Y	R2Y(cum)	Q2	Q2(cum)
1	0.705	0.705	0.482	0.482	0.326	0.326
2	0.292	0.997	0.233	0.716	0.282	0.516

The VIP-plot in figure 15 shows that the Theil-slope of EMEP SO_4^{2-} was the most important variable, followed by Theil-slope of precipitation and amount of SO_4^{2-} deposited in 1980. The permutations plot in figure 16 meets the second criteria for validity as the regression line of Q^2 intersects the vertical axis at below zero.

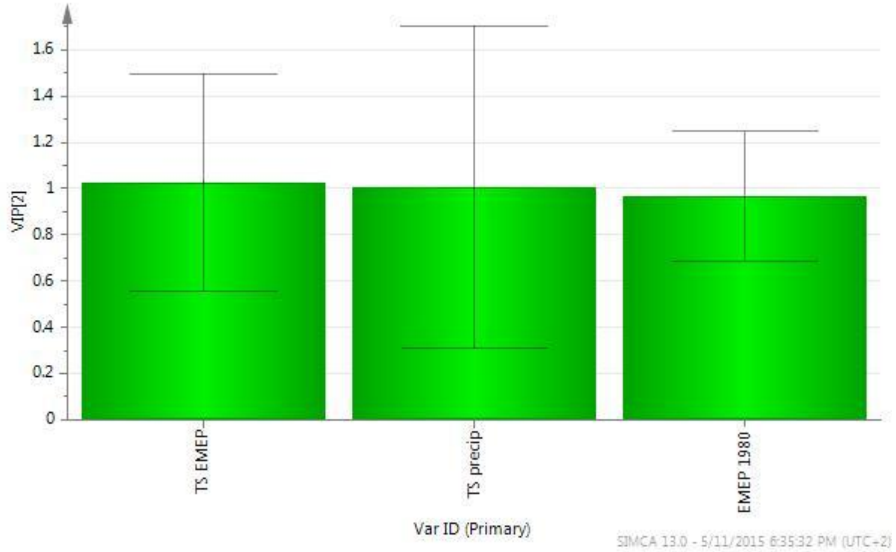


Figure 15. VIP-plot showing which variables that had the most influence on the

‘

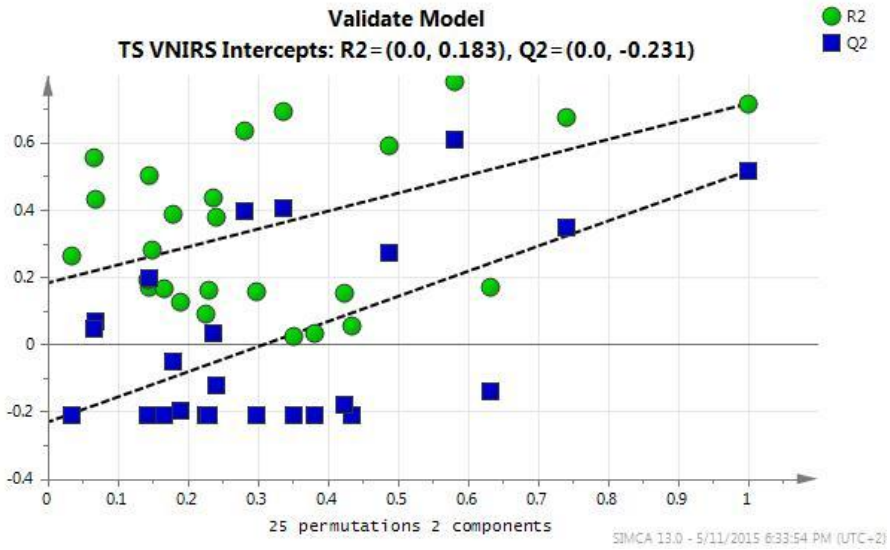


Figure 16. Permutations plot. The regression line of Q^2 intersects the vertical axis at below zero meeting the criteria for validity.

5.7.2 Annual average TOC

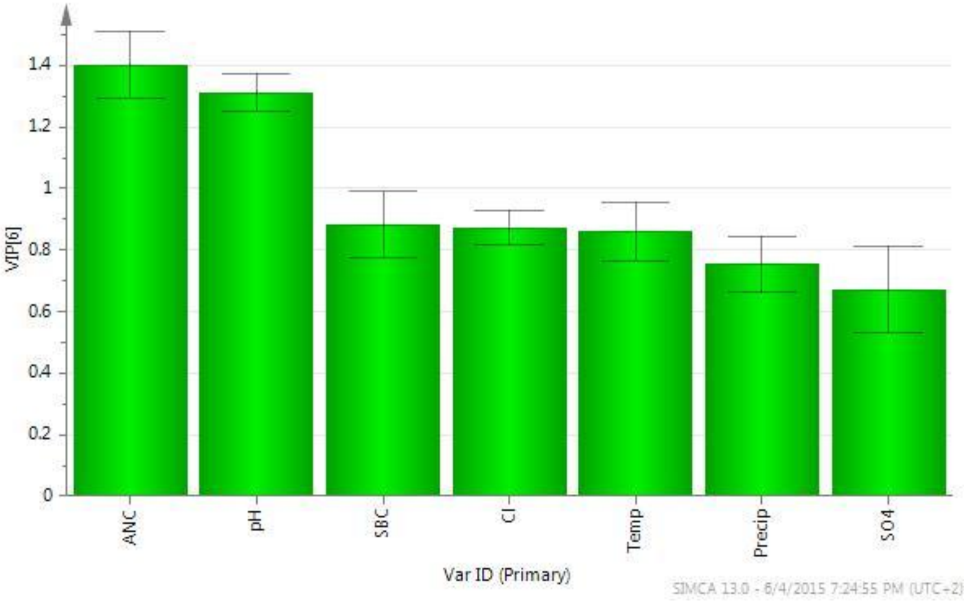
A PLS regression model was made on annual averages between 1987 and 2013 of the predictor variables in table 5 to predict the annual average of TOC. The PLS analysis reduced the predictor variables into five significant components, seen in table 11. Together the components made up for 97.7% of the variation in the X-variables (R^2X cum) and 54.9% of the Y-variable (TOC). The cumulated Q^2 value was 0.525 which means that 52.5% of the variation in Y could be predicted by the model according to cross validation. The regression equation can be seen in equation 11.

$$\text{TOC} = 8.46 - 0.41[\log \text{precip}] - 0.48[\text{temp}] + 0.15[\log SO_4^{2-}] - 2.58[\text{pH}] \\ - 3.67[\text{BC}] + 6.17[\text{ANC}] + 2.31[Cl^-] \qquad (11)$$

Table 4. Summary of the PLS components

Component	R2X	R2X(cum)	Eigenvalue	R2Y	R2Y(cum)	Q2	Q2(cum)
1	0.397	0.397	2.78	0.185	0.185	0.179	0.179
2	0.266	0.664	1.87	0.142	0.327	0.171	0.319
3	0.0792	0.743	0.555	0.156	0.483	0.22	0.469
4	0.0869	0.83	0.608	0.0157	0.498	0.0142	0.476
5	0.122	0.952	0.856	0.0148	0.513	0.0277	0.491
6	0.0245	0.977	0.171	0.0363	0.549	0.0664	0.525

The VIP-plot in figure 17 shows that the most important variable was ANC, followed by pH, ƩBC, Cl^{-1}, Temp, Precip and SO_4^{2-}. The permutations plot in figure 18 shows the cumulative R^2Y and Q^2-value of the original model to the right and the permuted models R^2Y and Q^2 values to the left. The horizontal axis shows the correlation between the permuted Y-vector and the original Y-vector. The original Y vector has a correlation of 1 with its self, which can be seen in the figure to the top right. The model met the criteria for validity as all the blue values were lower than the green and the regression line of Q^2 intersects the vertical axis below zero.



Figur 17. VIP-plot showing which variables that has most influece on the model.

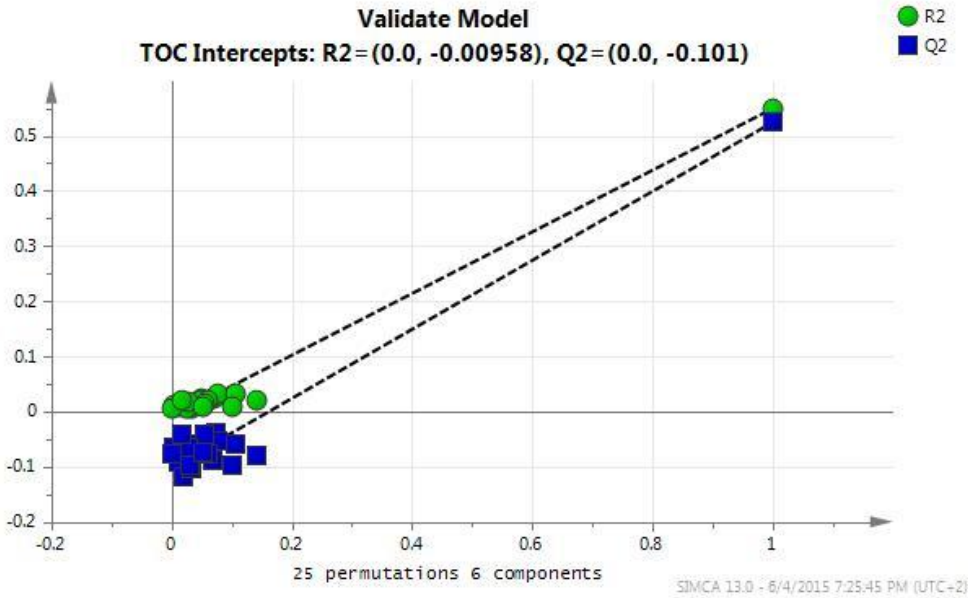


Figure 18. Permutations plot. All the blue values are below the green, and the regression line for Q^2 intersects the vertical axis at below zero indicating that the model is not spurious.

6 Discussion

6.1 Trends in measured TOC and VNIRS-TOC reconstructions

The results from the Mann-Kendall trend test showed that TOC concentrations have increased significantly in all lakes since the measurements began. They results also showed that the rate of increase in TOC after 1980 has been faster than the rate of decrease in TOC from reference conditions in most lakes, confirming what was noted in a previous study (Valinia et al., 2014).

The VNIRS-TOC-reconstructions in figure 10 and 11 all showed a decreasing trend in TOC from as far back as the reconstructions reached until 1980 (except Bösjön), which may be explained by anthropogenic activity in the form of land use and/or sulfur deposition. The VNIRS-TOC reconstructions in figure 10 exhibited a similar pattern in response to sulfate deposition; a decline of TOC concentrations began in the early 1900s, reached minima around 1980, whereafter TOC concentrations started to increase. The reconstructions after 1980 were not as accurate as before 1980 because the top sediment is sensitive to handling and recent liming may have influenced the reconstructions. However all measurement data shows that TOC concentrations have increased after 1987 when monitoring of TOC started, although it is not clear in the reconstructed VNIRS-TOC data. The TOC-reconstructions in figure 11 show signs of anthropogenic influence or show no response to sulfate deposition. Örvattnet, Ejgdesjön and Ulvsjön exhibits increasing TOC-concentrations before and during peak sulfur deposition which is likely due to land management practices (Meyer-Jabob et al., 2015). Gyslättasjön shows very little change from the beginning of the 1900s, which may be due to environmental factors which has made the catchment less sensitive to the effects of sulfate deposition.

6.2 Linear regression models

Linear regression and stepwise multiple linear regression was used to see which climatic and chemical parameters that could help explain the spatial variation and/or the rate of change in TOC before and after 1980. The multiple linear regression with Theil-slopes of TOC for the different lakes during the time period 1987-2013 on the Y-axis, showed that the slope could be explained by the site median temperature and site median SO_4^{2-} concentration. The lakes Älgsjön and Västra Skälsjön were outliers and removed from the data set. Älgsjön had the next highest Theil-slope of TOC and had the highest site median value of TOC. It was also the most nutrient rich lake and had the highest ANC, which means that the lake has been less sensitive to the effects of sulfate deposition. These factors resulted in a much faster TOC increase than the model predicted and made it an outlier. In Västra Skälsjön the rate of increase of TOC was much slower than in the rest of the lakes. This could be explained by that it is the lake with the lowest site median concentration of TOC, making the trend smaller in absolute terms. It was also the lake with the lowest site median of plant nutrients (Tot-N and Tot-P) which correlate strongly to TOC.

It was found that the ratio between Theil-slopes of TOC after and before 1980, i.e. how many times faster the rate of increase of TOC was than the rate of decrease before 1980, correlated with the Theil-slope of precipitation and the Theil-slope of pH. This means that the lakes where the rate of increase in TOC after 1980 was much faster than the rate of decrease before 1980 coincided with the lakes that had the highest rate of increase in precipitation and pH. The regression with Theil-slope of precipitation as X-variable (figure 13) gave an R^2 of 0.43 with a p-value of 0.056 being only slightly insignificant. Although an R^2 of 0.43 is only a moderate connection, it is still interesting as it may help to explain the discrepancy between TOC rates before and after 1980, and may be worth investigating further as it is possible that the connection would improve with more lakes included in the analysis. The regression with pH as X-variable (figure 14) gave an R^2 of 0.44, indicating that pH has increased faster than it decrease before 1980 and could also help to explain the discrepancy.

Stepwise multiple linear regression was also used in attempts to create a model with the predictor variables in table 5, with at least one climate variable included among the X-variables, to predict the annual average, annual median value, site average or site median value of TOC, with little success. A recurring problem was that the residuals in the multiple regression were not normally distributed and therefore did not meet the requirements for regression.

6.3 PLS regression models

The PLS model with annual averages of TOC after 1987 in the Y-matrix and variables in table 5 in the X-matrix, showed that ANC and pH had VIP-values above 1 and thereby being the most important variables for predicting the annual average of TOC. Also ΣBC, Cl^- and temperature had high VIP-values, followed by precipitation and SO_4^{2-} that also had a relatively large influence on the model.

The PLS model with Theil-slopes of VNIRS-TOC in the Y-matrix and Theil-slopes of variables in table 6 as predictor variables showed that the most important predictor variable was the Theil-slope of sulfate deposition (1880-1980), followed by the Theil-slope of precipitation (1901-1980), and the amount of sulfur deposition in the year 1980 during peak acidification. The two lakes with the largest Theil-slopes were outliers and had to be removed, leaving only 7 lakes in the model. These lakes where Bysjön and Lien, where the Theil-slopes were much larger than the rest of the lakes. The model gave a Q^2 above 0.5 indicating good predictivity, although it is possible that the model would perform a better Q^2 with more lakes included in the model.

6.4 The role of sulfate deposition

The trend test of sulfur deposition showed that deposition decreased 6-7 times faster after 1980 than it increased between 1880 and 1980. This implies that that the rate of increase in pH may have been faster after 1980 than the rate of decrease before 1980. This could help to explain why TOC concentrations have risen faster after 1980 than they decreased before 1980.

The trend analysis of lake water chemistry showed that concentrations of SO_4^{2-} have decreased in all lakes since the 1980s. As a result, the concentration of base cations has decreased in most lakes, as SO_4^{2-} is no longer competing with base cations for soil sorption sites. This in turn has led to an increased acid neutralizing capacity, alkalinity and pH, which several studies have linked to increasing TOC concentrations. The concentrations of SO_4^{2-} should in theory decrease at the same rate in surface waters, but during the period of high sulfur deposition sulfur has accumulated in the soil, delaying recovery from acidification (Wilander, 2008; Futter et al., 2014). This indicates that an increase in pH alone could not have been responsible for all of the increase in TOC.

The PLS model with Theil-slopes of VNIRS-TOC in the Y-matrix showed that the most important predictor variable was the Theil-slope of sulphate deposition (1880-1980), followed by Theil-slope of precipitation (1901-1980) and the amount of sulfur deposition in the year 1980 during peak acidification. Since precipitation did not change between 1901-1980, the results indicate that the decrease of TOC before 1980 can be mainly attributed to sulfate deposition.

The results from the PLS model with annual averages of TOC between 1987-2013 in the Y-matrix indicate that the ability to withstand the effects of acid deposition has been the governing process in TOC-dynamics, implying that it is in fact acid deposition that has been responsible for most of the increase in TOC since the measurements began in 1987. Since acid deposition is almost back to pre-industrial levels it is likely that the role of recovery from acidification will be smaller in the future and the role of precipitation and temperature will be larger as a result of climate change.

6.5 The role of temperature

Temperature has increased significantly in most locations since 1901, with the main part of the increase occurring after 1980 and the rate of increase being 3-6 times faster after than before 1980. The linear regression model with Theil-slopes of TOC during the time period 1987-2013 on the Y-axis showed that the rate of change of TOC decreases with increasing site median SO_4^{2-} and site median temperature. That a higher site median concentration of SO_4^{2-} leads to a lower rate of change of TOC was not surprising as a higher concentration of SO_4^{2-} will inhibit TOC mobility. It was more surprising to find that the rate of change of TOC has been slower on sites with a higher site median temperature. This means that the rate of increase of TOC has been faster in colder areas in northern Sweden and slower in the warmer areas in the south. This is however consistent with previous findings of Lucas et al. (2013) who showed that streams in southern Sweden that received a higher acid deposition are still responding to declines in deposition, while water chemistry in streams in the north are more closely related to climate variability.

The connection between TOC and temperature is under debate and it has been shown that temperature can affect TOC by a number of different mechanisms. For example, increased temperatures may have a decreasing effect by affecting soil drainage conditions and/or enhancing microbial activity which removes TOC by cellular respiration (Kalbitz et al., 2000). Increased temperatures could also lead to more vegetation, improving the soil structure which may prevent leaching of TOC (Kalbitz et al., 2000). Furthermore, temperature may lead to an increased evaporation and decreased runoff, which could have a decreasing effect on TOC (Erlandson et al., 2008). The mentioned mechanisms may explain why the rate of change of TOC has been slower in warmer areas and faster in cold. There are however other studies that have found that temperature has an increasing effect on TOC by an increased primary production (Weyhenmeyer and Karlsson, 2009).

The PLS with annual averages of TOC from 1987-2013 in the Y-matrix and annual averages of the variables in table 5 as predictor variables showed that temperature had a VIP value of 0.86, which is below 1 but still considered to be relatively high. In PLS modelling it is not possible to look at the sign of the coefficients to see if the variable has a positive or negative influence on the model as the coefficients are not independent and do not reflect a causal relationship. Temperature has been shown to have both positive and negative effect on TOC. Which mechanism that has been dominating in this study is not possible to say.

6.6 The role of precipitation

Precipitation has increased significantly in most locations since 1901, with the main part of the increase occurring after 1980. After 1980 the increase in precipitation has been in one order of magnitude larger than before 1980 and is the only parameter that increases in the same order of magnitude as TOC, which may indicate a connection.

The results from the linear regression with the ratio of Theil-slopes of TOC after and before 1980, showed that lakes where the rate of increase in TOC after 1980 had been much faster than the rate of decrease before 1980 correlated with the lakes that had the highest rate of increase in precipitation. Also the PLS model with annual averages of TOC between 1987-2013 in the Y-matrix, and variables in table 5 as predictor variables showed that precipitation was a relatively important variable for predicting the annual average TOC, which is consistent with previous studies (e.g. Worall and Burt, 2006). This indicates that that precipitation may explain a part of the discrepancy between the rates of change of TOC before and after 1980.

6.7 The role of runoff

The trend analysis on runoff showed no significant trend. This could be because the time series available from SMHI only extends back to 1999, a 19 year shorter time period than the trend analysis of temperature and precipitation, and also because increase temperatures may lead to an increased evaporation and thereby counteracting the effect of increased precipitation. Initial exploratory correlation analysis showed a strong correlation between TOC and runoff, but it did not help in explaining the increasing TOC-trend.

6.8 The role of marine Cl^-

Sea-salt deposition episodes have been linked to decadal cycles of storm intensities driven by the North Atlantic Oscillation (NAO). The trend test of Cl^- showed that deposition of Cl^- has decreased significantly in most places, which is a result of decreased atmospheric deposition of sea-salt. A pre-condition for performing Mann-Kendall trend tests is that the trend is monotonic, i.e. it is either entirely increasing or decreasing. A closer look at plots of Cl^- concentrations showed that concentrations of Cl rather had an oscillating than monotonic decreasing trend, which makes the result of the trend test uncertain, although it was clear that Cl^- deposition had decreased on most sites.

Deposition of marine base cations like Cl^- has been shown to cause sea-salt related acidification episodes (Heath et al., 1992), which may increase the solubility of TOC. A reduction of Cl^- deposition will also lead to a reduced ionic strength which is another mechanism that may increase the solubility of TOC. Furthermore, Cl^- is an anion that competes for soil sorption sites whereby TOC may be displaced (Kalbitz et al., 2000).

The results from the PLS model with annual averages of TOC between 1987-2013 in the Y-matrix and variables in table 5 as predictor variables showed that a decline in atmospheric deposition of sea-salt has had a large influence on TOC, which is consistent with prior research (Monteith et al., 2007).

6.9 The role of phosphorus and nitrogen

The trend analysis of Tot-P showed that concentrations have decreased on most sites. Most of the lakes in the study are still acidified and have been limed, which can inhibit the release of phosphorus (Hu and Huser, 2014). Phosphorus is a growth limiting plant nutrient and a decrease of Tot-P could lead to less primary production, counterbalancing the rate of increase of TOC. An additional counterbalancing mechanism is that phosphate (PO_4^{3-}) is an anion that can affect the adsorption of DOC by displacing it from sorption sites, and lower PO_4^{3-} concentrations will thereby inhibit TOC release. The trend in Tot-N was not clear as it was only significant on two sites and trends go both up and down on the different sites. Results from the initial correlation analysis showed a strong correlation between TOC and Tot-N, which can be expected since nitrogen is an important plant nutrient. Since Tot-N concentrations have not changed significantly over time it does not help to explain the increase in TOC-concentrations.

6.10 What will TOC concentrations in Swedish surface waters be like in the future?

The results from the PLS model with annual averages of TOC after 1987 in the Y-matrix and variables in table 5 as predictor variables indicate that the most important driver in TOC change since measurements began in 1986 has been the decline of acid deposition and subsequent recovery from acidification. Since there is still accumulated SO_4^{2-} stored in the soil it is likely that sulphate is still inhibiting TOC mobility, which means that TOC concentrations will continue to increase until the stored SO_4^{2-} has depleted and TOC concentrations have returned to naturally high levels, whereafter the increase can be expected to slow down. The results also indicate that increased precipitation has contributed to increased TOC concentrations. SMHI predicts that annual average precipitation in Sweden will increase with 20-60% from the time period 1961-1990 by the end of the century, depending on what climate scenario that is used (SMHI, 2015). Most of the increase is expected to take place in northern Sweden, which means that TOC concentrations will increase more rapidly in the north.

The annual average temperature in Sweden is expected to rise between 2-6°C from the time period 1961-1990 by the end of the century depending on what climate scenario that is used (SMHI, 2015). This could help counter balance the effect of precipitation to some degree. Temperatures are expected to increase at a faster rate in Southern than Northern Sweden, which means that the rate of change of TOC concentrations will be slower in the south than in the north. It can however not be ruled out that rising temperatures will have an increasing effect on TOC as different studies have shown different results.

The last PLS model showed that sea salt was an important variable for predicting TOC. The effects of climate change on the NAO and if changes will be associated with more severe sea-salt episodes is yet unknown (Hindar et al., 2004), making it hard to predict the effect of Cl^- on TOC in the future.

6.11 Uncertainties

Initially the idea was to compare the Theil-slope of TOC from reference conditions in 1860 to 1980, and from 1980 up until today, but the VNIRS reconstructions gave TOC-values at irregular time intervals for the different lakes. For some lakes concentrations were given every 5-10 years while others only gave 5 data points in total between 1860 and 1980. Some reconstructions extended back to the 1100s and others to the mid-1800s, although values before 1800 are extrapolated and therefore not as reliable. Since some lakes had too few data points to make reliable statistical analysis between the time period 1860 and 1980, the trend analysis was extended to as far back as the reconstruction reached up until 1980, which adds uncertainty to the trend analysis. Even though reference conditions are defined as the state assumed to have existed prior to 1860 with minor influence of anthropogenic activity, studies show that considerable anthropogenic activity had already altered the environment substantially before then (Renberg et al., 2009). Furthermore, the reconstructions from the lakes Örvattnet, Ulvsjön and Ejgdesjön showed increases in TOC during peak sulfate indicating anthropogenic activity in the form of land management, making the Theil-slope of TOC up until 1980 smaller than it would have been otherwise. VNIRS-TOC in Stora Härsjön also went up and down from reference conditions, which could be due to anthropogenic activity or perhaps due to changes in the North Atlantic Oscillation (NAO), making the trend analysis uncertain. Due to technical problems with the VNIRS-spectrophotometer

TOC-reconstructions could only be made for 9 of the analysed 17 lakes, providing less lakes for the statistical analysis and making it harder to find significant correlations.

There are also a number of uncertainties with regards to the VNIRS-analysis. The pre-treatment of samples include air drying, crushing and passing through a 2 mm sieve and additional grinding. Grinding of soil particles can have a substantial effect on the spectra as clay aggregates are crushed and differences between samples may have occurred due to manual handling.

Although not all Theil-slopes were significant for climate and in-lake chemical parameters they were used in the regression and PLS analysis to get more data to work with. For temperature and precipitation p-values for the slopes that were not significant were still close to 0.05, and for chemical parameters the insignificant Theil-slopes were the lowest ones, meaning that the trend is more uncertain where the rate of change is low.

PLS analysis is a useful tool for making regressions when variables are highly correlated, something which is not possible while using multiple linear regression. The degree of explanation is usually slightly lower than with multiple linear regression, but is often better at predictions. It would have been desirable to obtain a higher Q^2 for the PLS models, and higher R^2-values for the regression models with the ratio between the Theil-slope of measured TOC after 1980 and the Theil-slope of VNIRS TOC as Y-variable, but considering the uncertainties in calculating the Theil-slopes of VNIRS-TOC and the uncertainties in the reconstructions themselves, the results are still interesting and worth further investigation. It would also have been desirable to test the models on an independent data set, this was not done due to lack of time and the lack of VNIRS-analysed lakes. PLS analysis is useful to help explain which processes that are important, but it cannot be used to quantify one X-variables influence on Y. It was therefore not possible to quantify how much climate variables have affected TOC.

It is clear that many natural processes and anthropogenic factors can influence TOC-concentrations. To disentangle processes from each other and to quantify the influence of each process on TOC is not an easy task. This means that one has to be careful when interpreting statistical relationships. The results may still be used to discuss which variables have been important in the past and which variables may be important in the future rather than providing deterministic relationships.

7 Conclusions

- The results from the statistical analysis showed that TOC-concentrations have increased faster after 1980 than they decreased from reference conditions due to sulfate deposition before 1980. It is clear that many natural processes and anthropogenic factors can influence TOC-concentrations. To disentangle different processes from each other and to quantify the influence of each process on TOC is not an easy task. The results from the statistical analysis indicate that it is likely that the discrepancy between the rate of change of TOC before and after 1980 can be explained by increases in precipitation and a sharp reduction in sulfate emissions.
- Trend tests of lake chemical parameters showed that alkalinity, ANC and pH are increasing in most lakes while concentrations of base cations are decreasing. These are signs of recovery from acidification due to a substantial decrease in sulfate deposition.
- Results from the multiple linear regression analysis showed that the Theil-slope of TOC after 1980 could be predicted by the site median temperature and site median concentration of sulfate. Both temperature and sulfate exerted a negative effect on the model, which means that the rate of change of TOC has been slower on sites with higher sulfate loading and high temperatures. That the rate of increase has been slower in areas with a high sulfate deposition was not surprising. That the rate of increase of TOC has been slower in warmer areas was more surprising ant not in accordance with the original hypothesis that TOC concentrations would increase more on sites with warmer temperatures. This may be explained by, for example, an enhanced microbial activity which removes organic carbon by respiration and/or by an increased evaporation which leads to less runoff.
- Annual averages of TOC could be predicted with an acceptable degree of explanation in the PLS analysis. The VIP-plot showed that the most important variables for predicting TOC was ANC and pH, but also ΣBC, Cl^{-1}, temperature, precipitation and SO_4^{2-} were important variables. This supports the conclusion that increasing TOC concentrations have been due to both recovery from acidification and changes in precipitation. The effect of temperature is not known as the regression coefficients in PLS do not describe a causal relationship, and studies have shown that temperatures can have both a positive and negative effect on TOC. Furthermore, decreasing deposition of sea-salt may also contribute to increased TOC-concentrations.
- Different hypothesis of the primary drivers of increasing TOC have different implications for quantifying preindustrial levels and for future predictions of TOC, which in turn has different implications for water classification, management and drinking water treatment. The results from this study indicate that TOC are returning to naturally high pre-industrial levels of TOC and will increase further to un-preceded levels due to increased precipitation. Moreover, the results showed that the rate of increase of TOC will be faster in colder areas

in the north than warmer areas in southern Sweden. This will be of importance for drinking water treatment plants that will need to adapt their treatment processes.

8 References

Abdi, Hervé., 2007. Partial Least Square Regression PLS-Regression. *Encyclopedia for research methods for the social sciences, pp. 792-795*

Angers, D.A., Bolinder, M.A., Carter, M.R., Gregorich, E.G., Drury, C.F., Liang, B.C., Voroney, R.P., Simard, R.R., Donald, R.G., Beyaert, R.P., Martel, J., 1997. Impact of tillage practices on organic carbon and nitrogen storage in cool, humid soils of eastern Canada. *Soil and Tillage Research Vol. 41, pp. 191-201*

Appleby, P.G., 2001. Chronostratigraphic Techniques in Recent Sediments. In *Tracking environmental change using lake sediment, pp. 171-203.* Springer Netherlands

Ashworth, D.J., Alloway, B.J., 2007. Complexation of Copper by Sewage Sludge-derived Dissolved Organic Matter: Effects on Soil Sorption Behaviour and Plant Uptake. Water. *Air. Soil Pollut. Vol. 182, pp. 187–196.*

Austnes, K., Vestgarden, L.S., 2008. Prolonged frost increases release of C and N from a montane heathland soil in southern Norway. *Soil Biology and Biochemistry Vol. 40.10 pp 2540-2546.*

Boyer, E.W., Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1997. Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes Vol. 11, pp. 1635-1647*

Centre for Environmental Data Archival, 2015. Dataset Collection Record [WWW Document]. URL http://catalogue.ceda.ac.uk/uuid/3f8944800cc48e1cbc29a5ee12d8542d (accessed 4.22.15).

Chan, K.Y., Heenan, D.P., 1999. Lime-induced loss of soil organic carbon and effect on aggregate stability. *Soil Science of America Vol. 63, pp. 1841-1844*

Chantigny, M.H., 2002. Dissolved and water-extractable organic matter in soils: a review on the influence of land use and management practices. *Geoderma Vol. 113, pp- 357-380*

Chantigny, M.H., Angers, D.A., Prévost, D., Simard, R.R., 1998. Dynamics of soluble organic C and C mineralization in cultivated solid with varying N fertilization. *Soil Biology and Biochemistry Vol. 31, pp. 543-550*

Chow, Alex. T., Tanji, Kenneth K., Gao, Suduan., 2003. Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils. *Water Research Vol. 37, pp 4475-4485*

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

Clark, J.M., Heijden, G.M.F.V. der, Palmer, S.M., Chapman, P.J., Bottrell, S.H., 2011. Variation in the sensitivity of DOC release between different organic soils following H2SO4 and sea salt additions. *European Journal of Soil Science Vol. 62, pp- 267-284*

Couture, S., Houle, D., Gagnon, C., 2011. Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. *Environmental Science and Pollution Research Vol. 19, pp. 361-371*

Cunningham, L., Bishop, K., 2010. Paleoecological evidence of major declines in total organic carbon concentrations since the 19th century in four nemoboreal lakes. *Journal of Paleolimnology Vol. 45, pp. 507-518*

Davidson, Eric A., Janssens, Ivan A., Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, 2006. *Nature Vol. 440, pp. 165-173*

Delprat, L., Chassin, P., Linères, M., Jambert, C., 1997. Characterization of dissolved organic carbon in cleared forest soils converted to maize cultivation. *Developments in Crop Science Vol. 25, pp. 257-266*

De Paolis, F., Kukkonen, J., 1997. Binding of organic pollutants to humic and fulvic acids: Influence of pH and the structure of humic material. *Chemosphere Vol. 34, pp. 1693–1704.*

Don, A., Schulze, E.-D., 2008. Controls on fluxes and export of dissolved organic carbon in grasslands with contrasting soil types. *Biogeochemistry Vol. 91. pp. 117-131*

Dosskey, M.G., Bertsch, P.M., 1997. Transport of Dissolved Organic Matter through a Sandy Forest Soil. *Soil Science Society of America Journal Vol. 61.3, pp. 920-927*

EC Directive 2000/60/EC), 2000. EC Directive 2000/60/EC of the European Parliament and on the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.

Eriksson, L., Johansson, E., Kettaneh-Wold, N., Trygg, J., Wikström, C., Wold, S., 2006. Multi- and Megavariate Data Analysis, Part 1. Basic Principles and Applications. Umetrics Academy

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

Erlandsson, M., Cory, N., Köhler, S., Bishop, K., 2009. Direct and indirect effects of increasing dissolved organic carbon levels on pH in lakes recovering from acidification. *Journal of Geophysical Research Vol. 115*

Evans, C.D., Chapman, P.J., Clark, J.M., Monteith, D.T., Cresser, M.S., 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology Vol. 12, pp. 2044-2053*

Evans, C.D., Good ale, C.L., Capron, S.J.M., Dies, N.B., Emmett, B.A., Fernandez, I.J., Field, C.D., Findlay, S.E.G., Lovett, G.M., Meese burg, H., Malden, F., Sheppard, L.J., 2008. Does elevated nitrogen deposition or ecosystem recovery from acidification drive increased dissolved organic carbon loss from upland soil? A review of evidence from field nitrogen addition experiments. *Biogeochemistry Vol. 91, pp. 13-35*

Evans, C.D., Jones, T.G., Burden, A., Ostle, N., Zieliński, P., Cooper, M.D.A., Peacock, M., Clark, J.M., Oulehle, F., Cooper, D., Freeman, C., 2012. Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology Vol. 18, pp 3317-3331*

Evans, C.., Monteith, D.., Cooper, D.., 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental pollution Vol. 137, pp.55-71*

Fenner, N., Freeman, C., 2011. Drought-induced carbon loss in peat lands. *Nature Geoscience Vol. 4(12), pp. 895-900*

Findlay, S.E.G., 2005. Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? *Frontiers in Ecology and the Environment Vol. 3, pp 133-137*

Freeman, C., Evans, C.D., Monteith, D.T., Reynolds, B., Fenner, N., 2001. Export of organic carbon from peat soils. *Nature Vol. 412, pp. 785-785*

Freeman, C., Fenner, N., Ostle, N.J., Kang, H., Dowrick, D.J., Reynolds, B., M. A. Lock, Sleep, D., Huges, S., Hudson, J., 2004. Export of dissolved organic carbon from peat lands under elevated carbon dioxide levels. *Nature Vol. 430*

Futter, M.N., Valinia, S., Löfgren, S., Köhler, S.J., Fölster, J., 2014. Long-term trends in water chemistry of acid-sensitive Swedish lakes show slow recovery from historic acidification. *Ambio Vol. 43, pp. 77-90*

Fölster, J., Johnson, R.K., Futter, M.N., 2014. The Swedish monitoring of surface waters: 50 years of adaptive monitoring. *Ambio Vol. 43, pp. 3-18*

Giardina, C.P., Ryan, M.G., 2000. Evidence that decomposition rates of organic carbon in mineral soil do not vary with temperature. *Nature Vol. 404, pp. 858-861*

Gorham, E., 1991. Northern peatlands: Role in the carbon cycle and probable responses to climatic warming. *Ecological applications Vol. 1(2), pp. 182-195*

Heath, R.H., Kahl, H.S., Norton, S.A., Fernandez, I.J., 1992. Episodic Stream Acidification Caused by Atmospheric Deposition of Sea Salts at Acadia National Park, Maine, United States. *Water Resources Research Vol. 28, pp. 1081-1088*

Heikkinen, K., 1994. Organic matter, iron and nutrient transport and nature of dissolved organic matter in the drainage basin of a boreal humic river in northern Finland. *Science of the total environment Vol. 152, pp 81-89*

Hessen, D.O., Andersen, T., Larsen, S., Skjelkvåle, B.L., Wit, H.A. de, 2009. Nitrogen deposition, catchment productivity, and climate as determinants of lake stoichiometry. *Limnol. Oceanogr. Vol. 54(6, part 2). pp 2520-2528*

Hindar, A., Tørteth, K., Henriksen, A., Orsolini, Y., 2004. The Significance of the North Atlantic Oscillation (NAO) for Sea-Salt Episodes and Acidification-Related Effects in Norwegian Rivers. *Environmental Science and Technology Vol. 38, pp 26-33*

Hongve, D., 1999. Production of dissolved organic carbon in forested catchments. *Journal of Hydrology Vol. 224, pp. 91-99*

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

Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry Vol. 25, pp. 147-165*

Hruška, J., Krám, P., McDowell, W.H., Oulehle, F., 2009. Increased Dissolved Organic Carbon (DOC) in Central European Streams is driven by reductions in Ionic Strength Rather than Climate Change or decreasing Acidity. *Environmental Science and Technology Vol. 43, pp. 4320-4326*

Hudson, J.J., Dillon, P.J., Somers, K.M., 2003. Long term patterns in dissolved organic carbon in boreal lakes: the role of incident radiation, precipitation, air temperature, southern oscillation and acid deposition. *Hydrology and Earth Sciences Vol. 7(3), pp. 390-398)*

Hu, Q., Huser, B.J., 2014. Anthropogenic oligotrophication via liming: Long-term phosphorus trends in acidified, limed, and neutral reference lakes in Sweden. *Ambio Vol. 43, pp. 104-112*

IPCC, 2014. *Climate Change 2014 Synthesis report, Summary for Policymakers*.

Jenkinson, D.., Adams, D.., Wild, A., 1991. Model estimates of CO2 emissions from soil in response to global warming. *Nature Vol. 351, pp. 304-306*

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Science Vol. 165.4, pp. 227-304*

Karlik, B., 1995. Liming effect on dissolved organic matter leaching. *Water, Air, and Soil Pollution Vol. 85, 949-954*

Kellerman, A.M., Dittmar, T., Kothawala, D.N., Tranvik, L.J., 2014. Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. *Nature Communications 5*

Kirschbaum, M.U.F., 1995. The temperature dependence of soil organic matter decomposition and the effect of global warming on soil organic C storage. *Soil Biology and Biochemistry Vol. 27.6, pp 753-760*

Klaminder, J., Bindler, R., Laudon, H., Bishop, K., Emteryd, O., Renberg, I., 2006. Flux Rates of Atmospheric Lead Pollution within Soils of a Small Catchment in Northern Sweden and Their Implications for Future Stream Water Quality. *Environ. Sci. Technol. Vol. 40, pp. 4639–4645*

Larsen, S., Andersen, T., Hessen, D.O., 2010. Climate change predicted to cause severe increase of organic carbon in lakes. *Global Change Biology Vol. 17, pp 1186-1192*

Laudon, H., Bishop, K.H., 2001. The rapid and extensive recovery from episodic acidification in northern Sweden due to declines in SO2-4 deposition. *Geophysical Research Letters Vol. 29*

Laudon, H., Köhler, S., Buffam, I., 2003. Seasonal TOC export from seven boreal catchments in northern Sweden. *Aquat. Sci. Vol. 66, pp 223-230*

Ledesma, J.L.., Köhler, S.J., Futter, M.N., 2012. Long-term dynamics of dissolved organic carbon: Implications for drinking water supply. *Science of the Total Environment Vol. 432, pp. 1-11*

Leenheer, J.A., Croué, J.-P., 2003. Characterizing Dissolved Aquatic Organic Matter. *Environmental Science and Technology Vol. 37, pp 18-26*

Lepistö, A., Futter, M.N., Kortelainen, P., 2014. Almost 50 years of monitoring shows that climate, not forestry, controls long-term organic carbon fluxes in a large boreal watershed. *Global Change Biology Vol. 20.4, pp. 1225-1237*

Lucas, R.W., Sponseller, R.A., Laudon, H., 2013. Controls Over Base Cation Concentrations in Stream and River Waters: A Long-Term Analysis on the Role of Deposition and Climate. *Ecosystems Vol. 16, pp. 707-721*

Matson, P., Lohse, K.A., Hall, S.J., 2002. The Globalization of Nitrogen Deposition: Consequences for Terrestrial Ecosystems. *Ambio Vol. 31, pp- 113-119*

Meyer-Jabob, C., Tolu, J., Bigler, C., Yang, H., Bindler, R., 2015. Early land use and centennial scale changes in lake-water organic carbon prior to contemporary monitoring. *Proceedings of the National Academy of Sciences, 201501505*

Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry - an overview of indicators of organic matter sources and diagenesis in lake sediments. *Ecological applications Vol. 1(2), pp. 182-195*

Miljöstatistik, 2015a. Mann-Kendall test [WWW Document]. URL http://www.miljostatistik.se/mannkendall.html (accessed 4.21.15).

Miljöstatistik, 2015b. Linjär regression [WWW Document]. URL http://www.miljostatistik.se/lregression.html (accessed 4.22.15).

Miljöstatistik, 2015c. Principalkomponentanalys [WWW Document]. URL http://www.miljostatistik.se/PCA.html (accessed 4.17.15).

Miljöstatistik, 2015d. PLS [WWW Document]. URL http://www.miljostatistik.se/PLS.html (accessed 4.21.15).

Monteith, D.T., Stoddard, J.L., Evans, C.D., Wit, H.A. de, Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopácek, J., Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature Vol. 450*

Monteith, D.T., Henrys, P.A., Evans, C.D., Malcolm, I., Shilland, E.M., Pereira, M.G., 2015. Spatial controls on dissolved organic carbon in upland waters inferred from a simple statistical model. Biogeochemistry *Vol. 123, pp 363–377.*

Moser, R.N., 1992. A comparison of methods for the determination of the dating-nuclides 210 Pb and 226 Ra. *Journal of radioanalytical and nuclear chemistry Vol. 171, pp. 283-292*

Multiple Regression Analysis, 2015. Multiple Regression Analysis: Use Adjusted R-Squared and Predicted R-Squared to Include the Correct Number of Variables [WWW Document]. URL http://blog.minitab.com/blog/adventures-in-statistics/multiple-regession-analysis-use-adjusted-r-squared-and-predicted-r-squared-to-include-the-correct-number-of-variables (accessed 4.22.15).

Multivariate Statistics [WWW Document], 2015. URL http://www.multivariatestatistics.org/ (accessed 4.17.15).

Mylona, S., 1996. Sulphur dioxide emissions in Europe 1880-1991 and their effect on sulphur concentrations and depositions. *Tellus B Vol. 48, pp 662-689*

Mylona, S., 1993. EMEP Co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe. EMEP data report

O'Brien, R.M., 2007. A Caution Regarding Rules of Thumb for Variance Inflation Factors. *Quality and Quantity Vol. 41. pp. 673-690*

Pärn, J., Mander, Ü., 2012. Increased organic carbon concentrations in Estonian rivers in the period 1992-2007 as affected by deepening droughts. *Biogeochemistry Vol. 108, pp. 351-358*

Paul, K.I., Polglase, P.J., Nyakuengama, J.G., Khanna, P.K., 2001. Change in soil carbon following afforestation. *Forest ecology and management, Vol. 168, pp. 241-257*

Pilleyre, T., Sanzelle, S., Miallier, D., Faïn, J., Courtine, F., 2006. Theoretical and experimental estimation of self-attenuation corrections in determination of 210Pb by γ-spectroscopy with well Ge detector. *Radiation measurements Vol. 41, pp. 323-329*

Qualls, R.G., Haines, B.L., Swank, W.T., Tyler, S.W., 2000. Soluble Organic and Inorganic Nutrient Fluxes in Clear-cut and Mature Deciduous Forests. *Soil Science Society of America Vol. 64, pp. 1068-1077*

Ravichandran, M., 2004. Interactions between mercury and dissolved organic matter—a review. *Chemosphere Vol. 55,pp. 319–331.*

Renberg, I., Bigler, C., Bindler, R., Norberg, M., Rydberg, J., Segerström, U., 2009. Environmental history: A piece in the puzzle for establishing plans environmental management. *Journal of Environmental management Vol. 90, pp. 2794-2800*

Renberg, I., Bindler, R., Brännvall, M.-L., 2001. Using the historical atmospheric lead-deposition record as a chronological marker in sediment deposits in Europe. *The Holocene Vol. 11.5, pp. 511-516*

Rosén, P., 2005. Total organic carbon (TOC) of lake water during the Holocene inferred from lake sediments and near-infrared spectroscopy (NIRS) in eight lakes from northern Sweden. *Biogeochemistry Vol. 76, pp 503-516*

Rosén, P., Bindler, R., Korsman, T., Bishop, K., 2011. The complementary power of pH and lake-water organic carbon reconstructions for discerning the influences on surface waters across decadal to millennial time scales. *Biogeosciences Vol. 8, pp 2717-2727*

Schindler, D.W., Curtis, P.J., Bayley, S., Parker, B.R., Beaty, K.G., Stainton, M.P., 1997. Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. *Biogeochemistry Vol. 36, pp. 9-28*

SLU, 2015. Partial Mann-Kendall tests - SLU - Sveriges lantbruksuniversitet [WWW Document]. URL http://www.slu.se/sv/institutioner/ekonomi/personal/von-bromssen-claudia/partial-mann-kendall-tests/ (accessed 6.10.15)

SMHI, 2015a. HYPE | SMHI [WWW Document]. URL http://www.smhi.se/en/research/research-departments/hydrology/hype-1.7994 (accessed 4.23.15).

SMHI, 2015b. Klimatindikator - nederbörd | SMHI [WWW Document]. URL http://www.smhi.se/klimatdata/meteorologi/nederbord/klimatindikator-nederbord-1.2887 (accessed 5.18.15).

Steinberg, C., 2003. *Ecology of Humic Substances in Freshwaters. Determinants from Geochemistry to Ecological Niches*. Springer Science & Business Media

Stenberg, B., Rossel, R.A.V., Mouazen, A.M., Wetterlind, J., 2010. Chapter 5, Visible and near infrared spectroscopy in soil science. *Advances in Agronomy, Academic Press. pp. 163-215*

Sundqvist, G., Letell, M., Lidskog, R., 2002. Science and policy in air pollution abatement strategies. *Environmental Science & Policy Vol. 5, pp 147-156*

Sven Erick Alm, Tom Britton, 2008. *Stokastik - Sannolikhetsteori och statistikteori med tillämpningar*. Liber

Tiessen, H., Stewart, J.W.B., Bettany, J.R., 1982. Cultivation Effects on the Amounts and Concentration of Carbon, Nitrogen and Phosphorus in Grassland Soils. *Agronomy Journal Vol. 5, pp. 831-835*

Tipping, E., Hurley, M.A., 1988. A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances. *Journal of Soil Science Vol. 39, pp 505-519*

Tipping, E., Rigg, E., Harrison, A.F., Taylor, K., Benham, D., Poskitt, J., Rowland, A.P., Bol, R., Harkness, D.D., 1999. Climatic influences on the leaching of dissolved organic matter from upland UK Moorland soils, investigated by a field manipulation experiment. *Environment International Vol. 25, pp. 83-95*

Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P., Finlay, K., Fortino, K., Knoll, L.B., Kortelainen, P.L., Kutser, T., Larsen, S., Laurion, I., Leech, D.M., McCallister, S.L., McKnight, D.M., Melack, J.M., Overholt, E., Porter, J.A., Prairie, Y., Renwich, W.H., Roland, F., Sherman, B.S., Schindler, D.W., Wachenfeldt, S. von, Tremblay, A., Vanni, M.J., Verschoor, A.M., Wachenfeldt, E. von, Weyhenmeyer, G.A., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnol. Oceanogr Vol. 54(6, part 2), pp. 2298-2314*

Tranvik, L.J., Jansson, M., 2002. Climate change (Communication arising): Terrestrial export of organic carbon. *Nature Vol. 415, pp. 861-862*

Turner, B.., Clark, W.C., Kates, R.W., Richards, J.F., Mathews, J.T., Meyer, W.B., 1990. *The Earth as Transformed by Human Action - Global and Regional Changes in the Biosphere over the past 300 years. CUP Archive*

Umetrics MVA FAQ, 2015. SIMCA-P and Multivariate Analysis, Frequently Asked Questions.

US EPA, 2015a. Ionic strength introduction | CADDIS: Sources, Stressors & Responses | US EPA [WWW Document]. URL http://www.epa.gov/caddis/ssr_ion_int.html (accessed 1.29.15).

US EPA, 2015b. Sediments | Sediments | US EPA [WWW Document]. URL http://water.epa.gov/polwaste/sediments/ (accessed 5.22.15).

US EPA, 2003. Response of surface Water Chemistry to the Clean Air Act Amendments of 1990. *EPA 620/R-03/001*

Valinia, S., Futter, M.N., Cosby, B.J., Rosén, P., Fölster, J., 2014. Simple Models to Estimate Historical and Recent Changes of Total Organic Carbon Concentrations in Lakes. *Environmental Science & Technology Vol.49, pp. 386-394*

West, T.O., Post, W.M., 2002. Soil Organic Carbon Sequestration Rates by Tillage and Crop Rotation: A Global Data Analysis. *Soil Science Society of America Vol. 66, pp. 1930-1946*

Weyhenmeyer, G.A., Karlsson, J., 2009. Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures. *Limnol. Oceanogr. Vol. 54(6, part 2), pp. 2513-2519*

Wilander, A., 2008. Förändringar i sulfatbelastning och sulfatkoncentrationer i IKEU-sjöar och vattendrag - ett underlag för anpassad kalkning. Institutionen för miljöövervakning, SLU.

Wilkinson, G.M., Pace, M.L., Cole, J.J., 2013. Terrestrial dominance of organic matter in north temperate lakes. *Global Biogeochemical Cycles Vol. 27, pp 43-51*

Worall, F., Burt, T.P., 2006. Flux of dissolved organic carbon from U.K rivers.

Yallop, A.R., Clutterbuck, B., 2009. Land management as a factor controlling dissolved organic carbon release from upland peat soils 1: Spatial variation in DOC productivity. *Science of the Total Environment Vol. 407, pp. 3803-3813*

Zsolnay, A., Görlitz, H., 1994. Water extractable organic matter in arable soils: effects of drought and long-term fertilization. *Soil Biology and Biochemistry Vol. 26, pp. 1257-1261*

9 Appendix A

Table A1. P-values for trend tests of precipitation and temperature. Significant p-values (≤0.05) are marked with *. Sign indicates positive or negative trend.

Lake	p-value precipitation (1901-2013)	p-value Temperature (1901-2013)
Älgsjön	+ 0.07	+ 0.0006*
Bösjön	+ 0.05*	+ 0.001*
Bysjön	+ 0.02*	+ 0.0008*
Ejgdesjön	+ 0.03*	+ 0.0003*
Fiolen	+ 0.002*	+ 0.02*
Gårdsjön	+ 0.003*	+ 0.006*
Gyslättasjön	+ 0.0002*	+ 0.03*
Lien	+ 0.06	+ 0.001*
Mäsen	+ 0.02*	+ 0.001*
Örvattnet	+ 0.01*	+ 0.0008*
Övre Skärsjön	+ 0.06	+ 0.001*
Skärgölen	+ 0.1	+ 0.0009*
Stengårdshultasjön	+ 0.00004*	+ 0.06
Stora Härsjön	+ 0.0006*	+ 0.005*
Tryssjön	+ 0.02*	+ 0.001*
Ulvsjön	+ 0.1	+ 0.0004*
V. Skälsjön	+ 0.06	+ 0.001*

Table A2. P-values for trend tests of precipitation and temperature. Significant p-values (≤0.05) are marked with *. Sign indicates positive or negative trend.

Lake	p-value precipitation (1901-1979)	p-value temperature (1901-1979)
Älgsjön	+ 0.4	+ 0.2
Bösjön	+ 0.4	+ 0.09
Bysjön	+ 0.5	+ 0.09
Ejgdesjön	+ 0.7	+ 0.07
Fiolen	+ 0.6	+ 0.08
Gårdsjön	+ 0.9	+ 0.2
Gyslättasjön	+ 0.3	+ 0.06
Lien	+ 0.2	+ 0.1
Mäsen	+ 0.1	+ 0.2
Örvattnet	+ 0.4	+ 0.08
Övre Skärsjön	+ 0.2	+ 0.1
Skärgölen	+ 0.7	+ 0.1
Stengårdshultasjön	+ 0.1	+ 0.04*
Stora Härsjön	+ 0.2	+ 0.2
Tryssjön	+ 0.1	+ 0.1
Ulvsjön	+ 0.8	+ 0.07
V. Skälsjön	+ 0.2	+ 0.1

Table A3. P-values for trend tests of precipitation, temperature and runoff. Significant p-values (≤0.05) are marked with *. Sign indicates positive or negative trend.

Lake	p-value precipitation (1980-2013)	p-value temperature (1980-2013)	p-value runoff (1999-2013)
Älgsjön	+ 0.04*	+ 0.03*	+ 0.9
Bösjön	+ 0.1	+ 0.08	+ 0.9
Bysjön	+ 0.05*	+ 0.06	- 0.1
Ejgdesjön	+ 0.1	+ 0.02*	- 0.2
Fiolen	+ 0.002*	+ 0.03*	- 0.4
Gyslättasjön	+ 0.003*	+ 0.03*	- 0.5
Lien	+ 0.06	+ 0.03*	- 0.5
Mäsen	+ 0.2	+ 0.05*	- 0.3
Örvattnet	+ 0.04*	+ 0.1	- 0.7
Övre Skärsjön	+ 0.06	+ 0.03*	- 0.5
Skärgölen	+ 0.05*	+ 0.03*	+ 1
Stengårdshultasjön	+ 0.002*	+ 0.03*	- 0.5
Stora Härsjön	+ 0.07	+ 0.08	+ 0.7
Tryssjön	+ 0.1	+ 0.05*	+ 0.5
Ulvsjön	+ 0.04*	+ 0.07	- 0.6
V. Skälsjön	+ 0.06	+ 0.03*	- 0.8

Table A4. P-values for Theil-slopes of water chemical parameters. Significant p-values (≤0.05) are marked with *

Lake	Alk	ANC	BC	Cl^-	pH	SO_4^{2-}	TOC	Tot-N	Tot-P
Älgsjön	0.03*	0.6	<0.001*	0.001*	1	<0.001*	0.001*	0.1	0.6
Bösjön	0.2	0.8	0.1	0.007*	0.4	<0.001*	<0.001*	0.7	<0.001*
Bysjön	<0.001*	<0.001*	<0.001*	0.004*	0.7	<0.001*	<0.001*	0.6	0.1
Ejgdesjön	<0.001*	<0.001*	0.6	0.04*	0.001*	<0.001*	<0.001*	0.4	<0.001*
Fiolen	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	0.7	0.2
Gyslättasjön	0.1	0.2	<0.001*	<0.001*	0.3	<0.001*	0.003*	0.05*	0.9
Lien	0.01*	0.4	<0.001*	0.01*	0.3	<0.001*	<0.001*	0.4	0.04*
Mäsen	<0.001*	<0.001*	<0.001*	0.5	0.04*	<0.001*	<0.001*	0.8	0.9
Örvattnet	0.009*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	0.4	0.2
Övre Skärsjön	<0.001*	<0.001*	<0.001*	0.3	<0.001*	<0.001*	<0.001*	0.03*	0.03*
Skärgölen	0.08	0.005*	<0.001*	0.02*	0.2	<0.001*	0.004*	0.4	0.002*
Stengårdshultasjön	0.2	0.3	0.03*	<0.001*	0.5	<0.001*	0.001*	0.3	0.01*
Stora Härsjön	0.005*	0.04*	0.003*	0.02*	0.04*	<0.001*	<0.001*	0.07	0.02*
Tryssjön	0.4	0.04*	0.9	0.2	0.2	<0.001*	0.04*	0.06	0.02*
Ulvsjön	<0.001*	<0.001*	<0.001*	0.2	0.008*	<0.001*	<0.001*	0.7	0.04*
V. Skälsjön	0.03*	0.02*	0.6	0.1	0.3	<0.001*	0.02*	0.3	<0.001*

Table A5. P-values for trend tests of EMEP sulfate deposition. Significant p-values (≤0.05) are marked with *. Sign indicates positive or negative trend.

Site	p-value 1980-2013	p-value (1880-1975)
Älgsjön	-0.005*	+0.000002*
Bösjön	-0.005*	+0.000002*
Bysjön	-0.005*	+0.000002*
Ejgdesjön	-0.005*	+0.000002*
Fiolen	-0.005*	+0.000002*
Gårdsjön	-0.005*	+0.000001*
Gyslättasjön	-0.005*	+0.000002*
Lien	-0.005*	+0.000001*
Mäsen	-0.005*	+0.000001*
Örvattnet	-0.005*	+0.000001*
Övre skärsjön	-0.005*	+0.000001*
Skärgölen	-0.005*	+0.000002*
Sten gårdshultasjön	-0.005*	+0.000002*
Stora Härsjön	-0.005*	+0.000002*
Tryssjön	-0.005*	+0.000001*
Ulvsjön	-0.005*	+0.000002*
V. Skälsjön	-0.005*	+0.000001*

Table A6. P-values for trend tests of VNIRS-TOC. Significant p-values (≤0.05) are marked with *. Sign indicates positive or negative trend.

Site	Time period	p-value
Stora Härsjön	1110-1979	-0.00005*
Ulvsjön	1498-1975	-0.000001*
Gyslättasjön	1566-1979	-0.000002*
Örvattnet	1813-1982	-0.05*
Stengårdshultasjön	1833-1978	-0.0007*
Bysjön	1849-1982	-0.00002*
Ejgdesjön	1849-1971	-0.0003*
Bösjön	1859-1978	+0.03*
Lien	1227-1977	-0.02*