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RELATION BETWEEN LAND USE CHANGE AND LONG-TERM TRENDS OF ORGANIC CARBON IN LAKE WATER AND ITS IMPORTANCE FOR ACIDIFICATION ASSESSMENT

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Preface

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Table of Content

Abstract

This study examines the changes of total organic carbon (TOC) concentrations in 20 Swedish lakes throughout Sweden using pre-industrial (1860) TOC_0 inferred from near-infrared spectrometry (TOC_{NIRS}) of lake sediments to determine if land use change over time could be a plausible explanation for changes in lake water TOC. The study also focuses on the importance of using inferred pre-industrial data of lake water pH and TOC for acidification assessment, in particular ANC_0. Most lakes in this study show a long-term decreasing trend of TOC from 1860 up to -0.45 mg/l/yr^{-1} to an identified breaking point where the TOC turns from decreasing to increasing. Fifteen of the lakes have a breaking point in the mid to late 20th century (1950-1980) while five lakes do not display a clear breaking point. The magnitude of the increasing trend of TOC after the breaking point is up to 0.16 mg/l/yr^{-1}. Changes in land use were studied by comparing historical maps with present databases of land use. Land use changes in the catchment area show substantial differences in forest cultivation; for instance the coniferous forest has increased by 26% on average. This increase is due to removal of native forest (deciduous forest) and removal of wetlands. Two major conclusions can be drawn from the effects of land use change on TOC levels: (I) No direct correlation between land use change and long-term trends of TOC could be identified in this study. Previous studies have identified the effects of land use change on the carbon storage in the catchment area that corresponds well with the findings of this study. (II) the character of the forest land plays an important role when discussing the effects of land use change for long term TOC trends. The change from open-ended forests with large trees to intense managed forest is considered as an important driving force for TOC.

To determine reference conditions there is a need to make good estimations of ANC_0 for acidification assessment in Swedish lakes. This study examines the precision of MAGIC model ANC_0 calculations ($ANC_{0\text{-MAGIC}}$) against ANC_0 calculated with TOC_{NIRS}, diatom-pH and calculated pCO_2 ($ANC_{0,\ \text{diatom-NIRS}}$). $ANC_{0,\ \text{diatom-NIRS}}$ shows a mean difference of (-31µeq/l) when comparing it with $ANC_{0\text{-MAGIC}}$. In comparison, when using contemporary TOC (TOC_t) mean lake value 1990-2005 ($ANC_{0,\text{diatom-TOC}}$) the results show a mean difference of (-0.45 µeq/l) in comparison with $ANC_{0\text{-MAGIC}}$. A better fit is generated with TOC_{NIRS} then TOC_t. This could be an indication that $ANC_{0\text{-MAGIC}}$ overestimates the acidification of Swedish lakes. The European Union's "Water

Framework Directive", which Sweden has implemented, requires that all surface waters within the Union's authority have achieved good ecological status by 2015. According to the ecological quality standard the differences between the pre-industrial pH and contemporary pH, i.e. $\Delta pH=pH_0-pH_t$, should not be more than 0.4 units. This study shows that the long-term trends have to be accounted for when calculating reference conditions and ecological status for acidification.

Sammanfattning

Denna studie utvärderar den historiska förändringen av den totala halten organiskt kol (TOC) i 20 svenska sjöar. Historiska data återskapades genom att extrahera förindustriella (1860) TOC_0-värden med metoden ”near-infrared spectrometry” (TOC_{NIRS}). Undersökningen syftar till att avgöra om förändring i markanvändning kan korrelera med fluktuationen av TOC i svenska sjöar. Studien fokuserar även på vikten av att använda modellerade förindustriella värden av pH och TOC för försurningsbedömning i svenska sjöar, i synnerhet ANC_0. De flesta sjöar i denna studie visar på en minskning av TOC från 1860, upp till -0.45 mg/l/år^{-1}, till en identifierad brytpunkt där TOC-trenden vänder från minskande till ökande. Femton av sjöarna har en brytpunkt mellan mitten och senare delen av 1900-talet (1950-1980) medan fem sjöar inte visar en tydlig brytpunkt. Styrkan på den nedåtgående trenden före brytpunkten och den ökande trenden efter brytpunkten är likartade med en medeldifferens på -0,08 mg/l/år^{-1}. Förändringar i markanvändning analyserades genom att jämföra historiska kartor med nutida kartdatabaser. Analysen visar att den största förändringen i markanvändning har skett för skogstyper; barrskogen i avrinningsområden har ökat med ett medelvärde på 26 % på bekostnad av ursprungskog (lövskog) samt avlägsnande av våtmarker. Två betydande slutsatser kan dras utifrån denna studie: (I) Ingen direkt korrelation mellan förändringen i markanvändning och långtidstrender av TOC har identifierats. Tidigare studier har påvisat effekterna av ändrad mark- eller vegetationstyp på kolförrådet i marken inom avrinningsområdet som stämmer väl överens med vad som visas i denna studie. (II) Skogens karaktär spelar en viktig roll när man diskuterar effekterna av förändrad marktyp på långtidstrender av TOC. Förändringen från glesskog med stora träd och betesområden till intensivt brukad skog antas vara en viktig drivkraft för de förändringar i TOC som har identifierats.

För att bedöma referenstillståndet och försurningsgraden i svenska sjöar finns det behov av goda uppskattningar av ANC_0. Denna studie utvärderar precisionen av MAGIC-modellens ANC_0-beräkningar ($ANC_{0\text{-MAGIC}}$) mot ANC_0 beräknat med TOC_{NIRS}, diatom-pH och pCO_2 ($ANC_{0\text{-diatom-NIRS}}$). Medeldifferensen mellan $ANC_{0\text{-diatom-NIRS}}$ och $ANC_{0\text{-MAGIC}}$ är (-31µeq/l). Beräkning av ANC_0 ($ANC_{0\text{-diatom-TOC}}$) med nutida TOC ($TOC_t$, sjö medelvärde 1990-2005) visar på en medeldifferens på (-45 µeq/l) i jämförelse med $ANC_{0\text{-MAGIC}}$. Detta tyder på att en bättre passform genereras med TOC_{NIRS} än TOC_t vilket även kan vara en indikation på att $ANC_{0\text{-MAGIC}}$ överskat-

tar försurningen i svenska sjöar. Europeiska unionens vattenvårdsdirektiv, som Sverige har antagit, yrkar på att ytvattnet inom EUs gränser ska uppnått ”god ekologisk status” vid 2015. Enligt den miljökvalitetsnorm som antagits så skall inte differensen (ΔpH) mellan förindustriell pH (pH_0) och nutida pH (pH_t) vara mer än 0,4 pH-enheter dvs. $\Delta pH = pH_0 - pH_t > 0{,}4$. Denna studie visar att långtidstrender bör tas hänsyn till när man beräknar referenstillstånd och bedömer ekologisk status för försurning.

1. Introduction

Sweden, as a member of the European Union, has implemented the EU Water Framework Directive (WFD 2000/60/EC). The overall goal for both the Swedish environmental objectives and the member EU countries are “good ecological quality” and within this, the concept of “undisturbed aquatic ecosystems” is embedded. Using the concept of “undisturbed” or “natural condition” as a goal for water management does imply some difficulties. Many questions can be asked: (I) what is natural? (II) how can we define the appropriate target for a natural state? (III) who should determine the natural state (Bishop et al 2009)?

Good ecological quality and natural aquatic ecosystems are usually defined by a reference condition. The reference condition can be determined in a number of ways: (I) spatially based reference conditions including historical data, (II) modelling empirical or dynamical, (III) a combination of I and II and (IV) expert judgement (Andersen et al 2004). One of the greatest challenges with EU-WFD is determining the reference condition since pre-industrial measurements are usually absent. The reference condition in Swedish lakes and streams is often defined as an undisturbed state, which is usually referred back to the pre-industrial time period. There are some factors that limit the use of reference conditions: (I) identification of sites where no human disturbance has occurred, (II) pre-industrial measurements are often hard to compare with present measurements due to method uncertainties and a shift in field praxis and (III) the natural variability in rivers and lakes is hard to foresee because natural variability varies both in space and time at different scales (Fölster et al 2007; Durfour & Piégay 2009; Erlandsson et al 2008a; Bennion & Battarbee 2007).

Estimating the change from reference conditions is an important part of the national environmental quality criteria (EQC) for acidification assessment. Significant acidification is defined in EQC as an alteration from reference pH of more than 0,4 units i.e. $\Delta pH = pH_0 - pH_t > 0{,}4$ (Fölster et al 2007). Erlandsson et al (2008a) show that the natural variability of lake water pH exceeds the EQC criteria used to determine significant acidification $\Delta pH > 0.4$. In Sweden, a geochemical dynamic model (MAGIC) is often used for determining the reference condition for acidification assessment. The MAGIC model has been applied to most of the around 100 lakes within the national monitoring programs with 1997 representing present conditions (Moldan et al 2003). The year 1860 was chosen to represent pre-industrial lake water chemistry and steady state conditions are assumed for Total Organic Carbon (TOC) and Partial Pressure of Carbon Dioxide (pCO_2) from pre-industrial time until present. Erlandsson et al (2008b) show the importance of natural changes in TOC and pCO_2 for determining pH_0 as a reference condition for acidification assessment.

Lake sediments can be used as a historical archive to assess changes in the environment across decal to millennial timescales. Studies have shown that there is correlation between the visible to near infrared spectra (VNIRS) from sediment and lake water TOC concentrations (Rosén 2005; Cunningham et al 2010). This correlation can be used to infer lake water TOC beyond the instrumental records. The different sediment layers can be dated by different techniques, for example Pb-210, radiocarbon dating and spheroidal carbonaceous particles (SCP) (Wik and Renberg 1996). This type of sediment dating can be used to correlate changes in inferred TOC and known historical changes.

Different studies discuss plausible explanations for the recent increase of TOC both in a long-term and short-term trend. Cunningham et al (2010) discuss that land use change could be a plausible explanation for the decreasing trend in lake water TOC around a century ago. Rapid changes in TOC can occur when the catchment changes from birch to alpine forest due to descending tree-line or be due to change in permafrost and mire dynamics (Rosén 2005; Rosén et al 2009; Kokfelt et al 2009). These studies show that the changes in the physical landscape are important factors to take into consideration when determining the natural state in lake water chemistry. Changes in TOC over a timescale of decades have been shown to depend both on changes in stream flow and on long-term changes in sulphur deposition (Monteith et al 2007; Erlandsson et al 2008b). In this report, TOC and DOC are considered the same chemical parameter.

Changes in organic carbon concentrations have also been linked to climate related parameters, such as rainfall, temperature and carbon dioxide (Clark et al 2010). Houghton & Goodale (2003) discuss the effects of land use change for the carbon balance in different land systems, where there is a major change in the carbon sink when the cultivation in the catchment area is changed. When the land use changes, it is difficult to estimate when the effects of the carbon balance will occur in the catchment area. Houghton and Goodale claim that the soils may lose carbon for several decades after the change in the catchment area and forests can accumulate carbon centuries after cutting.

Sweden has a unique and well-documented historical map archive from pre-industrial time period until present. Swedish terrain started to be documented in the mid-1600s (Sterner et al 2010). The maps used in this project are from the years 1900 to 1915. One way of understanding the trends of TOC is to identify how the land use has changed from pre-industrial time until present.

1.1 Aim and hypothesis

The aim of this study is to analyse the importance of land use change in correlation with the inferred TOC concentrations and its impact on acidification assessment on a time scale of approximately 150 years. The hypothesis is that long-term trends in NIRS inferred TOC can be explained by changes in land use.

2. Materials and Methods

2.1 Lake selection

The lakes in this study are a subset of 20 lakes from the national monitoring program. The lakes were originally selected to represent acidification sensitive lakes but not subject to mitigating liming activities. The lakes were subject to paleolimnological studies including reconstruction of TOC by NIRS-analysis of the sediments (Fig. 1). The subset was selected to represent a range of pH and TOC as well as spatial coverage.

2.2 Historical and present land use

Two major types of historical maps exist in Sweden, "Häradsekonomiska kartor" ("HärK") and Generalstabskartor ("GenK"). These maps give an overview of the topography and what dominating terrain existed in the catchment areas. This data can be compared with present land topography and give important information of changes in the catchment area. HärK for the years 1859-1954 was the first alternative for identifying the land topography. GenK was the second alternative for determining historical land use, the maps existed between the years 1850-1910. The main differences between these two historical map archives are the resolution and coverage. HärK maps have higher resolution and more information can be gathered, GenK on the other hand has a greater land-coverage on the Swedish landscape (Sterner et al 2010). For this report, historical land use is available for 15 of the 20 lakes. Ten of the lakes are analysed with HärK and five lakes are analysed with GenK. The lakes where the historical maps are missing are located in mid/northern Sweden were the map coverage is not complete (Table 1 and Fig. 1).

Table 1. Historical and present land use, the data shows the % change of land use. In some cases the historical land use does not sum to 100%.

Name of lake	**Land use**												
	TotArea km^2	*Coniferous Hist*	*Coniferous Pres*	*Mixed Hist*	*Mixed Pres*	*Deciduous Hist*	*Deciduous Pres*	*Wetland Hist*	*Wetland pres*	*Agricult. Hist*	*Agricult. Pres*	*Water Hist*	*Water Pres*
Remmarsjön	-	-	-	-	-	-	-	-	-	-	-	-	-
Tväringen	-	-	-	-	-	-	-	-	-	-	-	-	-
Sangen	-	-	-	-	-	-	-	-	-	-	-	-	-
Hällsjön	-	-	-	-	-	-	-	-	-	-	-	-	-
Siggeforasjön	21.5	0.23	0.76	0.00	0.01	0.02	0.01	0.07	0.13	0.01	0.01	0.02	0.07
Tärnan	-	-	-	-	-	-	-	-	-	-	-	-	-
Överudsjön	15.70	0.54	0.48	0.00	0.12	0.05	0.07	0.03	0.05	0.21	0.09	0.16	0.14
Djupa Holmsjön	2.12	0.56	0.74	0.00	0.10	0.00	0.00	0.08	0.05	0.00	0.00	0.10	0.10
Älgsjön	5.04	0.16	0.78	0.00	0.05	0.23	0.00	0.09	0.06	0.05	0.00	0.07	0.06
Rotehogsstjärn	3.82	0.50	0.55	0.00	0.04	0.00	0.01	0.18	0.20	0.00	0.08	0.02	0.08
Gryten	19.1	0.55	0.65	0.00	0.05	0.08	0.02	0.17	0.15	0	0.06	0.12	0.10
Grissjön	1.62	0.65	0.81	0.00	0.04	0.06	0.00	0.13	0.02	0.01	0.00	0.13	0.12
Fjärasjön	3.15	0.30	0.67	0.03	0.08	0.07	0.08	0.04	0.04	0.00	0.01	0.12	0.12
Lilla Öresjön	4.82	0.38	0.53	0.00	0.09	0.02	0.05	0.10	0.14	0.06	0.05	0.11	0.13
Skärsjön	5.10	0.34	0.52	0.00	0.12	0.11	0.03	0.04	0.02	0.01	0.00	0.31	0.30
Harasjön	5.63	0.40	0.58	0.00	0.03	0.08	0.08	0.21	0.18	0.00	0.00	0.10	0.10
Svartesjön	0.39	0.26	0.46	0.00	0.00	0.13	0.00	0.49	0.46	0.00	0.00	0.08	0.08
Tomeshultagölen	3.91	0.65	0.82	0.00	0.03	0.01	0.00	0.22	0.13	0.00	0.00	0.02	0.02
Örsjön	0.88	0.33	0.55	0.00	0.03	0.33	0.19	0.03	0.00	0.06	0.00	0.24	0.22
Lillesjö	1.00	0.00	0.34	0.00	0.10	0.93	0.54	0.03	0.00	0.00	0.00	0.05	0.04

Lake	X-SMHI	Y-SMHI	Acidification status
Remmarsjön	708619	162132	N
Tväringen	690345	149315	N
Sangen	686849	145214	N
Hällsjön	667151	149602	N
Siggeforasjön	665175	157559	N
Tärnan	660749	161885	N
Överudssjön	659105	133982	N
Djupa Holmsjön	656263	156963	N
Älgsjön	655275	153234	N
Rotehogstjärnen	652902	125783	A
Gryten	652840	151589	N
Grissjön	651578	146163	A
Fjärasjö	638725	146677	N
Lilla Öresjön	638665	129243	A
Skärsjön	637260	128728	N
Harasjön	632231	136476	A
Svartesjön	630558	134327	A
Tomeshultagölen	629026	147562	A
Örsjön	624038	143063	A
Lillesjö	623161	142148	A

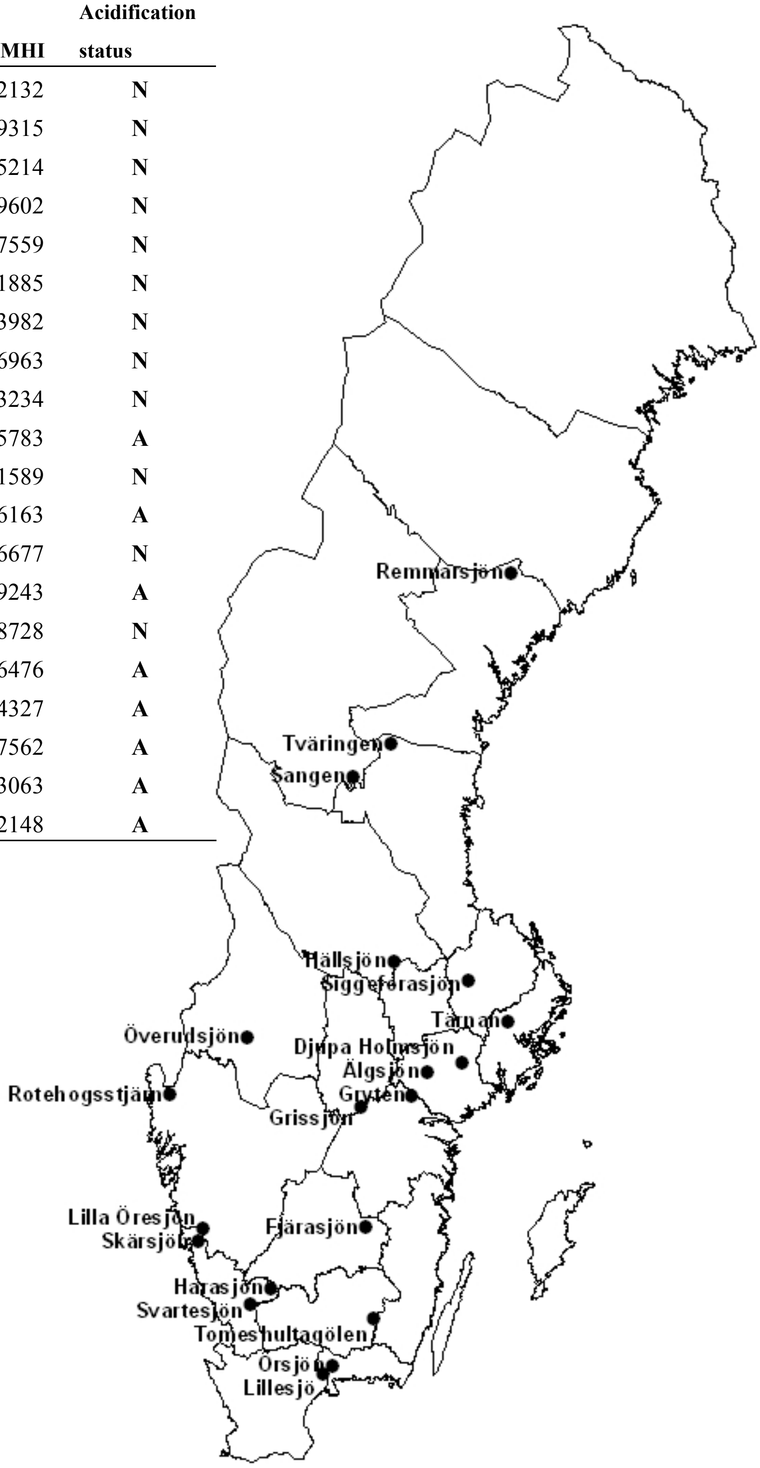


Fig 1. Overview of the lakes analysed in this report and their acidification status according to MAGIC pH (SEPA, 2007). N; non-acidified and A; acidified.

2.3 Modern Water Chemistry Data

National monitoring of reference lakes started in 1983, and TOC concentrations have been routinely measured since 1987 (SLU 2010). The lakes were sampled at least four times each year, i.e. one sample every season. When there were more than one sample during a season, only one of them has been used, and priority was then given to samples taken in the months of February, May, August and October. The parameters that have been sampled include Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, tot P, tot N, pH, Cl^{-}, SO_4, Alk (alkalinity), TOC and Al_{tot} (Table 2).

Table 2. Modern water chemistry, mean lake values for the period 1990-2005

Lake	X-SMHI	Y-SMHI	TOC mg/l	pH	Ca mekv/l	Mg mekv/l	Na mekv/l	K mekv/l	Alk./Acid mekv/l	SUM BC
Remmarsjön	708619	162132	9.5	6.2	0.09	0.04	0.06	0.01	0.06	0.2
Tväringen	690345	149315	7.6	6.6	0.13	0.05	0.06	0.01	0.12	0.25
Sangen	686849	145214	6.9	6.6	0.11	0.04	0.06	0.01	0.11	0.22
Hällsjön	667151	149602	8.0	6.1	0.11	0.05	0.07	0.01	0.04	0.24
Siggeforasjön	665175	157559	14.9	6.6	0.29	0.08	0.11	0.01	0.15	0.49
Tärnan	660749	161885	8.5	7.7	2.94	1.08	1.18	0.15	1.86	5.35
Överudssjön	659105	133982	9.6	6.7	0.19	0.14	0.15	0.03	0.18	0.51
Djupa Holmsjön	656263	156963	12.4	5.8	0.12	0.07	0.08	0.01	0.02	0.29
Älgsjön	655275	153234	17.8	6.6	0.31	0.18	0.15	0.02	0.22	0.66
Rotehogstjärnen	652902	125783	11.7	5.3	0.09	0.09	0.24	0.01	0	0.44
Gryten	652840	151589	16.6	6.6	0.39	0.12	0.16	0.02	0.16	0.69
Grissjön	651578	146163	9.9	5.4	0.12	0.06	0.11	0.01	0	0.29
Fjärasjö	638725	146677	9.2	6.8	0.27	0.15	0.18	0.01	0.14	0.61
Lilla Öresjön	638665	129243	5.3	5.0	0.09	0.09	0.3	0.02	-0.02	0.5
Skärsjön	637260	128728	1.9	4.9	0.1	0.1	0.33	0.01	-0.01	0.55
Harasjön	632231	136476	13.9	5.2	0.11	0.08	0.2	0.02	-0.01	0.41
Svartesjön	630558	134327	15.8	4.5	0.06	0.08	0.24	0.01	-0.05	0.39
Tomeshultagölen	629026	147562	18.8	5.1	0.11	0.12	0.22	0.02	-0.02	0.48
Örsjön	624038	143063	7.3	5.9	0.16	0.09	0.23	0.01	0.03	0.49
Lillesjö	623161	142148	2.2	4.7	0.12	0.09	0.25	0.01	-0.06	0.48

2.3.1 Partial pressure of carbon dioxide (pCO_2)

In the MAGIC model pCO_2 is given a steady state value of 0.63matm. In this report pCO_2 has been calculated using time series of contemporary pH, Alk and TOC. The time period chosen for calculation is with contemporary data for 1999-2009, because all lakes have similar number of measurements during this time period (see table 5). The calculated $pCO_{2(calc)}$ is a combination of ion balance (eq 1) and tri-protic model for organic acids given by Köhler et al (2000). To calculate the pCO_2 for lakes that have been strongly influenced by acidity pH (< 5.7) a regression between pCO_2 and TOC from Sobek et al (2003) was used instead $CO_{2(Sobek)}$= (107.9 * TOC (mg/l) +

233.2) x 10^{-6}. In addition a sensitivity analysis was performed where it was calculated how much 10 µeq/l affected pCO_2, if the relative change of pCO_2 was larger then 100 % or pH < 5,7 $pCO_{2(sobek)}$ was used otherwise $pCO_{2(calc)}$ was used (Table 3).

Table 3. Overview of the calculated pCO_2

Name of lake	$pCO_{2\ (calc)}$	$pCO_{2(Sobek)}$	pCO_2 (used)
Remmarsjön	0.0017	0.0013	0.0017
Tväringen	0.0015	0.0011	0.0015
Sangen	0.0012	0.0010	0.0012
Hällsjön	0.0012	0.0012	0.0012
Siggeforasjön	0.0017	0.0020	0.0017
Tärnan	0.0021	0.0013	0.0021
Överudsjön	0.0023	0.0015	0.0023
Djupa Holmsjön	0.0013	0.0017	0.0014
Älgsjön	0.0027	0.0022	0.0027
Rotehogsstjärn	0.0022	0.0016	0.0016
Gryten	0.0022	0.0022	0.0022
Grissjön	0.0011	0.0015	0.0015
Fjärasjön	0.0013	0.0013	0.0013
Lilla Öresjön	-	0.0009	0.0009
Skärsjön	0.0007	0.0004	0.0004
Harasjön	-	0.0021	0.0021
Svartesjön	-	0.0023	0.0023
Tomeshultagölen	-	0.0025	0.0025
Örsjön	0.0014	0.0011	0.0014
Lillesjö	-	0.0005	0.0005

2.3.2 Hydrogeochemical model MAGIC

MAGIC is a lumped-parameter model for estimations of long-term effects of acid depositions on water chemistry. MAGIC predicts annual average concentrations of major ions in the lake, in this case on an annual basis. In order to predict the concentrations, the MAGIC model simulates soil solutions and surface water chemistry. The required input to the MAGIC model is atmospheric deposition, uptake-release fluxes for base captions and strong acid anions, catchment characteristics, hydrology and run-off. MAGIC calculates the cation exchange using equilibrium (Gaines – Thomas) and mass balance equations. The equilibrium equation primarily considers coefficients for each base cation and Al and the mass balance primarily considers atmospheric deposition and decomposition and mineralization of organic material (Cosby & Wright 1998; Cosby et al 1985). MAGIC simulations have been done for the lakes by the Swedish environmental research centre (IVL). 1997 was used as a calibration year for the MAGIC model because that specific year had the most complete measurements of the parameters needed for MAGIC. The MAGIC simulations are supposed to simulate the pre-industrial condition that is referred to (1857). Steady state conditions are assumed for the lake water chemistry prior to that year (eq 1). Pre-industrial pH and ANC are two factors that the MAGIC model gives as output data (Moldan et al 2004 ; Cosby et al 2001). pH is calculated from ANC, TOC and pCO2 with a triprotic model for organic acids (Hruska et al 2001) In this report special focus has been put on the MAGIC calculations for pH, ANC and SO_4.

Table 4. Overview of the data used from MAGIC model.

Name of lake	MAGIC pH_0	MAGIC pH_{1990}	MAGIC pH_{2010}	MAGIC ANC_0 µeq/l	MAGIC ANC_{1990} µeq/l	MAGIC ANC_{2010} µeq/l	MAGIC $SO_{4,0}$ KgS/ha/yr	MAGIC $SO_{4\text{-}1990}$ KgS/ha/yr	MAGIC $SO_{4\text{-}2010}$ KgS/ha/yr
Remmarsjön	6.80	6.70	6.70	158.00	143.00	145.00	0	45	25
Tväringen	7.00	6.90	6.90	186.00	163.00	165.00	0	55	30
Sangen	7.00	6.90	6.90	187.00	163.00	166.00	0	38	22
Hällsjön	6.70	6.20	6.50	135.00	82.00	107.00	0	161	49
Siggeforasjön	7.30	7.10	7.20	354.00	298.00	316.00	0	175	74
Tärnan	-	-	-	-	-	-		-	-
Överudsjön	7.30	7.00	7.10	311.00	208.00	236.00	0	176	52
Djupa Holmsjön	6.60	6.20	6.40	151.00	115.00	130.00	0	132	68
Älgsjön	7.40	7.20	7.30	499.00	391.00	432.00	0	247	90
Rotehogsstjärn	4.74	4.34	4.50	21.64	-54.87	-7.88	0.06	73.75	17.82
Gryten	7.40	7.10	7.20	466.00	315.00	347.00	0	319	123
Grissjön	6.20	5.00	5.70	98.00	49.00	73.00	0	154	69
Fjärasjön	7.40	7.00	7.10	378.00	207.00	255.00	0	309	100
Lilla Öresjön	7.00	4.30	6.10	165.00	-115.00	52.00	0.2	247	59
Skärsjön	7.40	6.70	7.40	108.00	-42.00	35.00	0	2.4	0.6
Harasjön	6.40	4.60	5.30	149.00	45.00	87.00	0.1	205	56
Svartesjön	6.30	4.30	4.80	163.00	-27.00	80.00	0.1	185	46
Tomeshultagölen	6.00	4.80	5.10	174.00	108.00	126.00	0	177	69
Örsjön	6.90	5.50	6.4	149.00	47.00	92.00	0.1	272	87
Lillesjö	6.90	4.20	4.70	117.00	-186.00	-14.00	0.1	515	138

2.4 Paleolimnological reconstruction of lake water pH

Diatom community composition has been used to inferred lake water pH in Swedish reference lakes within the national monitoring group (Guhren et al 2003). The pre-industrial pH value has been estimated by using a calibration model which can translate the diatom community preserved in sediment to lake water pH (Guhrén et al 2003). The sediment samples were taken from a depth of 30 cm and the estimated age is between 100 and 400 years. The calibration model diatom inferred pH is based on weighted average (WA). The jack-knifed root mean squared error of prediction ($RMSEP_{jack}$) is ± 0.3 pH units. The pre-industrial pH has been calculated with two different calibration sets, 118 lakes in northern Sweden (Norrset) pH (N) (Korsman and Birks 1996) and 178 lakes from Sweden, Norway and Scotland (SWAP) pH (S) (Stevenson et al 1991). For this study, if both Norrset and SWAP calibrations have the same analogue, a mean between the two has been calculated. If Norrset or SWAP shows a stronger modern analogue situation than the other, the pH value with the strongest modern analogue has been chosen (Table 5).

Table 5. Paleolimnological reconstruction of lake water pH.

Name of lake	pH (S)	Analog (S)	pH (N)	Analog (N)	Used pH
Remmarsjön	6	++	6.3	+++	6.3
Tväringen	6.2	+++	6.7	+++	6.45
Sangen	6.3	+	6.7	+++	6.7
Hällsjön	5.9	+++	6.3	+++	6.1
Siggeforasjön	6.6	+++	6.9	+++	6.75
Fysingen	7.2	_	7.1	++	7.1
Överudssjön	6.7	++	6.9	+++	6.9
Djupa Holmsjön	6.4	+++	6.5	+++	6.45
Älgsjön	6.5	+++	6.6	++	6.5
Rotehogstjärnen	5.7	+++	6	+++	5.85
Gryten	6.4	+	6.7	+++	6.7
Grissjön	5.7	+++	6.1	+++	5.9
Fjärasjö	6.5	+++	6.9	+++	6.7
Lilla Öresjön	5.9	+++	6.3	+++	6.1
Skärsjön	6.8	+++	7.1	+++	6.95
Harasjön	5.7	+	6.3	+	6
Svartesjön	5.8	+++	6.1	+++	5.95
Tomeshultagölen	6.2	_	6	_	6.1
Örsjön	6.1	+	6.6	+++	6.6
Lillesjö	5.5	+++	5.9	+++	5.7

2.5 Total organic carbon inferred from Near-infrared spectrometry (NIRS-TOC)

Near-infrared spectrometry (NIRS) exploits that the organic portion of the lake sediment has a complex structure and a distinctive NIRS signature that can be summarized using multivariate statistics. The NIRS spectra of surface sediment have been shown to have a good correlation to lake water TOC (Rosén 2005). This correlation has been used to determine the historical TOC concentrations (Cunningham et al 2010). By using PLS regression the NIRS spectra of surface sediment and contemporary lake water TOC can be summarized into a few orthogonal components (Wold et al 1998). Three different calibrations sets have been used: a 100 lake calibration set from northern Sweden ($TOC_{NIRS\text{-}northern}$), 40 lake calibration set from southern Sweden ($TOC_{NIRS\text{-}southern}$) and a combined calibration set of 140 lakes across Sweden ($TOC_{NIRS\text{-}Alt}$).

All the lakes have been modelled using PLS with five and seven components ($TOC_{NIRS\text{-}5}$ and $TOC_{NIRS\text{-}7}$). $TOC_{NIRS\text{-}5}$ has been used in lakes where the TOC level is 6-14 mg/l, where the TOC level is <6 mg/l $TOC_{NIRS\text{-} northern}$ has been used and where the TOC level > 14 mg/l $TOC_{NIRS\text{-}southern}$ has been used (Table 3). To cover the range of individual lakes in this report a combination of three different NIRS-TOC calibration models has been used: $TOC_{NIRS\text{-}5}$, $TOC_{NIRS\text{-}northern}$ and $TOC_{NIRS\text{-}southern}$ have been combined and called Alternative NIRS-TOC ($TOC_{NIRS\text{-}Alt}$). $TOC_{NIRS\text{-}Alt}$ has been used for all lakes in this study (Table 6).

Table 6. Overview of calibrations set for the reconstructions of NIRS-TOC

Reconstruction	Calibration from	When used
NIRS-TOC7	140 Swedish lakes	Calculated for all lakes
NIRS-TOC5	140 Swedish lakes	TOC levels 6-14 mg/l
NIRS-TOC northern	100 Swedish lakes (northern Sweden)	TOC levels 0-6 mg/l
NIRS-TOCsouthern	40 Swedish Lakes (southern Sweden)	TOC levels >14 mg/l
NIRS-TOCAlt.	Combination of PLS 5, PLS northern and PLS southern	Used for all lakes

The sediment cores were sampled with a kajak corer and cover the topmost 22.5-30.5 cm. The samples were sliced into 0.5 cm intervals down to 15 cm and then 1 cm intervals for the bottom part of the core. The samples were freeze-dried and analysed with a Foss NIRSystem 6500 instrument. The sediment has been dated with Pb-210 using gamma spectrometry (Appleby 2001). Generally it is only possible to date sediment older than 100 years using the Pb-210 technique. Dates for sediment older than 100 years have therefore been extrapolated by using a depth age model for the top section of the cores.

Table 7. NIRS-TOC reconstructions, table shows the pre-industrial TOC levels with the different calibrations.

Name of lake	TOC_0PLS_7 mg/l	TOC_0 PLS_{Alt} mg/l
Remmarsjön	7.6	10.8
Tväringen	8.2	8.9
Sangen	6.3	6.7
Hällsjön	10.8	11.0
Siggeforasjön	9.3	14.9
Tärnan	11.5	8.3
Överudsjön	12.4	6.7
Djupa Holmsjön	10.2	10.5
Älgsjön	14.1	20.7
Rotehogsstjärn	14.3	12.5
Gryten	11.2	18.1
Grissjön	10.8	10.4
Fjärasjön	10.9	12.9
Lilla Öresjön	10.8	10.9
Skärsjön	10.1	4.0
Harasjön	11.2	22.1
Svartesjön	10.7	11.5
Tomeshultagölen	14.0	28.0
Örsjön	6.6	7.6
Lillesjö	11.5	7.0

2.6 Acid neutralizing capacity (ANC)

One of the primary results of MAGIC is the pre-industrial ANC (ANC_0). The MAGIC model calculates ANC using the difference between base cations (BC) and strong acid anions (SAA) ANC= BC-SAA (eq 1).

Where BC = $[Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}]$ and SAA = $[Cl^-] + [NO_3^-] + 2[SO_4^{2-}]$.

The calculation model used is this study is based on the ion balance where the difference of ions of weak acids and cations of weak bases are used. ANC is defined as:

(eq 2) $ANC = ([OH^-]+[HCO_3^-]+2 \times [CO_3^{2-}]) + [RCOO^-] - [H^+] - n \times [Al^{n+}])$.

In eq 2, the $[HCO_3^-]$ and $[CO_3^{2-}]$ are determined by pH and partial CO_2 pressure (pCO_2). The $[RCOO^-]$ is estimated from the organic acid model given by MAGIC, given pH and TOC concentrations. With modelled pre-industrial TOC values as well as calculated pCO_2 a different pre-industrial ANC could be calculated to complement and examine the MAGIC reliability (Erlandsson et al 2008b). In this report, calculations of ANC have been done with different TOC-levels and calculated pCO_2 (Table 8).

Table 8. Overview of calculated ANC with different TOC and paleo-pH estimates. The ANC data is presented as µeq/l.

Name of lake	MAGIC ANC_0	ANC_{PLS7} 0	$ANC_{Alt.\ TOC}$ 0	ANC_t
Remmarsjön	158	103	140	135
Tväringen	186	133	139	205
Sangen	187	151	155	164
Hällsjön	135	107	108	108
Siggeforasjön	354	233	284	270
Tärnan		524	494	511
Överudsjön	311	401	348	301
Djupa Holmsjön	151	149	152	131
Älgsjön	499	253	309	340
Rotehogsstjärn	21	121	108	84
Gryten	466	270	332	329
Grissjön	98	97	94	97
Fjärasjön	378	199	217	199
Lilla Öresjön	165	100	100	43
Skärsjön	108	152	95	10
Harasjön	149	116	199	115
Svartesjön	163	111	117	86
Tomeshultagölen	174	156	265	143
Örsjön	149	149	157	104
Lillesjö	117	83	52	14

2.7 Statistical methods

Change over time was quantified by Theils-slope and the statistical significance of the slopes was tested by Mann-Kendall approach. A level of significance ($p<0.05$) was accepted when determining long- term trends of TOC. Theils-slope analysis was performed to determine rates of change, i.e. change over time for TOC_{NIRS} and contemporary TOC (TOC_t). Linear regression was performed to determine strength and variation of NIRS-TOC calibration sets (PLS_7 and $PLS_{Alt.}$) and its correspondence with TOC_t.

3. Results

3.1 A comparison between NIRS-TOC and contemporary measured TOC

The NIRS-TOC for contemporary sediment layers was evaluated by comparison with average measured TOC for a period corresponding to the same time period as the sediment layer represented.

3.1.1 TOC_{NIRS-7} compared with TOC_t

NIRS-TOC calculated by TOC_{NIRS-7} shows quite poor correlation when comparing it with measured TOC for the same time period (mean lake value 1990-2005) with a R^2 value of 0.30. The errors were particularly substantial for high and low TOC levels (Fig. 2).

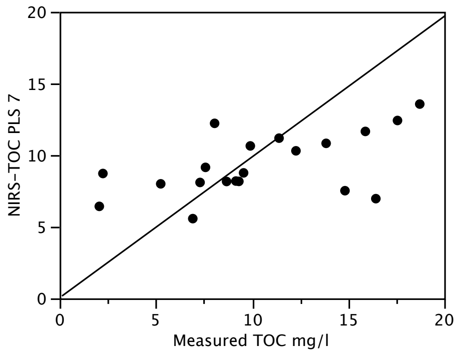


Figure 2. TOC modelled by NIRS (PLS_7) against measured TOC (TOC_t) for the time period 1990-2005. The 1:1 line is shown in the plot.

3.1.2 $TOC_{NIRS-ALT}$ compared with TOC_t

$TOC_{NIRS-Alt}$ showed a better correlation with contemporary measured TOC with a R^2 of 0.77 (Fig. 3). Unlike TOC_{NIRS-7}, the high and low TOC levels fit within the range when comparing it with TOC_t. From this point on, $TOC_{NIRS-Alt}$ is referred to as TOC_{NIRS}.

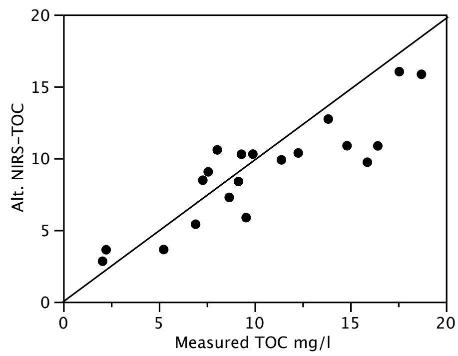
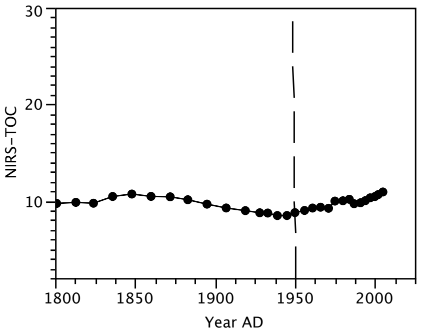


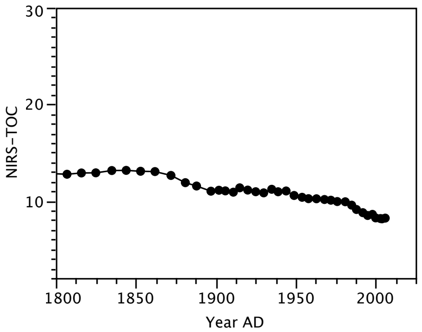
Figure 3. TOC modelled by NIRS (PLS_{Alt}) against measured TOC (TOC_t) for the time period 1990-2005. The 1:1 line is shown in the plot.

3.2 Long-term time series of TOC_{NIRS}

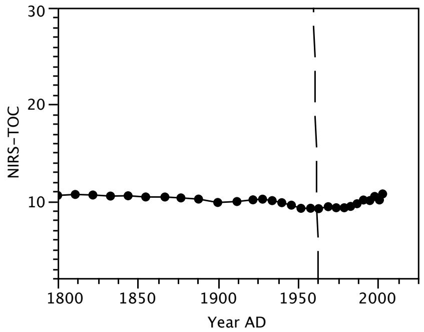
Long-term time series of TOC_{NIRS} gives an indication of how the evolution of TOC has changed through time. Some of the lakes show a substantial difference in TOC between 1800 and 2005 while some of the lakes have a very small difference within the same time period (Fig. 9). Harasjön, as an example, shows a substantial decrease in TOC of 15 mg/l between 1860 and 1950, but in recent time the values has increased c. 7 mg/l again. In contrast Harasjön and Tärnan does only show a small decrease in TOC since 1860 (Fig. 4 and table 10).



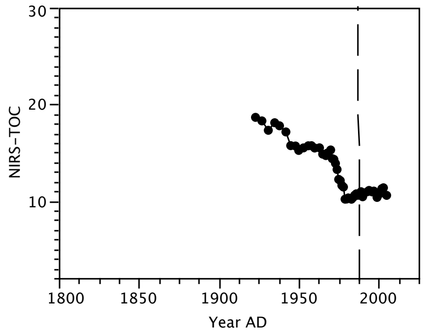
Plot for Lake=Djupa Holmsjön



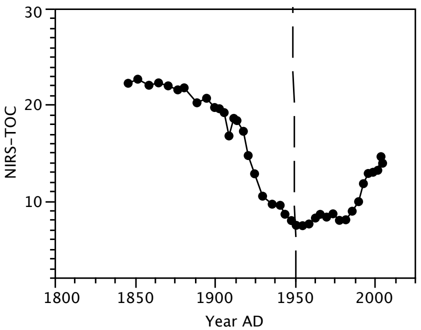
Plot for Lake=Fjärasjön



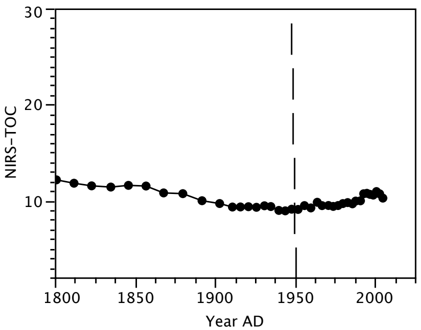
Plot for Lake=Grissjön



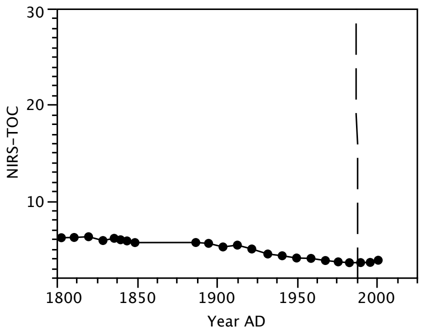
Plot for Lake=Gryten



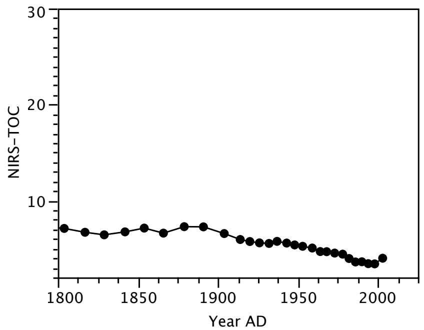
Plot for Lake=Harasjön



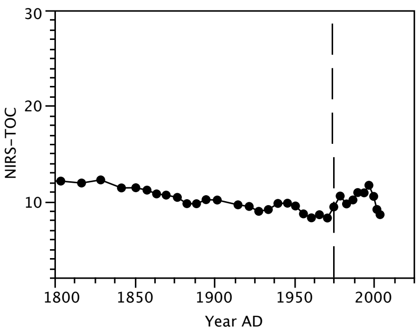
Plot for Lake=Hällsjön



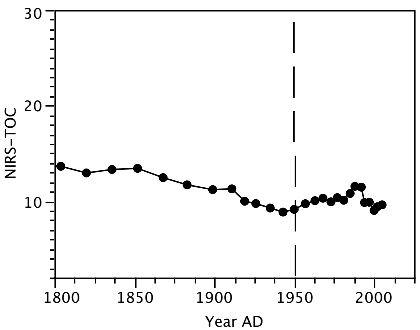
Plot for Lake=Lilla Öresjön



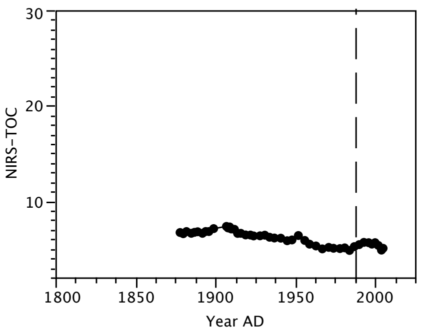
Plot for Lake=Lillesjö



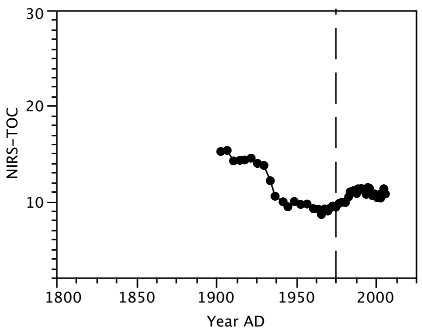
Plot for Lake=Remmarsjön



Plot for Lake=Rotehogsstjärn



Plot for Lake=Sangen



Plot for Lake=Siggeforasjön

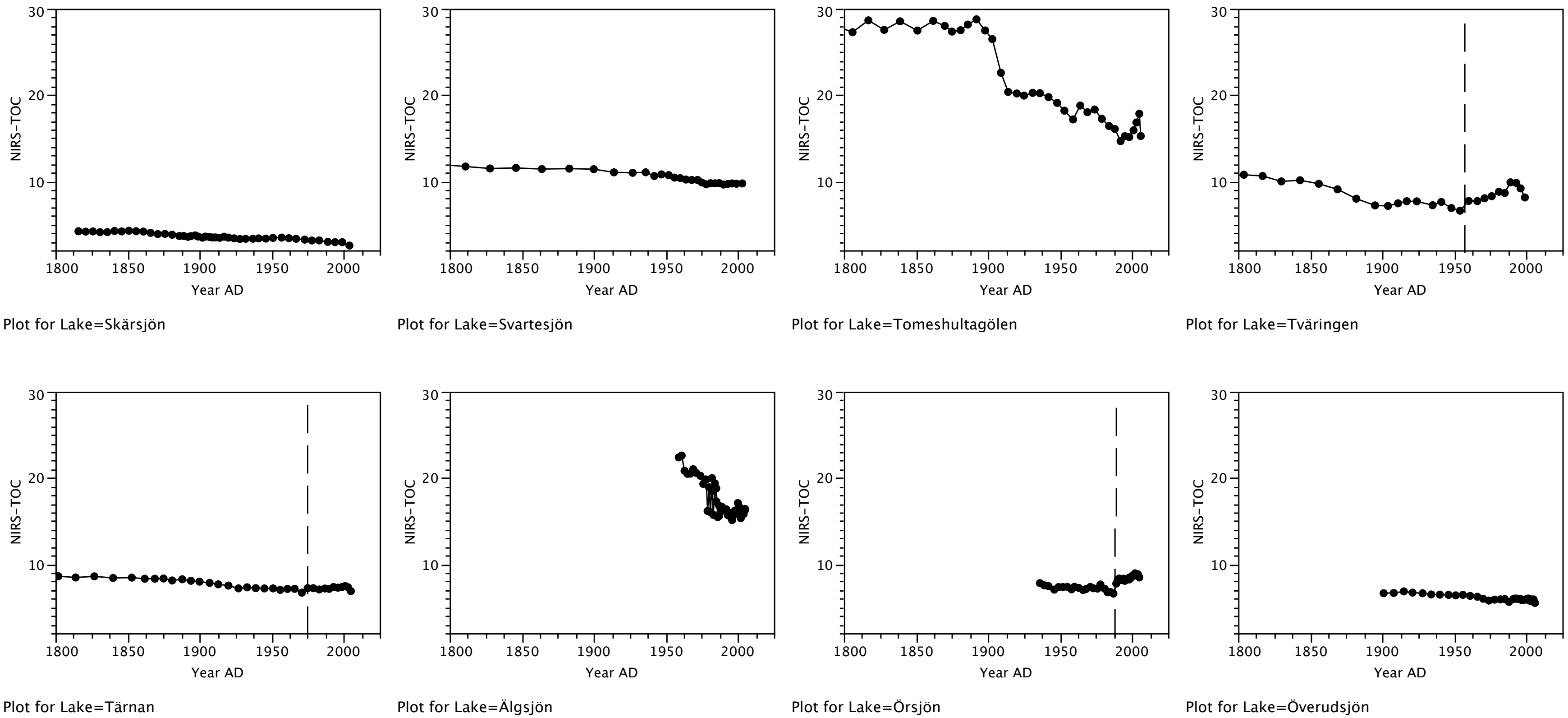


Figure 4. Lake water TOC inferred from near-infrared spectroscopy. Long-term time series of $TOC_{NIRS\text{-}Alt}$ for all lakes analysed in this report. The graphs show the time scale 1800 to 2020 AD. The dashed line in the graphs indicates the year of the breaking points. TOC is expressed in mg/l.

3.3 Trends of measured and NIRS inferred TOC

Trend analysis was done to identify both long-term trends for TOC_{NIRS} and contemporary time series of measured TOC (Table 9).

Table 9. Overview of the Theils-slope analysis on TOC

Theils-slope trend	TOC_{NIRS}	Measured TOC
Pre 1860	X	
1860- Breaking point	X	
Breaking point – 2005	X	
1990-2005	X	X

Trends were calculated for PLS_{Alt} and PLS_7 conducted before 1860 to identify trends before pre-industry. The length of the reconstructed time series varies between the different lakes. Some lakes have reconstructed TOC as far back as the 17th century, whereas others only go back to the early 20th century. Only two out of 16 lakes showed notable trends before 1860, with the same slope estimate regardless of NIRS-model (Fig. 5). The further analysis focuses on the period after 1860.

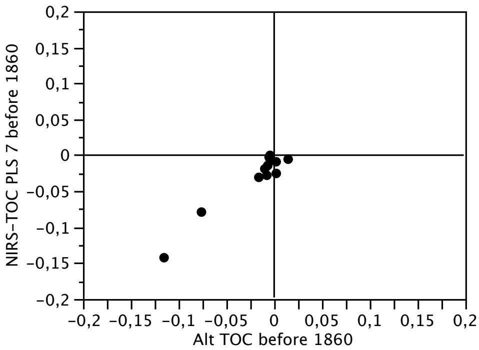


Figure 5. Theils-slope analysis on NIRS-TOC by the two models PLS_7 and PLS_{Alt} before 1860 for 8 lakes. Reference lines of 0 are shown in the figure. The trends are expressed in $mg/l/yr^{-1}$.

The long-term time series of TOC_{NIRS} show a breaking point (BP) where the TOC turns from decreasing to increasing for most of the lakes. The breaking points were identified visually (Fig. 4). The earliest breaking point is in the 1950s and the latest in 2000 (Table 9). A clear breaking point could be identified for 15 of the 20 lakes, five of the lakes that do not show a clear breaking point were set to the year 2000 (Fig 10). The lakes that had a breaking point set to the year 2000 still show significant increases of TOC in the last decade (Fig. 6).

TOC_{NIRS} showed a declining trend from 1860 to breaking points whereas the measured trend between 1990-2005 show an increase in TOC levels for 19 lakes with an R^2 value of 0.37 (Fig. 6 and table 10).

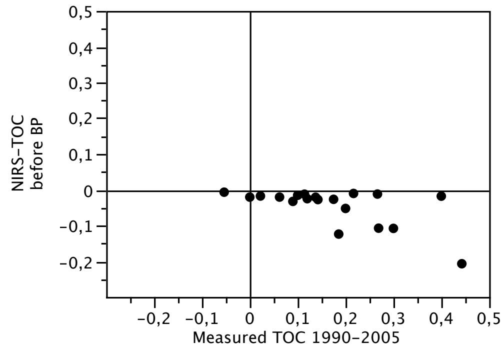


Figure 6. Theils-slope analysis on TOC_{NIRS} before breaking point and TOC_t between 1990-2005. Reference lines of 0 are in the plot. The trend is expressed in mg/l/yr^{-1}.

Table 10. Theils-slope for NIRS-TOC and measured TOC, the chosen interval for NIRS-TOC shown in the table. The trend is expressed in mg/l/yr^{-1}

Lake name	Year		Trend in NIRS-inferred TOC ($TOC_{NIRS-Alt}$) mg/l yr^{-1}				Trend in measured TOC
	Start	Breaking point	Before 1860	1860-BP	BP-2005	1990-2005	1990-2005
Remmarsjön	1860	1970	0.00	-0.02	0.03	-0.23	0.06
Tväringen	1860	1955		-0.02	0.05	-0.35	0.02
Sangen	1880	1980	-0.01	-0.02	0.001	-0.04	0
Hällsjön	1860	1950	0.01	-0.02	0.03	0.004	0.14
Siggeforasjön	1900	1970		-0.11	0.04	-0.04	0.3
Tärnan	1860	1970	0.00	-0.01	0.01	-0.002	0.1
Överudsjön	1900	2000	0.00	-0.01		-0.01	0.22
Djupa Holmsjön	1860	1950	0.00	-0.03	0.03	0.08	0.18
Rotehogsstjärn	1860	1950	-0.01	-0.05	-0.004	-0.14	0.2
Gryten	1920	1980		-0.12	0.04	0.03	0.19
Grissjön	1860	1960	-0.01	-0.01	0.04	0.05	0.27
Fjärasjön	1860	2000		-0.03		-0.04	0.14
Lilla Öresjön	1860	1980	0.00	-0.02	-0.003	0.001	0.12
Skärsjön	1860	2000		-0.01		-0.08	-0.05
Harasjön	1860	1950	-0.01	-0.20	0.14	0.22	0.44
Svartesjön	1850	2000		-0.02		0.01	0.4
Tomeshultagölen	1860	2000	-0.02	-0.11		0.14	0.27
Örsjön	1930	1988	-0.08	-0.01	0.05	0.04	0.11
Lillesjö	1860	2000		-0.03		0.01	0.09

When comparing TOC_{NIRS} before and after the breaking point, 13 of the 15 lakes change to an increasing trend while two of the lakes still have a decreasing TOC trend after the breaking points (Fig. 7). Five lakes had their breaking point in 2000 and are not counted in the analysis. The two lakes that still had a decreasing trend after BP show weak trends and no link between them could be identified (Table 10).

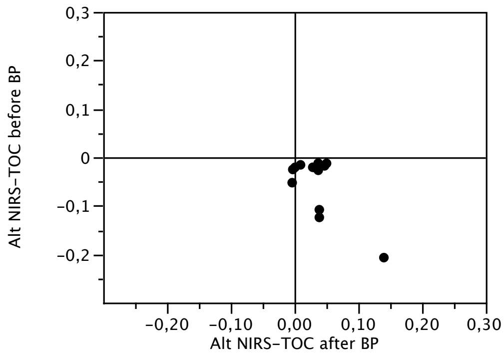


Figure 7. Theils-slope for PLS_{Alt} before and after breaking point (BP). Reference lines of 0 is shown in the plot. The trend is expressed in $mg/l/yr^{-1}$

The trends of TOC_{NIRS} and measured TOC between 1990-2005 show that six of the 19 lakes have a decreasing trend for TOC_{NIRS} 1990-2005 while 18 of 19 lakes with contemporary measured TOC show an increasing trend with an R^2 of 0.34 (Fig. 8).

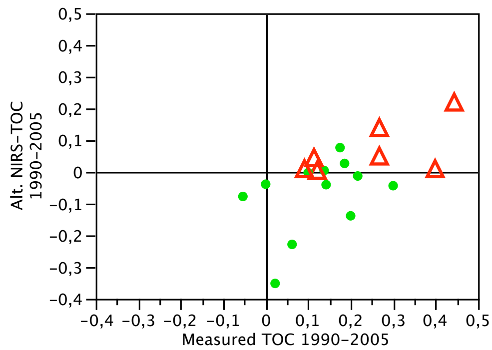


Figure 8. Theils – slope for NIRS TOC 1990-2005 plotted against measured TOC 1990-2005. The red data points show the level acidification; red triangles, acidified and green dots, non-acidified. The trend is expressed in $mg/l/yr^{-1}$

Despite the increasing trends since the break points, the overall pattern was that the lakes in this study had lower TOC today compared to 1860. This was shown both from the trends and long-term time series of the NIRS-data (Fig. 4 and 6) and by comparing measured TOC 1990-2005 with TOC_{NIRS}

1860 (Fig. 9). There has been a decrease in TOC between 1860 and 2005 in most of the lakes. Ten of the lakes show a decrease of TOC between 1860 and present while three lakes show an increase of TOC today compared with 1860 and seven lakes are around the same level as 1860. The lakes that show the greatest decrease of TOC are acidified according to MAGIC, approximately a decrease of 8-9 mg /l. The lakes that are close the 1:1 line follow the same levels of TOC 1860 until present and in most cases the lakes are not acidified (Fig. 9).

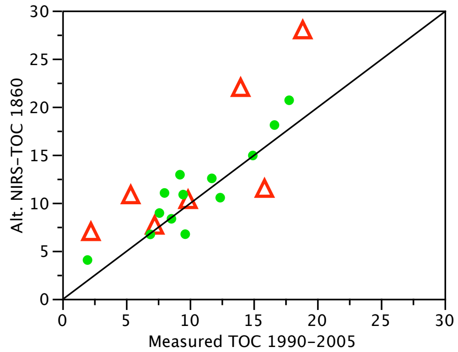


Figure 9. PLS_{Alt} 1860 (mg/l) plotted against measured TOC_t. The 1:1 line is shown. The red data points show acidified lakes while the green show non-acidified lakes.

3.4 Historical and present land use

The catchment areas for the lakes in this project are mostly covered by forest and wetlands with only a small proportion of agricultural cultivation. The different forest types that are present are mostly dominated by coniferous forest with smaller areas of deciduous forest and mixed forest (Fig. 11).

Significant changes in land use were found in the 15 lakes where historical maps were available (Fig. 11). One general change is that the coniferous forest has increased in the last century. The analysis shows that 14 of the 15 lakes have seen an increase of coniferous forest; in some cases up to a 70 % increase. Coverage of mixed forests has also increased, whereas the coverage of deciduous forests has decreased in many catchment areas. The proportion of agricultural land is small both in historical and contemporary maps, but has shown a minor decrease for most of the lakes. This indicates that the lakes are typically forest lakes where no large cultivations have taken place. Wetlands show a quite large change from historical to present time, in nine of the 15 lakes there had been a decrease of wetlands compared to historical land-use with up to 11 %. In five lakes there was an increase in wetlands and in one lake no change could be identified. Lake lowering and ditching are plausible factors that could explain the decrease of wetlands (Fig. 11). The areas of water in the catchment show some differences historically and present: seven of the lakes have decreased areas of water (< 5 %) while two of them have an increase and six catchment areas remain unchanged. The areas of grazing land in the catchment area are quite small, but a decrease in these areas can be distinguished for those lakes where grazing land is present. No direct correlation between the land use change and the trends of TOC_{NIRS} before break point can be identified (Fig. 10).

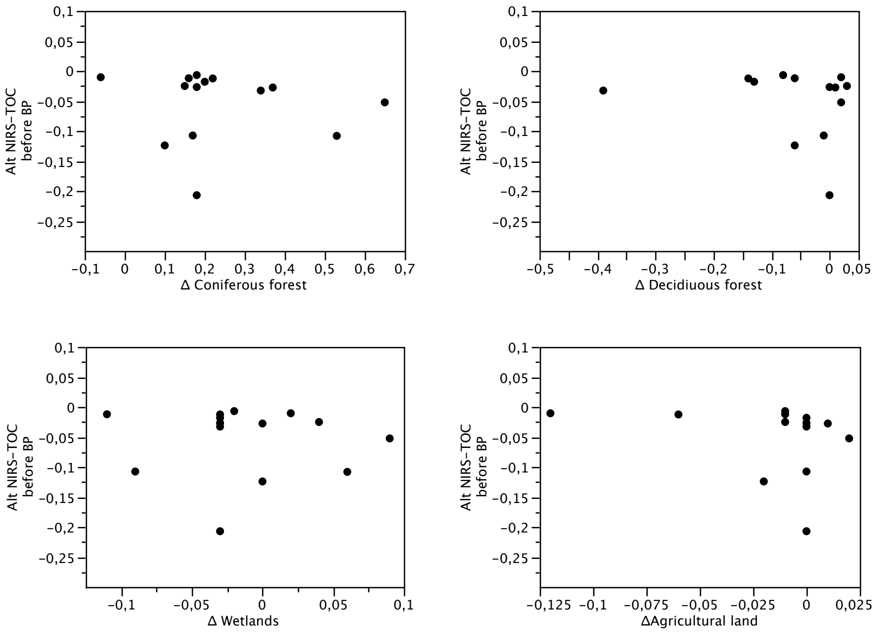


Figure 10. The percentile change in land use plotted against the trends of TOC_{NIRS} before breaking point.

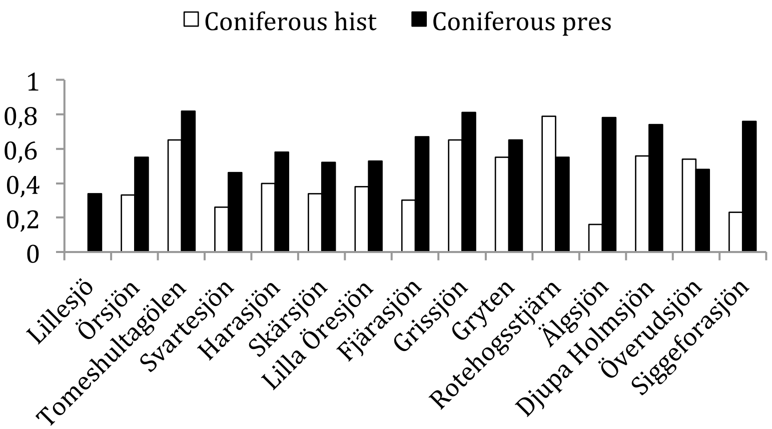
Small changes in the historical and present land use can be due to errors in the map material as well as different definitions of what particular land type was present in the catchment area.

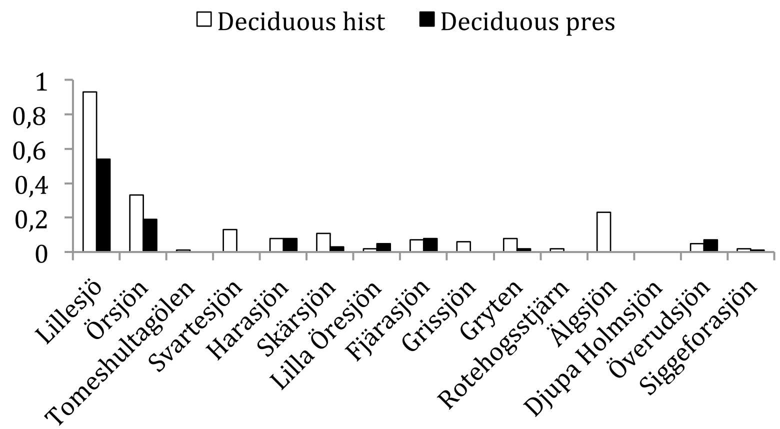
Information on known occasions of drainage or lake lowering has been collected for twelve lakes. Seven of the lakes show records of drainage or lake lowering, three of the lakes have no known events, for two of the lakes the records have been lost from the county administration board and for the remaining eight lakes no information has been gathered. The information has been collected from different county administration boards where the lakes are located. It is quite obvious that the catchment areas have been changed during 20th century. In most cases the changes in land use within the catchment have been made to enlarge areas for cultivation of agricultural land or forest land. The majority of the changes have been made mostly at the end of 19th or beginning of the 20th century. The records for lake lowering are the most extensive and can go back to the 1860s while the drainage and ditching are mostly in the beginning and mid 20th century (Table 11).

Table 11. Historical information about lake-drainage and lowering.

Name of lake	No known events	Drainage	Lake Lowering
Remmarsjön		1935	
Tväringen		No info gathered	No info gathered
Sangen		No info gathered	No info gathered
Hällsjön	X		
Siggeforasjön		No info gathered	No info gathered
Tärnan			1877
Överudsjön			1954
Djupa Holmsjön	X		
Älgsjön	X		
Rotehogsstjärn		No info	No info
Gryten		1946 &1948	1861
Grissjön		No info gathered	No info gathered
Fjärasjön		1987	
Lilla Öresjön		No info	No info
Skärsjön		No info gathered	No info gathered
Harasjön		1987	
Svartesjön		No info gathered	No info gathered
Tomeshultagölen		No info gathered	No info gathered
Örsjön		No info gathered	No info gathered
Lillesjö		1903 & 1913	

There is no direct correlation between the breaking points and the lake lowering/ditching where the landscape has been changed. It could be discussed when the effects of manmade operations in the catchment area will occur. No conclusive evidence can be seen when analysing the breaking points and the point operations.


Coniferous hist
Coniferous pres
1
0,8
0,6
0,4
0,2
0
Lillesjö
Örsjön
Tomeshultagölen
Svartesjön
Harasjön
Skärsjön
Lilla Öresjön
Fjärasjön
Grissjön
Gryten
Rotehogsstjärn
Älgsjön
Djupa Holmsjön
Överudsjön
Siggeforasjön


Deciduous hist
Deciduous pres
1
0,8
0,6
0,4
0,2
0
Lillesjö
Örsjön
Tomeshultagölen
Svartesjön
Harasjön
Skärsjön
Lilla Öresjön
Fjärasjön
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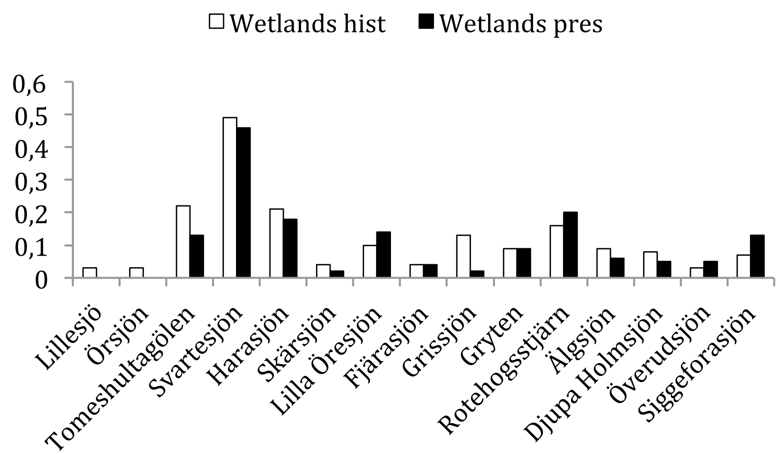
Älgsjön
Djupa Holmsjön
Överudsjön
Siggeforasjön


Wetlands hist
Wetlands pres
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0,5
0,4
0,3
0,2
0,1
0
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Örsjön
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Svartesjön
Harasjön
Skärsjön
Lilla Öresjön
Fjärasjön
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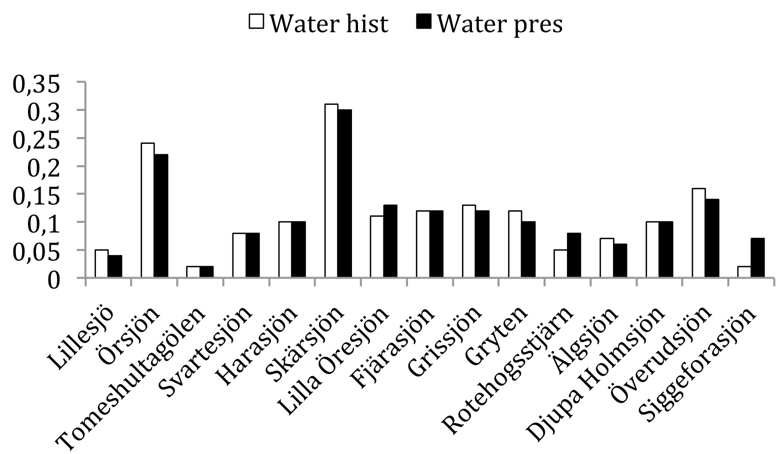
Gryten
Rotehogsstjärn
Älgsjön
Djupa Holmsjön
Överudsjön
Siggeforasjön


Water hist
Water pres
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0,25
0,2
0,15
0,1
0,05
0
Lillesjö
Örsjön
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Svartesjön
Harasjön
Skärsjön
Lilla Öresjön
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Överudsjön
Siggeforasjön

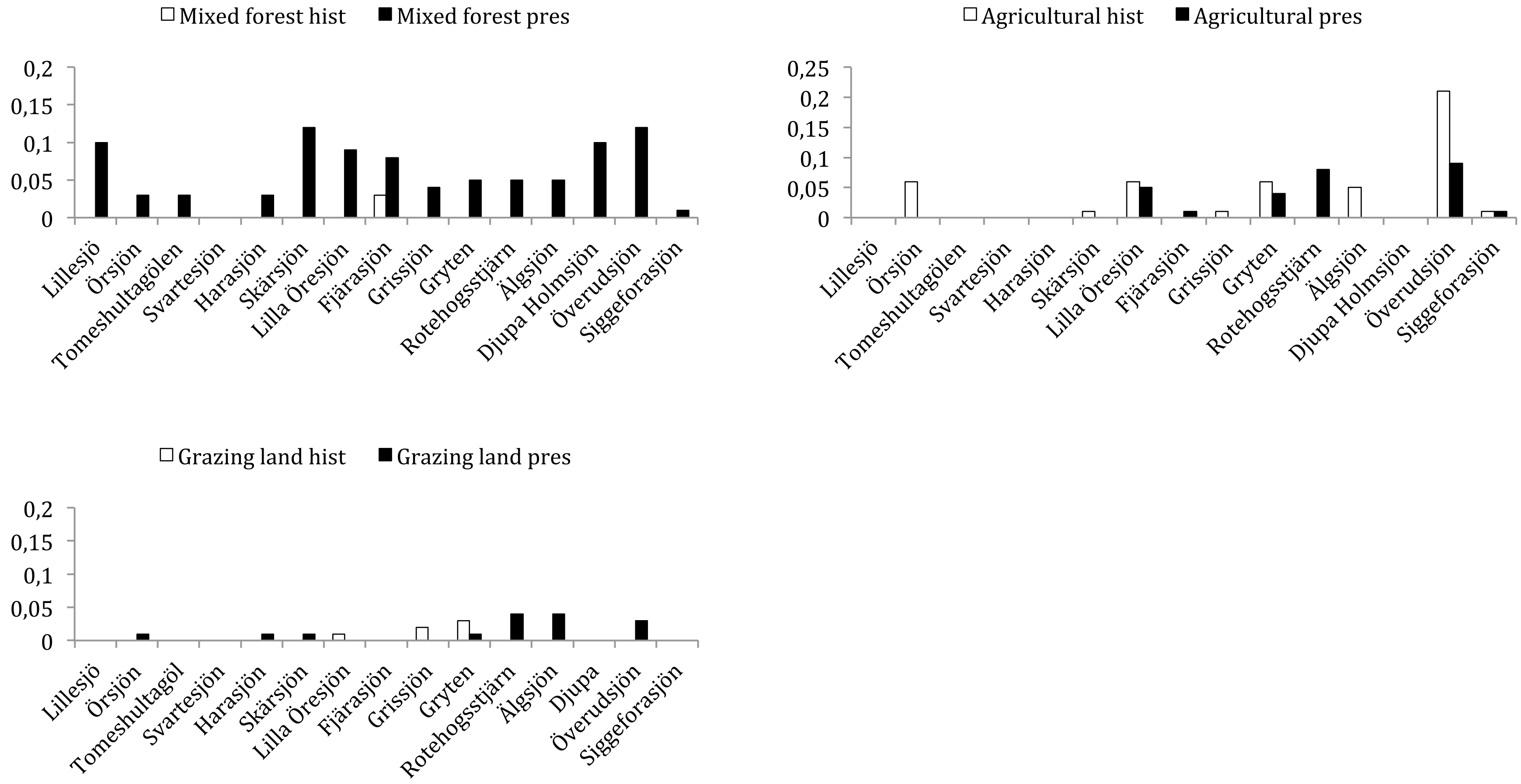

Figure 11. Overview of the historical and present land use, the numbers show the share of the total area. Not all correspond to 100 % between historical and present land use. The charts show the % of the total area of the catchment. Note that all plots do not have the same y-axis.

3.5 ANC calculated with diatom-pH and NIRS-TOC versus MAGIC ANC

ANC_0 was calculated from diatom-pH and NIRS-TOC by chemical equilibrium calculations and a triprotic model for organic acids (see method section). Two different values of TOC were used, measured TOC_t assuming constant concentration (mean lake value 1990-2005) over time as the MAGIC model does ($ANC_{0,diatom\text{-}TOC}$). The other method is to use long-term time series of TOC_{NIRS} assuming a change in TOC concentration over time as described by the paleo-reconstructions ($ANC_{0,\ diatom\text{-}NIRS}$) (Fig. 4 and table 12).

Table 12. Overview of data used for calculation of ANC_0

Calculated ANC_0	TOC used	pH
$ANC_{0,diatom\text{-}TOC}$	Measured TOC (mean lake value 1990-2005)	Diatom-pH
$ANC_{0,diatom\text{-}NIRS}$	TOC_{NIRS} 1860	Diatom pH

$ANC_{0,\ diatom\text{-}NIRS}$ and $ANC_{0,diatom\text{-}TOC}$ was then compared with $ANC_{0\text{-}MAGIC}$. A linear regression between $ANC_{0,diatom\text{-}TOC}$ and $ANC_{0\text{-}MAGIC}$ shows an R^2 of 0.63 (figure 12). An uncertainty factor of ± 0.3 for diatom-pH was taken into account and is shown as error bars (Birks et al 1990). The calculation shows that 13 of 19 lakes of $ANC_{0\text{-}MAGIC}$ were within the uncertainty interval of the $ANC_{0,diatom\ \text{-}TOC}$ (Fig. 11). The analysis shows a mean difference between $ANC_{0\text{-}MAGIC}$ and $ANC_{0,diatom\ \text{-}TOC}$ of -45µeq/l. The lakes that are outside the uncertainty interval show a large variation between $ANC_{0,diatom\ \text{-}TOC}$ and $ANC_{0\text{-}MAGIC}$. The six lakes outside the uncertainty interval show a substantial decrease of $ANC_{0\text{-}MAGIC}$ between 1860 and 1990 (mean difference -165 µeq/l) but show a recovery between 1990 and 2010 (mean difference between 1860 and 2010 -81 µeq/l). The mean difference between $ANC_{0\text{-}MAGIC}$ and $ANC_{0,diatom\ \text{-}TOC}$ shows that the MAGIC shows higher $ANC_{0\text{-}MAGIC}$ values than calculated $ANC_{0,\ diatom\ \text{-}TOC}$.

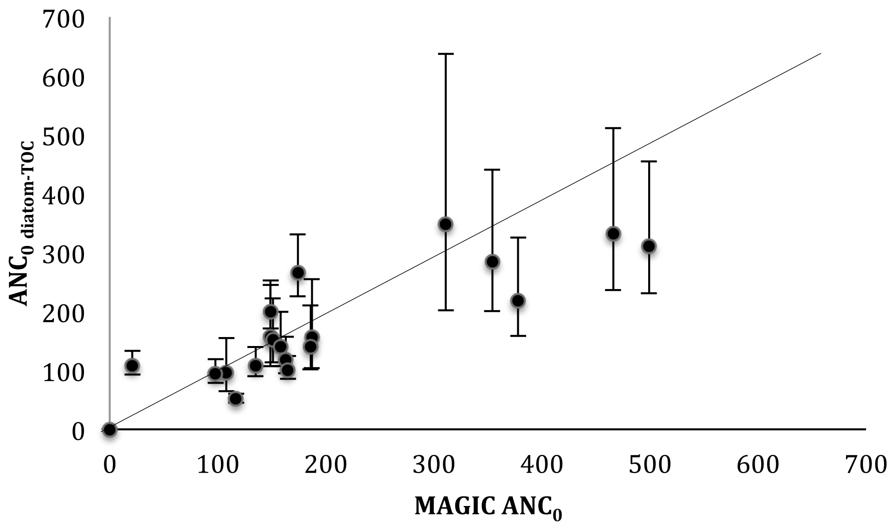

Figure 12. $ANC_{0\text{-MAGIC}}$ plotted against $ANC_{0,\ \text{diatom -TOC}}$. The error bars show the diatom-pH uncertainty interval of ±0.3 pH units. The 1:1 line is shown in the plot. ANC is expressed in µeq/l.

ANC calculated from Paleo-pH and NIRS-TOC ($ANC_{0,\text{diatom-NIRS}}$) shows different results when comparing it with $ANC_{0\text{-MAGIC}}$ (Fig. 13). $ANC_{0,\text{diatom -NIRS}}$ plotted against $ANC_{0\text{-MAGIC}}$ show a R^2 value of 0.68. Calculations show that $ANC_{0,\ \text{diatom -NIRS}}$ has eight of the 20 lakes outside the error bar. For 15 of the 19 lakes $ANC_{0,\ \text{diatom -NIRS}}$ showed lower results compared to $ANC_{0\text{-MAGIC}}$. The mean difference between $ANC_{0\text{-MAGIC}}$ and $ANC_{0,\ \text{diatom -NIRS}}$ is -31µeq/l. Analysing the mean difference of the lakes that fall outside the paleo-pH uncertainty interval shows a difference between $ANC_{0\text{-MAGIC}}$ and $ANC_{0,\ \text{diatom -NIRS}}$ of -38 µeq/l. The MAGIC model shows higher $ANC_{0\text{-MAGIC}}$ values compared to $ANC_{0,\text{diatom -NIRS}}$.

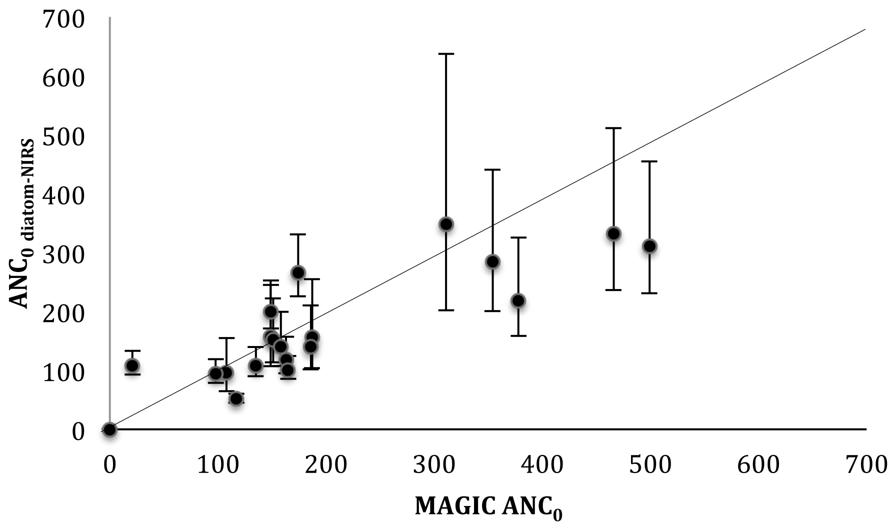

Figure 13. ANC calculated with $ANC_{0,\ diatom\ -NIRS}$ plotted against $ANC_{0\text{-}MAGIC}$, the error bars show the diatom-pH uncertainty interval of ±0.3 pH units. The 1:1 line is shown in the plot. ANC is expressed in µeq/l.

4. Discussion

When performing this study the main focus was to understand if the changes in land use could give a plausible explanation for the changes in lake water TOC in Swedish lakes. This report shows that there has been declining trends of NIRS-TOC from pre-industrial time until a breaking point were the TOC trends turns from decreasing to increasing for most of the lakes. The historical map archive shows that there is a shift in the land–use for most of the lakes. The largest change in the catchment area is an increase of coniferous forestland and a decrease of deciduous forestland and wetlands. This report also stresses the importance of a precise TOC level in acidification assessment and pH reconstructions. In this study we could not find a simple relationship between changes in land cover and TOC-trends, but there were indications on that the changes within the catchment could be a part of a larger explanation for the changes in TOC.

4.1 How reliable is the NIRS-TOC method?

The different NIRS-TOC models have different characteristics that determine how well it corresponds to measured TOC data (TOC_t). The reconstructions of TOC_{NIRS} do not follow a universal model, TOC_{NIRS-7} has been used for all lakes and is supposed to fit in with the wide range of TOC-levels in individual lakes. Due to the fact that TOC_{NIRS-7} has some difficulties reconstructing high TOC values (>13 mg/l) and low TOC (<6), different calibration models had been used. To be able to reconstruct low and high TOC values TOC_{NIRS-5} is used where the contemporary TOC measurements are 6-14 mg/l, $TOC_{NIRS-Northern}$ is used when the measurements are 0-6 mg/l and $TOC_{NIRS-Southern}$ is used when the TOC levels are high (>14 mg/l). To be able to meet the range of the TOC-levels, a compromise was made called Alternative NIRS-TOC (TOC_{NIRS}). This means that when lake water TOC is >14 / <6 mg/l $TOC_{NIRS-Northern}$ or $TOC_{NIRS-southern}$ calibration models are used. If the TOC level is 6-14 mg/l, TOC_{NIRS-5} is used in TOC_{NIRS}. Figure 2 and 3 show a substantial difference between the reconstructions. Therefore TOC_{NIRS-7} was not used for most of the analysis. $TOC_{NIRS-Alt}$ gave a much more satisfactory result when comparing it with TOC_t. This study shows one way of testing the robustness of the NIRS-TOC. The next step is to do a similar analogue testing that has been done for diatom-pH. It could be that samples which shows a poor fit to the monitoring data shows up as poor analogues. If that is the case we have a way to assess the robustness of the reconstructions.

The variety of lakes and their TOC_t content shows that there is a discrepancy between the NIRS-TOC and measured TOC (Fig. 8). The discrepancy could be due to the difference in the quality of the organic matter. As mentioned before, a universal model of TOC_{NIRS-7} is difficult to achieve due to the fact that there is a large variation of TOC depending on geographical location, lake and catchment characteristics and the quality of the produced carbon. It could be discussed whether the sensitivity of the NIRS is dependent on the quality of the organic matter derived from the lake and its catchment. This hypothesis was further developed when comparing TOC_{NIRS} and TOC_t between 1990 and 2005 (Fig. 8). Allot et al (1992) state that sediment mixing leads to loss of resolution of the sediment records and that the top layers of sediment are sensitive to change. This could also be an explanation as to why the trends between TOC_{NIRS} and TOC_t between 1990 and 2005 do not correspond well in some lakes. Another hypothesis is that the six lakes that show a decreasing trend 1990-2005 are not acidified according to MAGIC (Fig. 8). This could be an indication that there is a difference in quality of the organic matter in the sediment between acidified lakes and non-acidified lakes. It could also be argued if there are different processes driving the trends in acidified (recovering) lakes and non-acidified lakes. Earlier studies have shown that organic carbon is dependent on different driving factors. Erlandsson et al (2008a) argue that hydrology and sulphur deposition are factors driving the change in TOC. Monteith et al (2007) claim that sea salt deposition and sulphur depositions are factors that affect long-term change in TOC. Clark et al (2010) argue that the trend of organic carbon, regardless of the drivers, varies spatially with location. These different factors that are driving the change in TOC have to be taken into consideration when determining the long-term trends of NIRS-TOC and the sensitivity of the reconstructions can be affected by hydrological and depositional aspects that can affect the quality of the organic material.

4.2 Why is TOC changing?

4.2.1 Land use changes

The changes in land use could indicate some important factors to take into consideration. The acidified lakes that both show a large decrease between 1860 and present and also have the greatest increasing trend of TOC after the breaking point show considerable changes in land use. There are some common factors for the acidified lakes that show the greatest decrease of TOC between 1860 and present. All lakes have a substantial increase of coniferous forest, e.g. Lillesjö shows an increase of 34%, while the other three lakes show an increase up to 18%. The analysis shows that coniferous forest has replaced deciduous forest landscape in the catchment area. The amount of wetland has also been decreasing for all these lakes, Tomeshult-agölen shows a decrease of 9% of the wetlands in the catchment area. The other lakes have in most cases a decrease of wetlands, around 3 % (Fig. 11 and table 1). Houghton and Goodale (2003) discuss the effects of land use change for the carbon balance in the ecosystem. Looking at the quite large catchment area changes identified in this report it could be discussed what effects the change had on the carbon balances in the catchment area. The authors argue that there is a reduction in the upper meter soil carbon by 25-30 % as a result of cultivation from natural ecosystem to cropland. The analysis in this report shows that the change in agriculture has decreased from 1900 until present, by up to 12% (Fig. 11). The cultivated land has in most cases been replaced by forest, more specifically coniferous and/or mixed forest. It could be argued that when there is a change from natural ecosystem to cropland there is a decrease of soil carbon in the soil due to the fact that forestland can hold more carbon then agricultural land. If the procedure is reversed, from cropland to forestland, this increases the amount of soil carbon will increase in the upper meter. Johnson (1992) states that when the land has been reverted from former agricultural to forests the soil carbon increases substantially. Depending on the soil type there can be increases of soil carbon of 30-100% in the catchment area. The effects of change from agricultural land to forest may not be substantial in this analysis due to the fact that the conversion is quite small in the catchment area, at the same time the leaching of carbon into the lakes has to be taken into consideration. The greatest change shown in this analysis is the increase of coniferous forest by replacing the deciduous forest in the catchment area. Gou and Gifford (2002) state that when a change from native forest to plantation (coniferous forest) takes place the C stocks are reduced by 15 % and in areas where precipitation >1500 mm a reduction of 56 % occurred. Another important factor that the authors discuss is that the age of the plantation plays an important role for the carbon stocks – while there is a decrease of carbon for young plantations < 40 years the carbon stocks were later restored to the same level as before when the plantation reached an age > 40 years. The structure of the forest has changed historically just as the forest type. Historically, forest areas consisted of large trees and an open area where grazing of cattle were common. Today, the forests consist of fast growing trees and managed forests. The major changes of the character of the forest is decline in standing volume, stand age of the trees and the forest density (Linder and Östlund 1998). The analysis of TOC_{NIRS} shows that there is a decreasing trend of TOC_{NIRS} in lake water until a breaking point between the 1940s and 1960s. It could be argued that it is the effects of the losses of carbon storage from the changes in forest plantation that are identified as the increasing trends of TOC_{NIRS} between the 1940s and 1960s. It is difficult to predict when the effects of changes in plantation will occur. It might be the effects of change in forest type that are seen in the trends of the last 20-30 years. The land use change in the catchment area, in particular the change from cultivation to forest, change in forest to plantation, decrease of wetlands through lake lowering and drainage could be a plausible explanation for the increasing TOC trends identified in this report.

4.2.3 Hydrological activities

Analysing the trends of TOC_{NIRS} for the time period 1860-breaking point (Table 10), TOC_{NIRS} shows a declining trend within the chosen interval. The highest decreasing trend for this time period is -20 mg/l for Harasjön (Fig. 6). The lake Harasjön shows the greatest decrease in TOC_{NIRS} between 1860-breaking point (BP) also shows the greatest increase of TOC after BP 0.45 mg/l/ yr^{-1} (Fig. 6). The breaking points could be an indication that there could be some activities in the catchment area that had released a higher quantity of carbon into the lake and therefore the TOC_{NIRS} trend turns from decreasing to increasing. No relationship between the different breaking points could be found, neither geographical location nor TOC_t levels can be seen as the common denominator. One hypothesis as to why the breaking points occur was that there had been drainage activities or lake lowering in the catchment area. For the lakes where data on point sources is available, no direct links between the breaking points and drainage or lake lowering could be identified. There are some factors of drainage and lakes lowering that are important to highlight: (I) the data collected from the county administrations boards are not complete; there have been different rules and regulations on how to report ditching and lake lowering and during a time period, the reporting of ditching and lake lowering was not obligatory, (II) it is very difficult to estimate with certainty when the effects of the drainage and lake lowering were seen. These activities have to be taken into consideration due to the fact that they can be a part of a larger process that is affecting the increasing trends of TOC in Swedish lakes.

4.2.3 Acidification

When making a direct comparison between TOC_{NIRS} and TOC_t, the absolute changes show quite evident results. The levels of TOC_{NIRS} had decreased from 1860 to present in most of the lakes. A decrease was found in 14 of the lakes while three lakes showed an increase and three lakes show very little change from 1860 to present. The lakes that are acidified according to MAGIC are those lakes that show the greatest decrease in TOC_{NIRS} levels between 1860 and 2005 (Fig. 9). At the same time, the acidified lakes show the greatest decreasing change of TOC_{NIRS} before the breaking point and have the greatest increasing trend of TOC after the breaking point (>0.24 mg/l / y^{-1}). Studies have shown a relationship between decreasing atmospheric SO_4 deposition and the increasing trend of TOC (Clark et al 2010; Monteith et al 2007). For this study a clear increase of SO_4 occurs between 1860 and 1990 with the peak of sulphur deposition in 1970 that can be linked to the decreasing trend of TOC between these years. The decrease of atmospheric sulphur deposition occurs after 1990 and it can be argued that the decrease of sulphur deposition can be a driving factor for the increasing trends of TOC (Fig. 8).

4.3 The importance of TOC for estimating the reference ANC in acidification assessments

The determination of the reference condition relies in many cases on precise calculations of pH_0 and ANC_0. The MAGIC simulation for classification of ecological status (Moldan et al 2003) assumes TOC-concentration and pCO_2 as a constant equal the concentration of 1997. Comparing $ANC_{0\text{-MAGIC}}$ with $ANC_{0,\text{ Paleo-NIRS}}$ and $ANC_{0,\text{Paleo-TOC}}$ some clear distinctions can be made (Fig. 12 and 13).

In a comparison, $ANC_{0\text{-MAGIC}}$ shows higher ANC values than $ANC_{0,\text{Paleo-TOC}}$. 14 lakes show lower $ANC_{0,\text{Paleo-TOC t}}$ levels then $ANC_{0\text{-}}$. Six of the 20 lakes are outside the uncertainty interval of paleo-pH ±0.3 (see figure 12). $ANC_{0,\text{ Paleo-NIRS}}$ shows different results when comparing it with $ANC_{0\text{-MAGIC}}$ (see figure 13). $ANC_{0,\text{ Paleo-NIRS}}$ plotted against $ANC_{0\text{-MAGIC}}$ shows that eight lakes fall outside the uncertainty interval. Calculation with $ANC_{0,\text{ Paleo-NIRS}}$ shows that 15 of the 19 lakes show higher results with $ANC_{0\text{-MAGIC}}$.

As seen from the calculations and figure 12 and 13, some conclusions can be drawn by using present or historically inferred NIRS-TOC for calculations of ANC_0. No difference between $ANC_{0,\ Paleo\text{-}NIRS}$ and $ANC_{0,Paleo\text{-}TOC}$ could be established when considering the number of lakes in the uncertainty interval (paleo-pH ± 0.3) the differences could be due to random uncertainty. $ANC_{0,\ Paleo\text{-}NIRS}$ has eight lakes and $ANC_{0,\ Paleo\text{-}TOC}$ has six lakes outside the uncertainty interval. Five of these lakes outside the uncertainty interval are recurring for both calculations. Three of the lakes, Lillesjö, Lilla Öresjön and Rotehogstjärnen are acidified according to MAGIC. Lillesjö and Lilla Öresjön showed large changes in ANC over time. Lillesjö shows a difference of -131µeq/l, Lilla Öresjön shows a decrease of -113 µeq/l from 1860 until 2010. Rotehogstjärnen shows a quite small decrease of -26 µeq/l. The lakes that do not show acidification show quite large changes in ANC according to MAGIC. Älgsjön and Fjärasjön are outside the uncertainty interval but not acidified according to MAGIC. The lakes show a decrease of $ANC_{0\text{-}MAGIC} - ANC_{2010\text{-}MAGIC}$, Fjärasjö (-123 µeq/l) and Älgsjön (-67 µeq/l). The non-acidified lakes show a stronger recovery of ANC between 1990 and 2010 than the acidified lakes.

When calculating $ANC_{0,\ Paleo\text{-}TOC}$, a lower ANC is shown compared with $ANC_{0\text{-}MAGIC}$, but the mean difference is high so the fit is not optimal. Using $ANC_{0,\ Paleo\text{-}NIRS}$ a clear improvement of the fit occurs when comparing with $ANC_{0,\ Paleo\text{-}NIRS}$ and $ANC_{0\text{-}MAGIC}$, but $ANC_{0\text{-}MAGIC}$ still shows higher than $ANC_{0,\ Paleo\text{-}NIRS}$. As Erlandsson (2008a) suggests, there is a substantial importance of using TOC_{NIRS} and pCO_2 for determining ANC_0 for acidification assessment. By using pre-industrial estimations of TOC_{NIRS} and pH using paleolimnological reconstructions a lower ANC_0 than $ANC_{0\text{-}MAGIC}$ was calculated. The TOC_{NIRS} indicates a clear declining trend until present for most of the lakes and still MAGIC shows higher ANC_0 values than if used TOC_{NIRS}. It could be further analysed whether the MAGIC model overestimates the ANC of the analysed lakes in this report, in which case the overestimation of ANC would also lead to an exaggeration of the acidification in Swedish lakes.

5. Conclusions

- The long-term trends of TOC_{NIRS} show a decrease from 1860 until present for most of the lakes. There is a clear decrease of TOC until an identified breaking point where the TOC turns from decreasing to increasing.
- The most substantial difference in land use is change in forest cultivation. The increase of coniferous forest and the decrease of deciduous forest are the foremost changes in the catchment areas. A clear decrease of wetlands can be identified in the analysis.
- No direct correlation between change in land use and long-term trends of TOC_{NIRS} could be identified. Other studies have shown the effect land use can have on carbon storage, which could be linked to the trends of TOC_{NIRS} presented in this report. As discussed in this study, the character of the land use, in particular forest type, from open-ended forests with large trees to intensely managed plantation, influences and is an important driving force for TOC in the catchment area interrelated with the land use changes.
- Our result indicates that the estimations of acidification done by MAGIC for Swedish lakes might overestimate acidification by assuming the 1997 TOC concentration as a constant value.

References

Allot, T., Harriman, R., & Battarbee, R., (1997). Reversibility of lake acidification at the Round Loch of Glenhead, Galloway, Scotland. *Environmental pollution 77, 219-225*.

Andersen, J., Conely, D., Hedal, S., (2004). Palaeoecology, reference conditions and classification of ecological status: EU water framework directive in practice. *Marine Pollution Bulletin 42, 283 – 290*.

Appleby, P. G,. (2001). Chronostratigraphic techniques in recent sediments, p. 171–204. In W. M. Last and J. P. Smol [eds.], Tracking environmental change using lake sediments, v. 1: Basin analysis, coring and chronological techniques. Kluwer.

Bennion, H., Battarbee, R., (2007). The European union water framework directive: Opportunities of paleolimnology. *Journal of Paleolimnology. 38, 285-295*.

Birks, H. J. B., Line, J. Juggins, S., Stevenson, A., Terbraak, C.J.F. (1990). Diatoms and pH reconstruction *Philosophical Transactions of the Royal Society B. 327, 263-278.*

Bishop, K,. Beven, K.,Destouni, G., Abrahamsson, K., Andersson, L., Johnson, R. K. Rodhe, J., Hjerdt, N. (2009). Nature as the "natural" goal for water management: A conversation. *Ambio. 38, 4, 209-214*.

Clark, J.M Clark, J. M., Bottrell, S. H., Evans, C. D., Monteith, D. T., Bartlett, R. Rose, R., Newton, R. J., Chapman, P. J. (2010). The importance of the relationships between scale and process in understanding long-term DOC dynamics. *Science of the total environment 408, 2268-2275.*

Cosby, B., Ferrier, R, C., Jenkins, A., Wright, R., (2001) Modelling the effects of acid deposition refinemnets, adjustments and inclusion of nitrogen dynamics in the MAGIC model. *Hydrology and Earth system sciences. 5, 499-517*.

Cosby, B., & Wright, F., (1998). Modelling regional response of lake water chemistry in acidic deposition: the MAGIC model applied to lakes surveys in southernmost Norway 1974-1986-1995. *Hydrology and earth system sciences. 2, 563-576.*

Cosby, B. J., Wright, R. F., Hornberger, G. M.; Galloway, J. N. (1985). Modelling the effects of acid deposition: Estimation of longterm water quality responses in a small forested catchment. *Water Resources Research. 21*, 1591–1601.

Cunningham, L., Bishop, K., Mettävaimio, E., Rosén, P., (2010). Paleoecological evidence of major declines in total organic carbon concentrations since the 19th century in four nemoboreal lakes. *Journal of paleolimnology DOI: 10.1007/s10933-010-9420-x*

Durfour, S., & Piégay, H., (2009). From the myth of a lost paradise to targeted river restoration ; Forget natural references and focus on human benefits. *River Research and Applications. 25, 568-581.*

European Union, (2000). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 on establishing a framework for community action in the field of water policy. *J Eur Commun L 327, 1–72*.

Erlandsson, M., Fölster, J., Laudon, H., Weyhenmeyer, G., Bishop, K., (2008a). Natural variability in lake pH on seasonal, interannual and decadal time scales: implications for assessment of human impact. *Environment, Science & Technology. 42, 5594-5599*.

Erlandsson, M., Bishop, K., Fölster, J., Guhrén, M,., Korsman, T., Kronnäs, V., & Moldan, F., (2008b). A Comparison of MAGIC and Paleolimnological Predictions of Preindustrial pH for 55 Swedish Lakes. *Environment, Science & Technology. 42, 43–48.*

Fölster, J., Andrén, C., Bishop, K., Buffam, I., Cory, N., Goedkoop, W., Holmgren, K., Johnson, R,. Laudon, H., Wilander, A., (2007). A novel environmental quality criterion for acidification in Swedish lakes- An application of studies on the relationship between biota and water chemistry. *Water Air Soil pollution. 7, 331-338*.

Gou, L., and Gifford, M., (2002). Soil carbon stocks and land use change: a meta analysis. *Global change biology. 8, 345-360*.

Guhrén, M., P. Rosén, T. Korsman and I. Renberg (2003). Tidigare pH i referenssjöar i Sverige*. Inst. för Ekologi och Miljövård, Umeå Univeristet. ISBN 91-7305-448-8*

Helsel, D,. Hirsch, M. (1992). Statistical methods in water resources. Studies in environmental science. Elsevier, Amsterdam

Houghton, R., Goodale, C,. (2003). Effects of land-use change on the carbon balance of terrestrial ecosystems. *Geophysical Monograph Series 153. DOI: 12029/153GM08*.

Hruška, J., Laudon, H., Johnson, C.E., Köhler, S. and Bishop, K. (2001). Acid/base character of organic acids in a boreal stream during snowmelt,. *Water Resources Research.* 37, 1043.

Johnson, D., (1992). Effects of forest management on soil carbon storage. *Water Air & Soil pollution, 64: 83-120*.

Korsman, T., Birks, H.J.B., (1996). Diatom-based water chemistry reconstructions from northern Sweden: a comparison of reconstruction techniques. *Journal of Paleolimnology 15: 65-77,*

Kokfelt, U.,Rosén, P., Schoning, K., Christensen, T. R., Förster, J., Karlsson, J., Reuss, N., Rundgren, M., Callaghan, T. V., Jonasson, C., Hammarlund, D., (2009). Ecosystem responses to increased precipitation and permafrost decay in subarctic Sweden inferred from peat and lake sediments. *Global Change Biology. 7, 1652-1663*.

Köhler, S., Laudon, H., Wilander, A., Bishop, K., (2000). Estimating organic acid dissociation in natural surface waters using total alkalinity and TOC. *Water Research. 34*, *1425–1434.*

Linder, P., Östlund, L., (1998). Structural changes in three mid-boreal Swedish forest landscapes, 1885-1996. *Biological Conservation. 85, 9-19*.

Moldan, F., Kronnäs, V., Wilander, A., Karltun, E., Cosby, B. J. (2003). Modelling acidification and recovery of Swedish lakes. *Water, Air and Soil Pollutions: Focus, 4, 139-160.*

Monteith, D,T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Hogasen, T., Wilander, A. Skjelkvale, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B.. Kopacek, J. Vesely, J., (2008). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature. 450, 537-U9.*

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 76: 503–516.*

Rosén, P., & Hammarlund, D., (2007). Effects of climate, fire and vegetation development on Holocene changes in total organic carbon concentration in three boreal forest lakes in northern Sweden. Biogeosciences, 4, 975–984.

Rosén, P., Cunningham, L., Vonk, J., Karlsson, J., (2009). Effects of climate on organic carbon and the ratio of planktonic to benthic primary producers in a subarctic lake during the pas 45 years. *Limnology and Oceanography. 54, 1723-1732.*

Stevenson, AC., Juggins, S., Birks, H,J,B., Anderson, D,S., Anderson N,J., Battarbee, R,W., Berge, F., Davis R,B., Flower, R,J., Haworth, E,Y., Jones, V,J., Kingston, J,C., Kreiser, A,M., Line, J,M, Munro., M,A,R., Renberg, I., (1991). The surface waters acidification project paleolimnologyprogramme: Modern diatom/lake-water chemistry data-set. *ENSIS Publishing, London, 86 pp*

Sterner, M., Fölster, J., Nisell, J., (2010). Förändring av markanvändningen sedan förindustriell tid i avrinningsområden till sjöar. Rapport 2010:14.

Sobek, S., Algesten, G., Bergstrom, A.,Jansson, K., Tranvik, L. (2003). The catchment and climate regulation of pCO(2) in boreal lakes. *Global change boilogy. 9, 630-641.*

Swedish University of Agricultural sciences (SLU), Analysmetoder. (2010). available at www.ma.slu.se (accessed July 20, 2010).

Wold, S., Antti, H., Lindgren, F., and Öhman, J. (1998) Orthogonal signal correction of NIR spectra. *Chemometrics and Intelligent Laboratory Systems 44, 175–85.*

Wik, M., & Renberg, I., (1996). Environmental records of carbonaceous fly-ash particles from fossil-fuel combustion. *Journal of Paleolimnology 15, 193-206.*

Wollebæk- Toset H-P, Gleditsch N-P & Hegre H,. (2000). Shared rivers and interstate conflict. *Political Geography. 19, 971–996.*