Credible Acidification Assessments in a Changeable Environment

Estimating the Natural Acidity of Boreal Lakes in Sweden

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Abstract

Despite major reductions in acidifying deposition and varying degrees of recovery in acidified surface waters, there is still an urgent need to improve tools for acidification assessments on regional scales. The most accepted models for estimating acidification reference values are often too complex for this purpose. Here, a meta-model is derived from the established, dynamic MAGIC acidification model. The meta-model (meta$_{\mathrm{MAGIC}}$) relates generally available variables of contemporary water chemistry to the pre-industrial buffering capacity predicted by MAGIC. Meta$_{\mathrm{MAGIC}}$ was able to reproduce the pre-industrial ANC (Acid Neutralizing Capacity) predicted by MAGIC with an absolute median error of 13.2 μeq/l (or 8 %), for 95 Swedish lakes. This approach ultimately relies on the accuracy of the MAGIC reconstructions themselves, which were compared to a set of paleolimnological reconstructions of pre-industrial pH. No bias was detected between the two reconstructions (mean difference was 0.03 pH-units for 55 lakes), provided that lake specific estimates of TOC (Total organic carbon) and partial pressure of CO_2 are used when converting MAGIC ANC to pH.

A complication in acidification assessments is that surface water acidity varies on all time scales, from diel to centennial. The variability in pH is here compared to the criteria for acidification in the Swedish EQC (Environmental Quality Criteria), where a decline in pH of 0.4 units or more from the natural state is defined as significant acidification. When reference time series of pH were reconstructed for 95 lakes, it was found that the seasonal variability exceeded 0.4 units over 15 years in all lakes. On a longer time scale, a decade of TOC increase in many lakes has lowered pH. For 24 lakes with 30-140 % increases in TOC, the median effect on pH was 0.24 pH-units. The TOC increase affects the recovery from acidification and raises questions about what the "natural state" really is. The answer will have a profound impact on assessments of acidification.

Keywords: pH modelling, reference values, temporal variability, environmental quality criteria, ecological status, MAGIC, ANC, DOC, CO_2

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Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Erlandsson, M., Bishop, K., Fölster, J., Guhrén, M., Korsman, T., Kronnäs, V., Moldan, F. (2008). A comparison of MAGIC and paleolimnological predictions of pre-industrial pH for 55 Swedish lakes. *Environmental Science and Technology* 42: 43-48.

II Erlandsson, M., Fölster, J., Wilander, A., Bishop, K. (2008). A metamodel based on MAGIC to predict the pre-industrial acidity status of surface waters. *Aquatic Sciences* 70: 238-247.

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

IV Erlandsson, M., Cory, N., Köhler, S., Bishop, K. Changes in acidification status for 24 Swedish lakes due to increasing levels of organic acids. (manuscript).

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Abbreviations

(S)EPA	(Swedish) Environmental Protection Agency
DOC	Dissolved organic carbon
SSWC	Steady State Water Chemistry
EQC	Environmental Quality Criteria
MAGIC	Model of Acidification of Groundwater in Catchments
ANC	Acid neutralizing capacity
TOC	Total organic carbon
pCO_2	Partial pressure of CO_2
WHAM	Windemere Humic Aqueous Model
WFD	EU´s Water Framework Directive
ΔpH, ΔANC	Difference between reference and measured pH/ANC
RMSE	Root mean square error

1 Background

In the middle of the 19th century, levels of acidifying deposition began to increase in Europe (Mylona 1996). The effects on Swedish freshwaters began to manifest themselves towards the end of the 19th century (Renberg *et al.* 1993, Moldan *et al.* 2004). The emissions of sulphate and the acidification of freshwaters accelerated during the 20th century, but it was not until the 1960s that the problem came to the attention of the scientific community and the public. Sulphate deposition peaked around the end of the 1970s, and in the national survey of 1990, 16 % of the lakes in Sweden were classified as significantly acidified (SEPA 1991). Around this time, acidification could be considered as the major environmental problem in Sweden, with respect to the consequences for the biota, the proportion of water bodies affected, and the time perspective for recovery (Håkanson 1999). Since then, the freshwaters in Sweden, as well as other parts of N. Europe and N. North America, have begun to recover from acidification (Stoddard *et al.* 1999, Skjelkvåle *et al.* 2001). Through the Geneva Convention on Long Range Transboundary Air Pollution and its associated protocols (The Helsinki Protocol (1985), The Oslo Protocol (1994), The Gothenburg Protocol (1999)), commitments to reduce sulphate emissions have been successfully implemented. Sulphate deposition is now down to the same levels as of a century ago, whereas nitrogen deposition decreases to a lesser extent (Fig. 1). Acidifying deposition has been reduced to a level that most Swedish lakes should be able to tolerate, according to calculations of the "Critical Load" (SEPA 2008). In 2005, 5.6 % of the lakes in Sweden were classified as significantly acidified (Wilander and Fölster 2007).

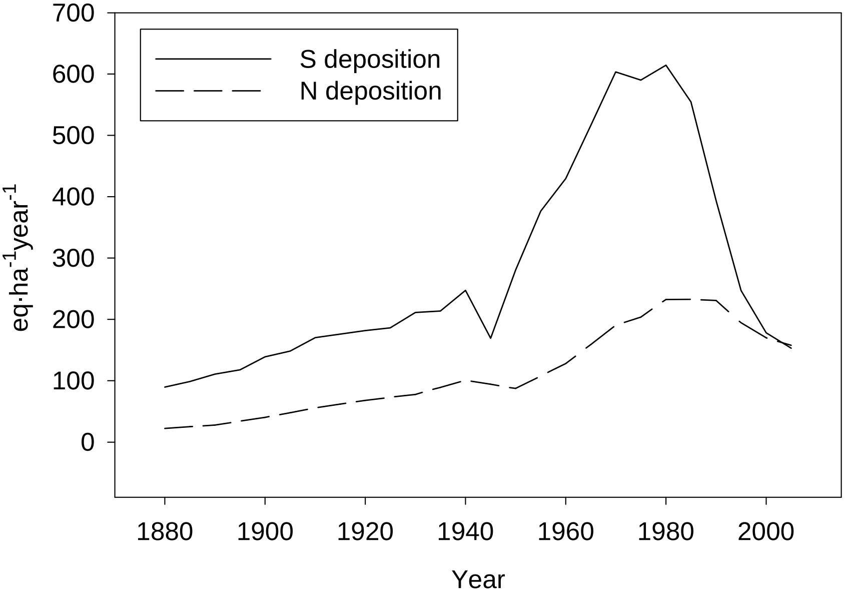

Figure 1: Mean deposition in Sweden of sulphur and nitrogen 1880-2005 (CCE 2007).

With the decreasing sulphate emissions and the recovery from acidification that has been observed over large areas in Europe and N. North America, the interest of the scientific community has largely been redirected towards other environmental problems. However, there are several reasons to still be concerned about acidification. First, the recovery will take several decades, and many of the most severely acidified lakes can not be expected to be fully recovered even after another 50 years. Due to the depletion of base cations in the soil, acidified lakes will also be more sensitive to acidic episodes in the future, such as a sudden storm event with sea salt deposition (Likens *et al.* 1996, Hruška *et al.* 2002). Furthermore, increased harvesting of biomass in forestry is likely to delay the recovery, or even increase the acidification in some areas (Aherne *et al.* 2008). The effects of global warming could potentially affect the recovery process in both directions (Wright *et al.* 2006), including the effects on acidity of a possible continuing increase in DOC concentrations (Freeman *et al.* 2001, Freeman *et al.* 2004). Concerns have been raised that soils may saturate with nitrogen and begin leaching nitrate, thus causing re-acidification (Aber *et al.* 1989). There are also other parts of the world where emissions of acidifying substances continue to increase. This is most notable in China, where concerns of forthcoming and widespread acidification have been raised (Larssen *et al.* 2006). Last but not least, as the recovery progresses, and acidity is moving closer to the natural levels, policy implications put higher demands on the accuracy of acidification assessments (Fölster *et al.* 2007). The national environmental goals in Sweden (Miljömålsrådet 2008) and the demands of the European Union's "Water Framework Directive" (2000) requires that good ecological status is achieved, meaning no significant ecosystem differences compared to pre-industrial conditions. Furthermore, the annual cost for liming lakes in Sweden is currently about 23 000 000 EUR/year. To evaluate whether these legislative demands are met, and to end liming treatments when no longer needed, precise assessments of acidification are required.

This thesis is focused on how to improve acidification assessments on a regional scale. The problems associated with acidification assessments are primarily questions about how the natural state of a water body should be described. We know that the acidified lakes and streams in Sweden are recovering, but we need to know which target to reach, so that we know when to direct remediation efforts to other environmental problems. Or in other words: Where are we going, and how shall we know when we have got there?

2 Complications for acidification assessments

2.1 How to define reference values

Defining reference values against which the present state is measured is the key to assessing human impact on climate, nutrient status, acidity, metals, organic contaminants, etc. Generally speaking, reference values are set with the "natural state" as a measure. Some types of environmental stressors, such as POPs (Persistent Organic Pollutants), should simply not be present in the environment. For such types of environmental problems, the target may be set to zero, or to the levels that the most sensitive organisms can tolerate. For stressors such as acidification and/or eutrophication, finding suitable targets is more difficult, since there is a large natural heterogeneity in acidity and nutrient status among different water bodies. For acidification, the reference state is usually defined as the pH or buffering capacity in the "pre-industrial period" of the mid 1800s, prior to the increased anthropogenic emission of sulphur and nitrogen associated with the burning of fossil fuels.

There are sophisticated methods to estimate the pre-industrial acidity in freshwaters, most notably dynamic modelling and paleolimnology. In dynamic modelling, information on catchments, mineralogy, hydrology, land use, atmospheric deposition over time and contemporary surface water chemistry are used to simulate lake chemistry over longer (centennial) time scales (Forsius et al. 1998). In paleolimnology, the historical archives in lake sediments are examined, for example the diatom community (Birks et al. 1990), or the reflectance spectrum (Korsman et al. 1992), and then related to the water chemistry when the material was deposited. In the lake rich landscapes formed by glaciation, it is not realistic to use such methods for acidification assessments on a routine basis, since they require a large amount of input parameters as well as operational skills. A simpler approach is then needed to assess acidification on a regional scale. The recovery of freshwaters in Sweden and other parts of the northern hemisphere has made improvements of the methods for defining reference conditions urgent, since the method previously used for assessment purposes in Sweden, the SSWC model (Henriksen 1982, Henriksen et al. 1990), was not intended to be used during the recovery phase. It relies on a parameter, the so-called "F-factor", which describes the degree to which acidifying deposition in the lake has been neutralized by soil processes. During the recovery phase that the acid sensitive lakes in S. Sweden are now in, the empirical relationships used to estimate the F-factor are no longer adequate (Rapp 2001). Currently, acidification in the Swedish EQC is assessed by matching a lake to a similar lake within a database of some 400 lakes for which the pre-industrial chemistry has been reconstructed by the MAGIC-model (SEPA 2008).

2.2 The variability of reference values

An issue that is seldom addressed is the temporal variability of reference values. With the water chemistry being subject to natural variations during both the contemporary and the pre-industrial time periods, this is anything but a trivial matter. Important acidity parameters such as pH, ANC and DOC are all subjects of natural variability. Still, for assessment purposes, the two periods are commonly represented as two single numbers to be compared. Sampling of the contemporary chemistry is theoretically possible, but there are of course financial and practical limitations. Estimating a reference value that accounts for the natural variability in the pre-industrial period is a more difficult task. One key issue is how to distinguish between different signals in a time series. Which signals can be considered as natural variability? Which signals should be filtered out when assessing anthropogenic disturbances? And what can be considered as ecologically relevant trends that are due to human activities? A theoretical definition would be that signals that are present in a reference state can be considered as "noise", whereas signals that are absent during reference conditions should be considered as a trend associated with human impact. However, this would seldom be a useful definition in a practical sense, since the established modelling approaches usually provide a reference value representing the mean chemistry from a longer time-period, typically from years to decades. Since it is practically impossible to make a reconstruction that completely captures both the temporal and the spatial variability of water chemistry, it is necessary to be aware which chemistry we compare and what it represents.

2.3 What is the "natural state"?

Changes in climate and in land use may result in "irreversible" changes in natural acidity, at least on a reasonable (centennial) time scale. One example is the increasing levels of organic matter noted in large parts of the Northern hemisphere which retards the recovery from acidification in many lakes by increasing the concentrations of organic acids (Evans *et al.* 2007). Changed patterns in temperature, precipitation and runoff will also affect the water chemistry (Schindler 1998). These changes will not only affect the recovery processes, they will also complicate assessments of the status and change the restoration targets. A further complication is when mechanisms behind changes in water chemistry are unknown. For example, the observed increasing concentrations of organic acids suppress the pH. Is this pH-decline a natural variation or is it caused by anthropogenic activities? Since the mechanisms behind the increasing levels of organic matter in fresh waters are not fully known, this question is difficult to answer accurately. One hypothesis is that sulphate deposition has suppressed the concentrations of dissolved organic matter, and that the observed increases in DOC concentrations are due to declining levels of acidifying deposition (Monteith *et al.* 2007). If this assumption is true, the DOC increase is a recovery from a disturbance caused by human impact. Other hypotheses link increases in DOC concentrations to changes in climate, such as higher temperatures and/or runoff (Freeman *et al.* 2001, Erlandsson *et al.* 2008). If this is the main driving factor, we must know what caused the climatic changes. Is it a consequence of anthropogenic global warming, due to increased emissions of greenhouse gases, or could it be a natural phenomenon? Given the current state of knowledge, it is not an easy task to define which levels of organic matter concentrations should be considered "natural". Considering all interactions between climate and acidity in freshwaters, should climate changes associated with human activities then be considered when assessing acidification? Questions like these may not only be up to the scientific community to answer, but just as much up to policy makers.

Natural acidity was discussed already in the end of the 1970s, when Rosenqvist (1977) argued that soil properties of the catchment, including DOC released by soils, were much more important factors than acid rain for the acidity status of streams and lakes. Several years later, there was a controversial suggestion that acid rain would just result in a replacement of organic acidity with anthropogenic acidity in the form of sulphuric acid (Krug and Frink 1983). These ideas were dismissed by most researchers at that time, but they have recently gained relevance again, with the sustained increases of DOC observed in waters recovering from acidification.

3 Objectives

The overall aim of this thesis was to improve acidification assessments by improving methods for defining reference values. First, a method to assess acidification is derived, and then the variation in natural acidity on different time scales is examined.

- Comparing the outcome of two regional applications of pre-industrial water chemistry reconstructions. One reconstruction was made with the dynamic hydrogeochemical model MAGIC, the other was a paleolimnological reconstruction (**Paper I)**.
- Developing an operational method for acidification assessments of freshwater on larger spatial scales, based on a set of MAGIC reconstructions of the pre-industrial chemistry (**Paper II)**.
- Examining the temporal variability of reference values for pH, on seasonal, interannual and decadal time scales, as well as the implications for acidification assessments (**Paper III)**.
- Examining the effects of increasing levels of organic matter on the recovery process (**Paper IV**).

4 Material and methods

4.1 Environmental Monitoring Data

All the water chemistry data used in this thesis are from reference lakes in the Swedish environmental monitoring program. Surveillance of fresh water quality on a systematic and regular basis has been undertaken in Sweden since the mid 1960s. The focus was originally on eutrophication in the four largest lakes in Sweden, and monitoring of river mouths to quantify the transport of nutrients to the Baltic Sea. The environmental surveillance program for monitoring lake acidification was initiated by the Swedish EPA in 1983 (SEPA 1985). At that time, liming had become a common countermeasure to mitigate the effects from acidification. The purpose with the new lake monitoring program was to follow the acidification process in a number of acid sensitive and unlimed reference lakes, with a temporal resolution that captured the seasonal dynamics. The program included almost 200 lakes, usually sampled four times each year (i.e. once each season). The monitoring program has since then been extended, and now covers most of the range of Swedish lake water chemistry (Johnson 1999).

Monitoring data of high quality is a very valuable asset, which can not only be used to follow the course of events in the monitored objects, but also to develop models, and to test hypotheses of large-scale changes in the environment. The chemical analyses in the Swedish monitoring program have been made in the same laboratory, and by using the same methodologies (mostly) during the entire study period. All data on water chemistry can be downloaded from the Swedish University of Agricultural Sciences' webpage (SLU 2008).

4.2 Model of Acidification of Groundwater in Catchments (MAGIC)

With the focus on different aspects of reference values for acidity, an estimate of the pre-industrial water chemistry was required. MAGIC is a hydrogeochemical model developed to predict long-term effects of acidifying deposition on a catchment scale. The development of MAGIC is described in a series of papers by Cosby et al. (Cosby *et al.* 1985a, Cosby *et al.* 1985b, Cosby *et al.* 1986, Hornberger *et al.* 1986). MAGIC has since then been used in a large number of studies, focused on both hindcasts (Hornberger *et al.* 1989, Cosby *et al.* 1990, Whitehead *et al.* 1997) and forecasts (Beier *et al.* 1995, Evans *et al.* 1998, Posch *et al.* 2003, Wright *et al.* 2005) of freshwater acidity. To define the reference conditions throughout this thesis, the pre-industrial ANC estimated from MAGIC simulations from 133 Swedish lakes was used, performed by Moldan et al. (2004). The model was calibrated to the median water chemistry from 1997, since good quality deposition data were available for that year. The 1997 hydrological conditions were assumed to be close to the long-term (1961-1990) average values. The pre-industrial chemistry was defined as the water chemistry of 1857, a year chosen as representative for pre-industrial conditions. Steady-state conditions were assumed for the pre-industrial period.

MAGIC gives pre-industrial ANC as well as pH as output data. However, in the study by Moldan et al., lake pH was not used in the calibrations, due to lack of measurements of aluminium. In this thesis, only the ANC from MAGIC is therefore used. Reference pH was then modelled afterwards, using certain assumptions regarding pre-industrial values of TOC, pCO_2 and Al (DOC and TOC being essentially equal in Swedish systems (Gadmar *et al.* 2002)). In the MAGIC simulations, pCO_2 is assumed to be constant over time in the lake water compartment, and TOC concentrations are assumed to be constant over time in both the lake water and the soil water compartment. TOC concentrations in the lake water compartment are lake specific (equal to the median of 1997), whereas TOC in the soil compartment and pCO_2 are uniform for all lakes. Changing TOC and pCO_2 in the lake water compartment will not affect the hindcasts of pre-industrial ANC. Therefore, when changing assumptions about stream TOC and pCO_2, the reference pH can be estimated separately afterwards, instead of repeating the MAGIC simulations.

The prerequisites to include lakes in the studies of this thesis were that they should be part of ongoing monitoring, that they should be acid sensitive (alkalinity < 220 μeq/l), and that they should not have been limed during the study period (1988-2006). Of the 133 lakes with pre-industrial buffering capacity reconstructed with MAGIC, 95 met these criteria and were chosen for further studies (Fig.1, Paper II). For two of these lakes, monitoring ended in 2003, whereas the rest are still subjects of ongoing monitoring. In Paper I, a subset of 55 lakes was used, i.e. the lakes for which a paleolimnological reconstruction of the pre-industrial water chemistry was available (Guhrén *et al.* 2003), in addition to the MAGIC reconstructions. In Paper IV, where the effects of increasing TOC on acidification assessments was studied, a subset of 24 lakes was used, i.e. lakes that showed an increase in TOC between 1990 and 2006 of at least 30 %.

4.3 Modelling of pH

In this thesis much attention is paid to modelling pH. Using parameters such as ANC or alkalinity for defining acidity would certainly make life easier for the scientist, since these constituents are often much easier to predict. However, variations in buffering capacity may not always be ecologically relevant. A reduction in ANC from 1000 μeq/l by 50 %, or by 500 μeq/l in absolute numbers, is only likely to change pH marginally, whereas a decline in ANC from 100 μeq/l by 50 %, or by 50 μeq/l in absolute numbers, could potentially decrease pH by up to 1 unit. Furthermore, variations in TOC and pCO_2, either natural, or associated with anthropogenic activities, will also affect pH, and hence the conditions for biota in surface waters. For these reasons, the estimates of pre-industrial buffering capacity are preferably converted to pH to achieve the most relevant reference value (Fölster *et al.* 2007).

The definition for ANC is the difference between the sum of weak acid anions and the sum of weak base cations (ANC in eq/l, right side in mol/l).

$$ANC = ([OH^-] + [HCO_3^-] + 2 \cdot [CO_3^{2-}] + [A^-] - [H^+] - n \cdot [Al^{n+}]) \qquad (1)$$

Where;

$[A^-]$ = concentration of organic anions (denoted $[RCOO^-]$ in the papers)

n = mean charge of $[Al_i]$

ANC can also be calculated from the difference between concentrations of strong base cations (BC) and strong acid anions (here ignoring $[NH_4^+]$ and $[F^-]$):

$$[ANC] = (2 \cdot [Ca^{2+}] + 2 \cdot [Mg^{2+}] + [Na^{+}] + [K^{+}]) - (2 \cdot [SO_4^{2-}] + [NO_3^{-}] + [Cl^{-}]) \quad (2)$$

Given an estimate of ANC from eq. 2 (modelled or measured), the pH can be given by solving eq. 1 iteratively. In eq. 1, $[HCO_3^-]$ and $[CO_3^{2-}]$ are determined by pH and pCO_2 (Stumm and Morgan 1996). The $[A^-]$ is estimated from an organic acid model, given pH and TOC concentrations, where the acid moieties in TOC are treated as a tri-protic acid. To calculate the average charge (n) for Al, a full speciation is necessary. No measurements of Al-speciation are available for the study lakes, but it is possible, although complex, to model the speciation. The ion-balance can thus be divided in three separate components, each of them describing a buffering system.

The carbonate buffering system

The pCO_2 is in equilibrium with $[H_2CO_3]$:

$$[H_2CO_3] = K_H \cdot pCO_2 \quad (3)$$

The $[H_2CO_3]$ can then act as a proton donor:

$$[HCO_3^{-}] = K_1 \frac{[H_2CO_3]}{[H^+]} \quad (4)$$

$$[CO_3^{2-}] = K_2 \frac{[HCO_3^{-}]}{[H^+]} \quad (5)$$

At 25°C (temperature at analysis) the equilibrium constants are;
$pK_H = 1.47$; $pK_1 = 6.35$; $pK_2 = 10.33$

The constituents in the carbonate buffer system can thus be determined from pCO_2 and pH. However, pCO_2 is not routinely measured in the Swedish monitoring programs, and this is often the main source of uncertainty when modelling pH. The approach throughout this thesis has been to estimate pCO_2 from contemporary time series using eq. 1, given measurements of pH, alkalinity and TOC, and then model pH under a different scenario (for example, during pre-industrial conditions), assuming pCO_2 equal to the contemporary estimates. For pH-values much below pK_1 (below ~5.7), pCO_2 can not be estimated from contemporary measurements. Under such conditions, pCO_2 was instead estimated from the empirical relationship between TOC and pCO_2 found by Sobek et al. (2003).

The organic acid buffering system

A large proportion of the TOC consists of organic acids that constitute an important buffer system in many freshwater systems. A number of conceptual models have been used to describe the acid/base-properties of organic matter. One commonly used model treats TOC as a tri-protic acid (Driscoll *et al.* 1994). The *site density* (SD) defines how many acid functional groups are carried by each unit mass of TOC, i.e the total number of protons that can be released by the organic acid when completely dissociated. Each tri-protic acid contains three acid functional groups, so that the total moles of organic acid are one third of the total equivalents of acid sites:

$$[A]_{tot} = \frac{SD \cdot TOC}{3} \tag{6}$$

$[A]_{tot}$ is the total amount of organic acids in [mol/l], and is calculated by multiplying the SD by the TOC. $[A]_{tot}$ is then assumed to act as a tri-protic acid:

$$[H_3A] = \frac{[A]_{tot}}{1 + \frac{Ka_1}{[H^+]} + \frac{Ka_1 \cdot Ka_2}{[H^+]^2} + \frac{Ka_1 \cdot Ka_2 \cdot Ka_3}{[H^+]^3}} \tag{7}$$

$$[H_2A^-] = Ka_1 \frac{[H_3A]}{[H^+]} \tag{8}$$

$$[HA^{2-}] = Ka_2 \frac{[H_2A^-]}{[H^+]} \tag{9}$$

$$[A^{3-}] = Ka_3 \frac{[HA^{2-}]}{[H^+]} \tag{10}$$

In Papers I and III, the calibration by Köhler et al. (2000) was used, and in Paper IV, the calibration by Hruška et al. (2003) was used. The two calibrations give similar results (less than 0.05 pH-units difference). The SD value is 10.2 μeq/mg(TOC) for both calibrations. For Köhler et al., the pKa-values were:

$pKa_1 = 3.04$; $pKa_2 = 4.51$; $pKa_3 = 6.46$

For Hruška et al., the pKa-values were:

$pKa_1 = 3.04$; $pKa_2 = 4.42$; $pKa_3 = 6.70$

The aluminium buffering system

Buffering from aluminium becomes important during acid conditions (pH below ~5.3). The speciation of [Al] is complex and depends on many factors, primarily pH, [F$^-$], and [TOC]. Without measurements of Al-speciation, it instead has to be modelled, for example by using the chemical equilibrium model WHAM (Tipping 1994), calibrated to Swedish surface waters (Cory *et al.* 2007). The speciation of Al has been treated differently in the three papers where pH has been modelled. In Paper I, Al-concentrations were ignored, since the mean Al-concentrations were presumed to be very low for pre-industrial conditions. In Paper III, an empirical model between pH and the mean Al-charge (n) was used, based on a set of WHAM generated Al-speciation of 1815 observations. In Paper IV, a full Al-speciation was made using WHAM.

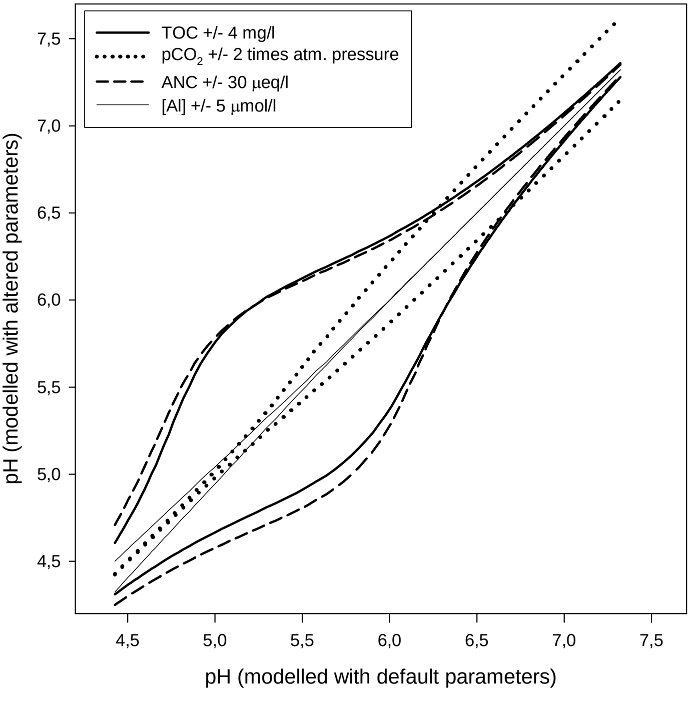

Figure 2: Sensitivity of pH-modelling to changes in TOC, ANC and Al-concentrations, and pCO2. The starting point was a TOC concentration of 8 mg/l, pCO_2 of 4 times equilibrium with the atmospheric value (1.27 matm), Al concentrations of 5 µmol/l and ANC concentrations ranging from -10 to 500 µeq/l, yielding pH-values between 4.4 and 7.3. While the other variables were kept constant, the TOC was changed by +/-4 mg/l, the pCO_2 by +/-2 times the atmospheric value, the ANC by +/-30 µeq/l, and the Al by +/- 5 µmol/l.

The sensitivity in pH of the different buffering systems depends on the pH-interval. The sensitivity for changes in ANC and TOC is largest for pH's between 5 and 6. Sensitivity of pCO_2 is small for low pH (<5.5), and fairly constant for pH above 6. The sensitivity of total Al concentrations is negligible for pH above 5.5, and fairly small even for lower pH (Fig. 2).

4.4 Environmental quality criteria – acidification assessments

To define the ecological status of surface waters with respect to acidification, it will not be sufficient to simply describe the present state of a water body (for example pH, buffering capacity or inorganic aluminium), without any consideration of the natural situation, since many lakes are naturally acidic (Wilander *et al.* 2003). To measure the "ecological status", as defined by the WFD, the present chemistry is compared to a reference value that describes the presumably natural, pre-industrial state. Thus, ecological status is a measure of the deviation from the natural state, as caused by human activities.

In the Swedish EQC, pH has been identified as the acidity variable to which biota show the strongest response (Fölster *et al.* 2007). The decision was therefore to let acidification assessments build upon pH, namely the difference between the reference pH (defined as the presumed natural, pre-industrial pH, pH_0) and the contemporary pH (pH_t) (SEPA 2007).

$$\Delta pH = pH_0 - pH_t \tag{11}$$

A lake can then be placed in 5 different classes with respect to their acidification status: Class 1: $\Delta pH < 0.2$. Class 2: $0.2 \leq \Delta pH < 0.4$. Class 3: $0.4 \leq \Delta pH < 0.6$. Class 4: $0.6 \leq \Delta pH < 0.8$. Class 5: $\Delta pH \geq 0.8$. Lakes in classes 3-5 ($\Delta pH \geq 0.4$) are defined as significantly acidified, and do not meet the criterion for good ecological status. Lakes in class 5 ($\Delta pH \geq 0.8$) are defined as severely acidified.

5 Results

5.1 An operational model for acidification assessments (Paper I, II)

The method proposed here to assess acidification ultimately relies on the accuracy of the MAGIC reconstructions. Even if MAGIC is a widely accepted model, there are uncertainties within the model, especially since regional applications demand many simplifications. Considering the lack of historical measurement data of water chemistry, it is difficult to validate the reconstructions of pre-industrial chemistry from MAGIC. A possibility to test the reliability of the MAGIC model is to compare it to a fundamentally different approach to reconstructing pre-industrial water chemistry, i.e. paleolimnology. In **Paper I**, two independent reconstructions of pre-industrial acidity in 55 Swedish lakes are compared, one using MAGIC (Moldan *et al.* 2004) and one using paleolimnology (Guhrén *et al.* 2003). The pre-industrial pH provided by MAGIC was calculated from ANC, with TOC concentrations equal to the median concentrations of 1997, and a uniform pCO_2 for all lakes equal to 0.63 matm. A different calibration of the tri-protic organic acid model by Hruška et al. (2001) was used. With these assumptions, pH_{MAGIC} fell into the pH_{Paleo} uncertainty interval of +/-0.3 units for 28 of 55 lakes. The median difference between the two reconstructions of pre-industrial pH ($pH_{MAGIC} - pH_{Paleo}$) was +0.23 units, i.e. MAGIC gave on average a higher estimate of pre-industrial pH than the paleolimnological method. As an alternative approach, the ANC from MAGIC can be converted to pH from eq. 1, using the long term contemporary means (1990-2004) of TOC concentrations and pCO_2, along with the tri-protic model for organic acids described by Köhler et al. (2000). With these assumptions, pH_{MAGIC} fell into the pH_{Paleo} uncertainty interval of +/-0.3 units for 43 of 55 lakes. The mean difference between pH_{MAGIC} and pH_{Paleo} was reduced by an order of magnitude to +0.03 units. The median *absolute* difference, $|pH_{MAGIC} - pH_{Paleo}|$, is 0.22 units, and hence, there are still considerable differences for the individual lakes. These are, however, mostly within the limits of uncertainty for the paleolimnological reconstructions, and the conversion from ANC_{MAGIC} to pH_{MAGIC}. The difference between the two sets of reconstructions was quantified by constructing a confidence interval for the mean difference in pH between the two models. The 95 % confidence interval for the mean difference between pH_{MAGIC} and pH_{Paleo} is: [-0.07, 0.13]. In other words, no significant differences between the two sets of reconstructions could be detected, provided lake specific estimates of TOC and pCO_2 equal to the contemporary long term means are used to convert the ANC given by MAGIC to pH.

With the satisfactory results from the comparison between MAGIC and the paleolimnological constructions in mind, the results from MAGIC were generalized by finding empirical relationships between easily measured parameters for contemporary conditions, and the pre-industrial ANC (ANC_0) estimated from MAGIC (**Paper II**). The result is a meta-model ($meta_{MAGIC}$) described by a regression equation, which aims to reproduce the pre-industrial estimates from MAGIC, but with far fewer input parameters. $Meta_{MAGIC}$ was calibrated for 95 Swedish lakes. In total, 18 parameters were tested as explanatory variables in $meta_{MAGIC}$, including contemporary lake chemistry, lake morphology, land use and regional climate parameters. By using stepwise multiple linear regression, the parameters with the highest correlations with pre-industrial ANC were selected. Since the relations between contemporary and pre-industrial chemistry change during the acidification/recovery-process, the equations of $meta_{MAGIC}$ will be specific to the year(s) used as input. To calibrate $meta_{MAGIC}$, median values from five years of observed water chemistry were used as contemporary data. $Meta_{MAGIC}$ was then calibrated for each year in the period 1990-2004. From the stepwise regression, the contemporary concentrations of [BC★], $[SO_4^{2-}★]$ and $[Cl^-]$ were identified as the best predictors of the pre-industrial ANC from MAGIC (★ denotes correction for sea-salt, (Umweltbundesamt 1996)). None of the lake morphology, land use or regional climate parameters could improve the r^2-values significantly. Stratifying the model by ecoregion or by buffering capacity did not improve the predictions either. With a squared term of [BC★] included, the resulting $meta_{MAGIC}$ equation became:

$$[ANC]_0 = b_1 \cdot [BC★]_t + b_2 \cdot [SO_4★]_t + b_3 \cdot [Cl^-] + b_4 \cdot [BC★]_t^2 + b_5 \qquad (12)$$

This model yielded r^2-values between 0.93 and 0.95 for the 15 calibration years 1990-2004. The median absolute error in predicted pre-industrial ANC for $meta_{MAGIC}$ (all years and lakes) was 13.2 µeq/l, when validated with the k-fold method (k = 19). An error in ANC of this size may result in an error in reference pH of up to approximately 0.4 units, in the most sensitive pH-interval. An advantage with $meta_{MAGIC}$ as an operational tool for acidification assessments is that it allows the reference values to vary in response to short term variations in surface water chemistry, and thereby may provide more stable assessments. This feature was examined by calculating time series of reference ANC from $meta_{MAGIC}$, with different time-spans of "centred" contemporary input data, from single measured values to 3-year medians. The stability of the parameter ΔANC, i.e. $ANC_0 - ANC_t$, was then calculated, using both time series of ANC_0 from $meta_{MAGIC}$, and a fixed ANC_0 from MAGIC, representing the pre-industrial long term mean. It was shown that for single measures of water chemistry, $meta_{MAGIC}$ gave a more stable, and on average also more accurate estimate of ΔANC, than a fixed reference value from MAGIC.

5.2 Variability in acidity on different time scales (Paper III, IV)

In order to examine the natural variability in pH during reference conditions, the time series of pH 1990-2004 were recreated for 95 Swedish lakes, as they would have been if there had been no anthropogenic acidification (**Paper III**). The approach was to reconstruct reference time series for each variable that affects pH, i.e. ANC, TOC, pCO_2 and [Al]. This was done by assigning a "baseline“ to each variable, presumably equal to the pre-industrial values. The baselines for ANC and [Al] were taken from the MAGIC simulations, whereas the mean pre-industrial TOC concentrations and pCO_2 were assumed equal to contemporary conditions. The variables were then varied around their baselines, on the basis of contemporary observations. Reference pH was then modelled from these reconstructed, "fictive", time series of ANC, TOC, pCO_2 and [Al]. The variability in reference pH was examined on seasonal (single measured values), interannual (1-year medians) and decadal (5-year medians) time scales. In the Swedish EQC, a decline from the reference pH by more than 0.4 units is defined as significant acidification. For single measured values, the range (between the 10th and the 90th percentile in the time series) in reference pH during the period 1990-2004 exceeded 0.4 units for all 95 lakes. If 5-year medians of reference pH are concerned, the range still exceeds 0.4 units for 12 of the 95 study lakes. The individual impact on variability in reference pH of each of the regulating variables ANC, TOC and pCO_2 was found to be of similar importance. To examine how the varying reference values affect the acidification assessments, ΔpH (eq. 11) was calculated for all time series, where the time series of contemporary pH was related to both a fixed reference pH, and the reconstructed variable reference pH. If pH has gone from a stable to an unstable pH-interval, the parameter ΔpH will be variable regardless whether the natural variability of the reference value is considered or not. If the pH is in a stable interval for both reference and contemporary conditions, ΔpH will be less variable if the variability of the reference value is considered. And finally, if pH has gone from an unstable to a more stable pH-interval, ΔpH will be more variable if the variability of the reference value is considered. Since seasonal fluctuations of reference pH exceeded 0.4 units (i.e. the criteria for significant acidification) for all the studied lakes, acidification assessments should be based upon longer term means of the contemporary chemistry. However, even if the chemistry is averaged over such a long time period as five years, the natural fluctuations of the reference pH may still be considerable.

Besides the presumed natural fluctuations in acidity, other factors may result in irreversible and substantial changes in natural acidity, such as the observed increase in TOC in many Swedish lakes during the last decades. Depending on the mechanism responsible for the TOC increase, this can be seen as either a delay in the recovery from acidification, or as a return to the natural state of organic acidity. In **Paper IV**, the impact of increased natural acidity from increasing TOC is examined for 24 acidified lakes, which had a TOC increase of at least 30 % between 1990 and 2006. Two alternative hypotheses were examined:

1) The acidification suppression scenario (AS-scenario): TOC was suppressed during the acidification phase and is now returning to its natural levels.

2) The climate change enhancement scenario (CCE-scenario): TOC is increasing to unprecedented levels due to some climatic factors.

For the AS-scenario, it was examined how much the suppression of TOC has buffered the acidifying deposition in terms of pH during the period of increasing acidification prior to 1990. TOC in 1990 was assumed equal to the concentrations of today (2006), and pH was modelled from eq. 1. For the CCE-scenario, today's TOC concentrations (2006) were assumed equal to the lower concentrations of 1990, and pH was then modelled to see how much the TOC increase since 1990 has delayed the recovery from acidification. The effects on pH due to changed concentrations of TOC were similar for the AS- and the CCE-scenarios. In the AS-scenario, the suppression of TOC would have buffered the decline in pH due to anthropogenic acidification by 0.30 units in median. In the CCE-scenario, the TOC increase set back the recovery by 0.29 units in median. Increasing TOC is also likely to increase pCO_2, as well as concentrations of BC and Al, all of which affect the pH. With the influence of these ancillary changes on pH considered, the median change in pH was 0.24 units for both the AS- and the CCE-scenarios. The largest effect on an individual lake was 0.80 units for the AS-scenario, and 0.74 units for the CCE-scenario. The effects on pH of increasing pCO_2 and [Al] accompanying higher TOC levels were small, and never affected the pH by more than 0.13 units. Increasing [Al] would however result in higher concentrations of inorganic forms of aluminium, which is toxic for biota. The effects of increased [BC] with TOC were small for most lakes in both scenarios, although it can reduce the effect from TOC by up to 0.5 units for individual lakes.

6 Discussion

6.1 Uncertainties in acidification assessments

In this thesis, an approach to define the reference status of a lake is suggested, as well as some of the difficulties associated with finding proper reference values. Each paper can be said to handle different sources of uncertainties when estimating a reference pH:

- Errors in the MAGIC simulations of pre-industrial chemistry. (**Paper I**).
- Errors when generalizing MAGIC into a meta-model that inevitably will arise from parameters that affect the relationship between pre-industrial and contemporary chemistry, but are not reflected in water chemistry data alone, such as soil thickness in the catchment (**Paper II**).
- Uncertainties due to natural variability in acidity on a shorter (seasonal to decadal) time scale, associated with limitations in the frequency and data record of sampled water chemistry (**Paper III**).
- Uncertainties associated with events that may change the chemical properties in the lake water irreversibly (for the foreseeable future), such as the observed increase of TOC concentrations over large parts of Sweden. This raises the question of what the natural state really is, and the outcome of an acidification assessment according to eq. 11 will be dependent on that decision (**Paper IV**).

6.2 Can the natural variability be captured in meta$_{MAGIC}$?

With all this error propagation, one may conclude that it will be impossible to achieve an estimate of anthropogenic acidification that is even remotely correct. However, one of the features of $\text{meta}_{\text{MAGIC}}$ is that it allows the natural variability to be reflected in the reference value, thereby reducing the errors associated with insufficient sampling frequency or length of data record. The error introduced when replacing MAGIC with a meta-model is then partly compensated.

If the simulated time series of pre-industrial ANC ($\text{ANC}_{0,\text{sim}}$) in Paper III are assumed to be the "true" reference level for ANC for 1990-2004, they can be compared to the time series generated from $\text{meta}_{\text{MAGIC}}$ ($\text{ANC}_{0,\text{meta}}$). The median RMSE for the 95 lakes when $\text{ANC}_{0,\text{sim}}$ and $\text{ANC}_{0,\text{meta}}$ are compared is 16.8 µeq/l. If $\text{ANC}_{0,\text{sim}}$ instead is compared to the fixed reference value $\text{ANC}_{0,\text{MAGIC}}$, the median RMSE is 20.9 µeq/l, and hence, the error introduced when replacing MAGIC with $\text{meta}_{\text{MAGIC}}$ is compensated by the reflection of the natural variability in $\text{meta}_{\text{MAGIC}}$. However, if long term water chemistry data are available, a full MAGIC reconstruction is still preferable to $\text{meta}_{\text{MAGIC}}$. For 1-year medians, the median RMSE for $\text{meta}_{\text{MAGIC}}$ is 15.0 µeq/l and for MAGIC it is 13.0 µeq/l. For 5-year medians, the median RMSE for $\text{meta}_{\text{MAGIC}}$ is 13.5 µeq/l and for MAGIC it is 6.4 µeq/l.

We can then go on to consider acidification assessments according to the Swedish EQC. ΔpH (eq. 11) was calculated with three different reference pH values:

1) The simulated time series of reference pH from Paper III ($\text{pH}_{0,\text{sim}}$), which are assumed to be the "ideal" reference value against which contemporary pH is measured.

2) Time series of pH_0 from $\text{meta}_{\text{MAGIC}}$ ($\text{pH}_{0,\text{meta}}$).

3) A fixed reference value, modelled from $\text{ANC}_{\text{MAGIC}}$ and contemporary long term means of TOC and pCO_2 ($\text{pH}_{0,\text{MAGIC}}$).

All observations were then classed with respect to "good ecological status" (i.e $\Delta\text{pH} < 0.4$) according to the criteria in the Swedish EQC. In these, aluminium is ignored, since there are no empirical methods to determine reference values for Al. Hence, the whole cation deficit in eq. 1 is assumed to be $[\text{H}^+]$-ions.

When single measurements are considered, $\text{meta}_{\text{MAGIC}}$ gives a correct assessment for 87 % of the 5052 lake chemistry observations from 1990-2004. In comparison, if a fixed reference pH is used, the assessment will only be correct for 79 % of the observations. Furthermore, the bias is considerable when using a fixed reference pH. The assessment will overestimate the acidification for 16 % of the observations, and underestimate acidification for only 5 % of the observations. For 1-year medians, both sets of assessments are equivalent, with 88 % of the observations correctly classed. However, assessments with the fixed reference value will still be more biased towards overestimation of acidification. When going up to 5-year medians, the variability is not enough to compensate for the errors in meta$_{\mathrm{MAGIC}}$, and the fixed reference value from MAGIC will be superior, with 94 % correctly classed observations, compared to 87 % for meta$_{\mathrm{MAGIC}}$ (Fig. 3).

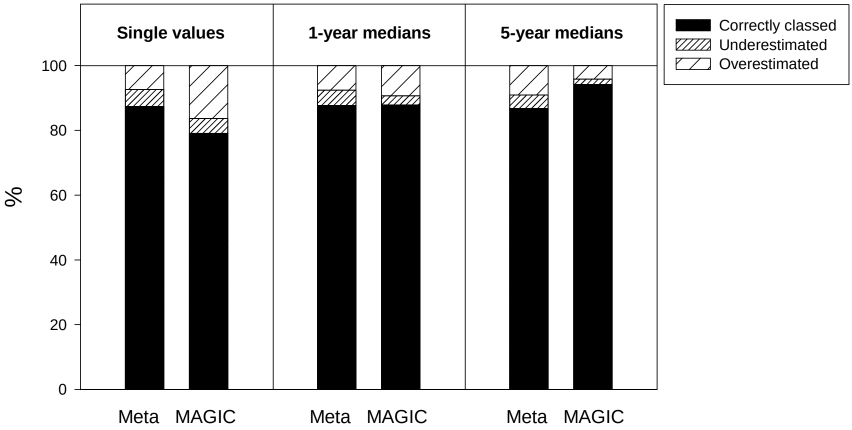

Figure 3: Acidification assessments according to the Swedish EQC for 95 lakes, 1990-2004, using a variable reference pH from meta$_{\mathrm{MAGIC}}$ and a fixed reference pH from MAGIC. The black bars represent correctly classed observations, fine grid bars represent underestimation of acidification, and coarse grid bars represent overestimation of acidification.

6.3 Effects of increasing TOC on reference pH

In **Paper IV** it is demonstrated how changing TOC-levels have affected acidification, either by buffering during the acidification phase, or by delaying the recovery from acidification. Changes in TOC will also have a profound impact on what state can be considered “natural”, and are likely to change the targets for the recovery from acidification. In the lakes where TOC is increasing, it will not be possible to reach the goals for acidity posed 20 years ago when TOC levels were generally lower.

So, how much does the reference pH differ, depending on the reference level selected for TOC? Reference pH was modelled for the same 24 lakes as in **Paper IV**, using TOC levels equal to those of 1990 and 2006 respectively. Mean values of pre-industrial ANC and [Al] were taken from the MAGIC reconstructions (Moldan *et al.* 2004), whereas all other parameters needed to model pH were assumed equal to the long term mean contemporary conditions (1990-2006). Furthermore, ancillary changes of [BC], pCO_2 and [Al] were treated in the same way as in **Paper IV**. The pre-industrial values for these were assumed to correspond to the mean TOC concentrations, i.e. $(TOC_{90} + TOC_{06})/2$. When adjusting these constituents to the lower (from 1990) or higher (from 2006) TOC, half the difference between TOC_{90} and TOC_{06} was therefore accounted for.

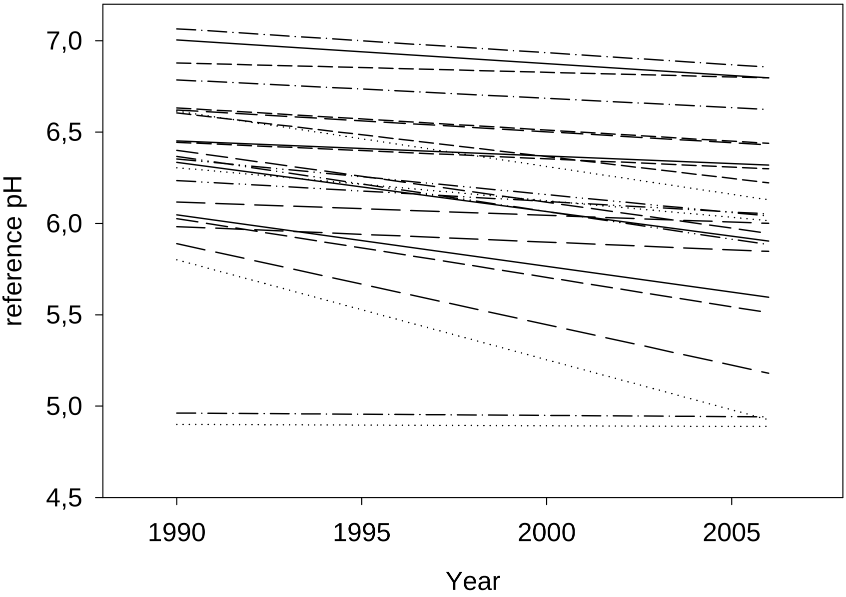

Figure 4: Reference pH modelled for 24 lakes with increasing TOC, 1990-2006, with ancillary changes in pCO_2, ANC and BC included.

With TOC levels equal to those in 1990, and pre-industrial levels of pCO_2, [Al] and ANC adjusted to this lower TOC, the range in reference pH was from 4.8 to 7.1, with a median of 6.4. With TOC levels equal to those in 2006, and pre-industrial levels of pCO_2, [Al] and ANC adjusted to the higher TOC, the range in reference pH was from 4.6 to 6.9, with a median of 6.0. Reference pH with TOC levels equal to 2006 are between 0.08 and 0.98 units lower than reference pH with TOC levels equal to 1990, and 0.22 units lower in median (Fig. 4).

Acidification assessments according to the Swedish EQC differ considerably between the two alternative TOC scenarios. With the lower TOC concentration used for setting the reference value, 21 of the 24 study lakes were significantly acidified ($\Delta pH \geq 0.4$) in 1990, and 14 of them were severely acidified ($\Delta pH \geq 0.8$). By 2006, the degree of acidification had decreased so that 7 remained significantly acidified, and only 1 lake severely acidified. If instead reference pH is calculated with higher TOC levels, only 15 of the lakes were significantly acidified in 1990, and 7 were severely acidified. By 2006, 3 of the lakes were significantly acidified in 2006, none of them severely (Fig. 5). This dramatic revision may reopen some questions about natural acidity raised over a quarter of a century ago that were generally discredited (Rosenqvist 1977, Krug and Frink 1983).

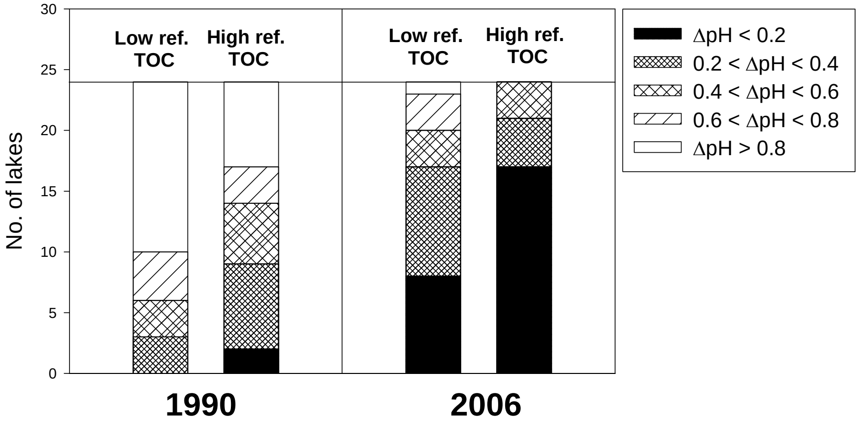

Figure 5: Acidification assessments of the 24 study lakes for 1990 (left) and 2006 (right), using reference TOC equal to 1990 (low ref. TOC) and equal to 2006 (high ref. TOC).

In **Paper III**, the variability in reference values for pH on seasonal, annual and decadal time-scales was discussed. Where that study was focused on "reversible" variations in reference pH, changing reference levels due to increasing TOC is in one sense "irreversible", in that the reference levels can not be expected to return to their previous state in the foreseeable future. This will mean that if restoration targets for pH were set one or two decades ago with lower TOC levels, they will be impossible to reach in the near future (if ever) without extensive countermeasures (i.e. liming) that have to compensate for organic acidity increases.

Three distinctly different alternatives for TOC levels can be identified when defining reference conditions:

- The TOC levels in 1990 prior to the subsequent increase are chosen as the reference level. This implies that TOC concentrations are increasing due to some mechanism that was not present in the pre-industrial state, and that the "natural" TOC-levels are the ones prior to the post-1990 increase. This would be the case if N-deposition or some of the variables linked to global warming are responsible for the TOC-increase, i.e. increasing temperature and/or increasing atmospheric CO_2.
- The TOC levels after the 1990-2006 increase are chosen as the reference level. This corresponds to scenarios where TOC concentrations are assumed to be returning to a higher, "natural" level. This would be the case if acidification had suppressed TOC concentrations in surface waters. This alternative would result in a major reassessment of acidification that would significantly reduce the extent of acidification in S. Sweden (Fig. 5). A complication here is that we do not yet know the final level to which TOC will recover since no attenuation in the rate of increase has been observed so far.
- Reference values for TOC concentrations are allowed to follow the observed, contemporary increase. This may be appropriate for reversible TOC changes such as the interannual fluctuations in runoff associated with "normal" climatic variability. But it is doubtful that this is appropriate for the 1990-2006 increase since most of the hypothesized reasons for the decadal trend were not present in the pre-industrial reference state. Furthermore, it will also lead to pedagogical problems. Some lakes would then in theory have recovered from acidification without any observed increases in pH, but merely due to decreasing reference pH associated with rising contemporary levels of TOC.

Of course, a fourth possibility may well be the most correct one, i.e. a combination of all three alternatives. Since there are studies that support both the AS- and the CCE-scenarios, the observed increases in TOC may be due to a combination of decreased acidifying deposition and a changed climate, so the reference levels would be somewhere between the levels observed in the 80s and the levels seen today. In addition, the signal might be enhanced by natural variations, for example hydrology, which should be reflected in the reference levels.

If the influence on TOC from athmospheric deposition, temperature, runoff, etc. can be described and quantified, it should also be possible to better define the reference state. In addition, much progress has been made recently in reconstructing reference levels of TOC with paleolimnological techniques (Rosén 2005, Rosén and Hammarlund 2007). However, which level of TOC to choose as a reference may not be a question only for the scientific community, but just as much for policy makers. Even if the lower TOC-concentrations observed during the 1980s actually describe the natural state, it may not be feasible to choose this as a reference value, since it may result in a target for pH that is impossible to reach with the present elevated TOC levels. Such conundrums are likely to become more common in many aspects of water resource management as climate change and associated changes in land use alter the amount and chemistry of runoff.

7 Main Conclusions

- The MAGIC reconstructions used to define pre-industrial chemistry throughout this thesis proved consistent with a set of paleolimnological reconstructions of pre-industrial pH for 55 of the study lakes, provided that lake specific estimates of TOC concentrations and pCO_2 were used.
- From the results of a regional application of MAGIC, it was possible to create a simplified meta-model ($\text{meta}_{\text{MAGIC}}$), which uses only measurements of contemporary water chemistry to predict the acidity of lakes in the pre-industrial period. $\text{Meta}_{\text{MAGIC}}$ reproduced the pre-industrial ANC from MAGIC with a median error of 13.2 µeq/l (8 %), when calibrated for 95 Swedish lakes. An error of this size may cause an error of up to approximately 0.4 pH-units in the most sensitive pH-interval.
- The natural variability of lake pH causes reference values for pH to vary by at least 0.4 pH-units on a seasonal basis, during a 15 year period in 95 Swedish lakes. For 12 of the lakes, variability exceeded 0.4 units, even when using 5 year medians of reference pH.
- The natural variability can be accounted for to some extent by using $\text{meta}_{\text{MAGIC}}$ as a tool for acidification assessments. The prediction error in $\text{meta}_{\text{MAGIC}}$ is thereby compensated for, at least when using one year or less of contemporary data to estimate pre-industrial conditions.
- In many Swedish lakes, increasing concentrations of TOC since 1990 has lowered pH. Depending on which mechanisms are responsible, the TOC increases may either be seen as a return to the natural state, or as a disturbance that sets back the recovery from acidification. In 24 lakes with a TOC increase of 30-140 % between 1990 and 2006, the median decrease in pH due to increasing TOC was 0.24 units.

- Changing levels of TOC will have a profound impact on acidification assessments, depending on which concentrations of TOC are chosen as the reference level.

Svensk sammanfattning

Tack vare betydande minskningar av försurande nedfall har tidigare försurade vatten i Sverige börjat återhämta sig under de senaste 15-20 åren. Ur många aspekter är försurningen ett åtgärdat miljöproblem, men det återstår fortfarande många goda anledningar att studera försurningsprocesserna. Dels kan faktorer som ökat uttag av biomassa i skogsbruket, kvävemättnad i markerna, och klimatförändringar orsaka återförsurning. Dels så ställs idag i och med de svenska miljömålen, och EU´s ramdirektiv för vatten, högre krav på en exakt bedömning av försurning, och det har saknats pålitliga modeller för försurningsbedömning som kan användas rutinmässigt. De erkända metoder som finns, dynamisk modellering och paleolimnologiska rekonstruktioner, är komplexa, kräver mycket indata, samt är svåra att använda. I den här avhandlingen utvecklas en meta-modell, som bygger på resultat från den dynamiska hydrogeokemiska modellen MAGIC (Model of Acidification of Groundwater in Catchments). Idén med meta-modellen ($\text{meta}_{\text{MAGIC}}$) är att finna korrelationer mellan nutida vattenkemi och den förindustriella vattenkemin predikterad av MAGIC. Med $\text{meta}_{\text{MAGIC}}$ kunde förindustriellt ANC (Acid neutralizing capacity) enligt MAGIC predikteras med ett medianfel av 13,2 μekv/l, när modellen kalibrerades för 95 svenska sjöar. Denna metod för försurningsbedömning förlitar sig i grund och botten på MAGIC´s tillförlitlighet. För att stärka denna jämfördes MAGIC´s rekonstruktioner av förindustriell kemi med paleolimnologiska rekonstruktioner av förindustriellt pH för 55 sjöar. De båda metoderna var konsistenta (medeldifferens 0,03 pH-enheter). För enskilda sjöar fanns ibland betydande skillnader (medeldifferens i absoluta tal var 0,22 pH-enheter), men dessa rymdes oftast inom felmarginalen för de paleolimnologiska rekonstruktionerna (+/- 0,3 pH-enheter), eller inom osäkerheterna för förindustriella värden av TOC-koncentrationer (totalt organiskt kol) och partialtryck av CO_2.

En komplikation vid bedömning av miljöproblem i allmänhet, och försurning i synnerhet, är att surhetsparametrar är variabla på alla tidsskalor, allt ifrån timmar till årtusenden. Att definiera det naturliga tillståndet för en sjö är därför ingen enkel uppgift. Den naturliga variabiliteten i pH kan jämföras med de gällande kriterierna för försurning i de svenska bedömningsgrunderna, nämligen en avvikelse i pH från det naturliga tillståndet på mer än 0,4 pH-enheter. I avhandlingen har tidsserier av referensvärdet för pH (det förmodade ”naturliga” pH-värdet) rekonstruerats från 1990 till 2004 för 95 svenska sjöar. Säsongsvariabiliteten i pH överskred 0,4 pH-enheter i samtliga sjöar. Även över längre tidsskalor (medianvärden över 5 år) överskred ofta variabiliteten 0,4 pH-enheter (för 12 av 95 sjöar). Ett annat exempel på variabilitet i referensvärden är de ökande halterna av organiska syror som observerats, både i Sverige och i andra delar av Nordeuropa och Nordamerika. Beroende på vilken orsak som ligger bakom får detta olika implikationer vid bedömning av försurning. En teori är att TOC är mindre lösligt under försurningsfasen, och att den observerade ökningen under återhämtningen är en återgång till det naturliga tillståndet. En annan teori är att klimatförändringar stimulerar ökad produktion av TOC, och att TOC därmed har ökat till högre koncentrationer än de naturliga. I avhandlingen har påverkan på pH från ökande TOC undersökts i 24 sjöar med minst 30 % ökning i TOC mellan 1990 och 2006. För dessa har TOC-ökningen sänkt pH med en median av 0,24 enheter, och upp till 0,80 enheter. Resultatet av försurningsbedömningar baserade på avvikelse i pH kommer att vara starkt beroende av vilket antagande som görs angående de naturliga TOC-koncentrationerna. Sammanfattningsvis så presenteras i denna avhandling en metod ($\text{meta}_{\text{MAGIC}}$) som kan användas vid försurningsbedömning, och som också till viss del kan uppfånga den naturliga variabiliteten. Andra aspekter vid försurningsbedömningen, som vilken TOC-koncentration som ska användas som referensnivå, kräver dock noggranna överväganden, och är lika mycket en policyfråga som ett vetenskapligt problem.

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