NOTICE: this is the author's version of a work that was accepted for publication in *Applied Geochemistry*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Applied Geochemistry* **35**, 221-229, 2013. <http://dx.doi.org/10.1016/j.apgeochem.2013.04.014>

Modelling of pH and inorganic aluminium after termination of liming in 3 000 Swedish lakes

Carin Sjöstedt^{a,*}, Cecilia Andrén^b, Jens Fölster^c and Jon Petter Gustafsson^{a,d}

^a Department of Land and Water Resources Engineering, KTH Royal Institute of Technology, Teknikringen 76, SE-100 44 Stockholm, Sweden.

^b Department of Applied Environmental Science, Stockholm University, 106 91 Stockholm, Sweden.

^c Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Box 7050, 750 07 Uppsala, Sweden.

^d Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, 750 07 Uppsala, Sweden.

*corresponding author, Present address: Department of Chemistry, Surface chemistry, KTH Royal Institute of Technology, Dr. Kristinas väg 51, SE-100 44 Stockholm, Sweden. Tel.: +46-8-790 99 26 E-mail address: carinsj@kth.se (C. Sjöstedt)

Editorial handling by M. Kersten

Abstract

Significant resources are spent on counteracting the effects of acidification, mainly by liming. Due to lower S and N deposition in Europe and North America, authorities are changing directives and strategies for remediation and reducing liming. However, as the acid-base buffer capacity differs in different water bodies, the desirable reduction of the lime dose is variable. In this study, a geochemical model is used to predict pH and inorganic monomeric Al (Al_i) when liming is reduced and finally terminated in the 3 000 Swedish lakes currently treated with lime. To estimate Ca and Mg concentrations not affected by liming for use in the model, the Ca/Mg ratio in nearby unlimed reference lakes was used. For the

modelling of pH and inorganic Al the Visual MINTEQ program including the Stockholm Humic Model recently calibrated for Swedish fresh water was used. The predictions were validated with modelling results from six monitored lakes, in which liming had been terminated. The use of geochemical modelling appeared to be a promising tool for the calculation of accurate lime requirements in acid waters. For simulations in which liming was completely terminated, the pH value decreased by, on average, 1 pH unit to pH 5.7, whereas Al_i increased from $17 \mu g L^{-1}$ to $32 \mu g L^{-1}$. If liming was reduced by half, the pH would drop only 0.3 pH units and Al_i would increase by $2 \mu g L^{-1}$. Lakes in the south-western part of Sweden were predicted to reach a lower pH and higher Al_i , which would be expected due to their greater historical S deposition. The results indicate that liming can be terminated in certain areas and in other areas be reduced without increases in the lake acidity.

1. Introduction

The effects of acidification peaked in the 1980s and the chemistry of many fresh waters has recovered since the 1990s in Europe and North America, but it still remains a problem in some areas and the recovery of the biosphere is more uncertain (Stoddard et al., 1999; Skjelkvåle et al., 2005). Furthermore, in other regions acidification is an increasing problem, e.g. in China (Larssen et al., 2006). Low pH and high inorganic monomeric Al (Al_i) concentrations reduce overall biodiversity and cause fish death (Gensemer and Playle, 1999). One remediation action for waters is to lime to increase the pH and decrease Al_i . However, liming is costly and might damage wetlands. The anthropogenic S emissions in Europe and USA were reduced between 1980 and 2010, while they increased in China and India during the same time period (Granier et al., 2011). The emissions of N started to decrease in the 1990s in Europe and the USA, but since the 1980s they have increased in China and India (Granier et al., 2011). Even though emissions have decreased in Europe and USA the acid neutralizing capacity (ANC) can still be too low locally to allow termination of liming. The cost for liming in Sweden is 208 million SEK (25 million euros; 32 million U.S. dollars) annually (Swedish Environmental Protection Agency, 2011). The knowledge of when and where liming can be reduced or terminated, therefore, has an economic incitement and cost-effective approaches are currently being sought. The Swedish liming targets, based on empiric observations of damage to biota, are to keep the pH above 5.6 and Al_i below $50 \mu g L^{-1}$ in brown trout (*Salmo trutta* L.) waters, and pH above 6.0 and Al_i below $30 \mu g L^{-1}$ in salmon (*Salmo salar*) waters (Swedish Environmental Protection Agency, 2010) in the

whole water body all of the time. This is monitored for lakes at least once a year during spring flood with one sample from the surface water in the middle of the lake.

One group of methods that is becoming increasingly used for scenario simulations of water chemistry involves the use of state-of-the-art geochemical equilibrium models. Different geochemical models have been developed that are capable of modelling pH and Al_i , which are the main toxic factors in acidified waters. Examples of models include WHAM (Tipping 1994, 1998), recently tested by Tipping and Carter (2011); the ALCHEMI model (Schecher and Driscoll, 1995) including different organic acid models (Driscoll et al., 1994); and a triprotic organic acid model (Hruška et al., 2003). Predicting what will happen with less added lime requires a model that can simulate pH and Al fractions simultaneously. Sjöstedt et al. (2010) presented such a model, which was calibrated and validated for pH and Al_i (as determined by the cation exchange method of Driscoll, 1984) on a large data set of Swedish lakes and streams.

The steady-state concentration of Ca when liming is terminated is needed for modelling pH. One approach involves the use of the Ca to Mg ratio in unlimed waters upstream or in nearby unlimed reference lakes (Göransson et al., 2006). This is possible since the Ca to Mg ratio is relatively stable both temporally and spatially. The Ca to Mg ratio in the limed lake after termination of liming is assumed to be the same as the one in the reference lake. Hence, the steady-state “unlimed” Ca concentrations can be calculated from the Mg concentrations in the limed lake (Göransson et al., 2006), as lime only contains small amounts of Mg.

The aim of this study is to evaluate the use of a geochemical modelling method that predicts the response in pH and Al_i after a changed lime dose or after termination of liming. The model setup is validated for six monitored lakes where liming has been terminated. If successful, this would permit more precise calculations of the requirement for liming in the present situation, and thus optimise (and when possible reduce) liming. The method is applied on a survey of all limed Swedish lakes ($n = 3\,043$) and used to predict water chemistry for stepwise reduction of lime doses down to a complete termination of liming.

2. Methods

2.1 Data sets

The 3 043 limed Swedish lakes and 1 807 unlimed corresponding reference lakes in their vicinity were sampled once in the autumn of 2007 (between September 2007 and January 2008) and once in the spring of 2008 (between March and June). Collected, unfiltered

samples were analysed (procedures described by Fölster et al., 2011b). A subset from the unlimed reference lakes in spring 2008 was chosen for Al_i determinations. A representative collection with classes of pH (<4.5, 4.5 to 5, 5 to 5.5, 5.5 to 6), total organic C (TOC) (>5, 5-10, 10-20, >20 mg L^{-1}), and regions (south and north Sweden) (Fölster et al., 2011b) was chosen. The Al_i was fractionated by the cation exchange method of Driscoll (1984) and determined with pyrocatechol violet (the method is described in Andrén and Rydin, 2009). The detection limit for this method is 3 $\mu\text{g L}^{-1}$ Al and the coefficient of variation is 11 % for duplicate samples. Calcium, Fe, Al, Mn and pH displayed the largest difference comparing the limed lakes with the unlimed lakes. The measured and simulated values were relatively similar between autumn 2007 and spring 2008 (Table 1). Samples with one missing variable were excluded from further data treatment, so the exact number of lakes studied varies between 2007 and 2008 (Table 1).

For six lakes in which liming had been terminated, the effects on water chemistry of lime reductions were simulated and evaluated. The lakes consisted of two groups; one group where liming had been performed directly in the lake for the ten years prior to the final liming: L. Skifsen, L. Rådsjön and L. Geten. In the other lake group, lime had also been distributed upstream of the lake within the ten years prior to the final liming: L. Trehörningen, L. Långsjön (Tyresta), and L. Långsjön (Örebro) (Table 2). The change in water chemistry of L. Trehörningen and L. Långsjön (Tyresta) after termination of liming has been examined previously by Wällstedt et al. (2009).

2.2 Geochemical equilibrium model

The geochemical equilibrium model used was the same as the one calibrated in Sjöstedt et al. (2010), which uses the Visual MINTEQ software (Gustafsson, 2012) with equilibrium equations for all relevant chemical species. The model was calibrated for pH as described in Sjöstedt et al. (2010) for the subset ($n = 322$) of the unlimed reference lakes. Briefly, the pH was simulated by an iterative approach from the charge balance for the cations Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{3+} , Al^{3+} , Mn^{2+} ; versus the anions SO_4^{2-} , Cl^- , F^- , inorganic C (mainly HCO_3^-) as well as organic acids. Fluoride was included because it is important for Al speciation, but its effect on the charge balance was low. Silicic acid was also included in the model, and was estimated to be 0.1 mmol L^{-1} in all lakes, as no data were available. The average value for silicic acid in the National Lake Survey 2000 (Wilander, 2003) was 0.06 mmol L^{-1} . However, this concentration is not critical for modelling of pH and Al_i . Nitrate was not included since,

generally, it was present in low concentrations and has no effect on the Al^{3+} speciation. Measured values were used directly, with the exception of inorganic C and organic acids for which some assumptions had to be made. For inorganic C the relationship between dissolved organic C (DOC) and pCO_2 proposed by Sobek et al. (2003) for open lakes in Sweden was used:

$$\text{pCO}_2 = (1.079 \cdot \text{DOC} + 2.332) \cdot 10^{-4} \quad (1)$$

where pCO_2 is the partial pressure of CO_2 in the lake in atmospheres and DOC is the measured DOC concentration in mg L^{-1} . The determined concentrations of TOC (total organic C) were used as estimates for DOC, since they differ by less than 5 % in Fennoscandian boreal waters (Gadmar et al., 2002). Equation 1 may be less valid for limed lakes with residual CaCO_3 in the sediment, but the aim was to predict the situation with no added lime for which the equation should be more valid.

The charge equivalents of organic acids were modelled with the Stockholm Humic Model (SHM) (Gustafsson, 2001) incorporated in Visual MINTEQ. The fraction of active dissolved organic matter (DOM) was calibrated to be 82.5 % of the total DOM, assuming that the organic matter contained 50 % C by weight.

The Al_i was also simulated with Visual MINTEQ, and there was a clear and significant relationship between analysed and simulated Al_i ($r^2 = 0.87$). However, there was a small systematic error with lower concentrations of simulated Al_i compared to the analysed contents. A correction function was, therefore, introduced:

$$\text{Al}_i\# = 12.4 + 1.10 \cdot \text{Al}_{i\text{MOD}} \quad (2)$$

where $\text{Al}_i\#$ is the corrected simulated concentration of Al_i in $\mu\text{g L}^{-1}$ and $\text{Al}_{i\text{MOD}}$ is the simulated concentration in $\mu\text{g L}^{-1}$ by Visual MINTEQ (Sjöstedt et al., 2010). Eq. 2 sets the lowest simulated Al_i concentration to $12.4 \mu\text{g L}^{-1}$.

2.3 Model scenarios

The model needed background steady-state concentrations of Ca and Mg not affected by liming. The method used to estimate these values was based upon the Ca to Mg ratio in unlimed reference lakes upstream or within 20 km of the limed lakes. This method relies on the assumption that Ca and Mg have similar chemical properties and, therefore, co-vary in time and space (Göransson et al., 2006; Fölster et al. 2011a). During liming the Ca to Mg ratio increases, as lime has a higher Ca to Mg ratio than lake water. Therefore, to calculate

the steady-state Ca concentration for the unlimed condition, the Ca to Mg ratio has to be adjusted in the limed lake to the ratio of the reference lake. The Mg concentrations also need adjustment because of the Mg content of lime. Data on Mg content of the different liming agents used was reported from the local county boards and a weighted three year average was calculated according to Fölster et al (2011b).

Thus for lakes subject to liming, the following three equations can be used to calculate the steady-state concentrations of Ca and Mg after termination of liming (Fölster et al., 2011a). Eq. 3 calculates a preliminary value of $Ca^{2+}_{unlimed}$, which is adjusted in Eq. 5 to compensate for the lime-added Mg. Eq. 3 to 5 are repeated iteratively until a stable value is reached.

$$[Ca^{2+}]_{unlimed, pre} = [Mg^{2+}]_{meas} \cdot \left(\frac{[Ca^{2+}]}{[Mg^{2+}]} \right)_{ref} \quad (3)$$

$$[Mg^{2+}]_{unlimed} = [Mg^{2+}]_{meas} - \left(\frac{[Mg^{2+}]}{[Ca^{2+}]} \right)_{lime} \cdot ([Ca^{2+}]_{meas} - [Ca^{2+}]_{unlimed, pre}) \quad (4)$$

$$[Ca^{2+}]_{unlimed} = [Mg^{2+}]_{unlimed} \cdot \left(\frac{[Ca^{2+}]}{[Mg^{2+}]} \right)_{ref} \quad (5)$$

where $[Ca^{2+}]_{unlimed}$ and $[Mg^{2+}]_{unlimed}$ are the projected steady-state concentrations of Ca and Mg after termination of liming, $([Ca^{2+}]/[Mg^{2+}])_{ref}$ is the ratio of Ca to Mg in nearby unlimed reference lakes, $[Ca^{2+}]_{meas}$ and $[Mg^{2+}]_{meas}$ are the measured concentrations (in the limed lake), whereas $([Mg^{2+}]/[Ca^{2+}])_{lime}$ is the weighted average of the ratio in the liming agents used for the lake or in the catchment of the lake.

For the limed lakes, pH and Al_i at “unlimed” conditions were predicted using values of Ca and Mg as calculated from Eq. 4 and 5 ($[Ca^{2+}]_{unlimed}$ and $[Mg^{2+}]_{unlimed}$). For spring 2008 model predictions of what would happen if liming was decreased in a step-wise manner were also performed, with progressively lower and lower concentrations of Ca and Mg. The concentrations of added Ca and Mg from lime were decreased from 100 % (determined levels for the present situation) down to 75 %, 50 %, 25 % and 0 % (calculated “unlimed” concentrations). These Ca and Mg concentrations were calculated according to:

$$[Ca^{2+}]_{x \% limed} = ([Ca^{2+}]_{meas} - [Ca^{2+}]_{unlimed}) \cdot x + [Ca^{2+}]_{unlimed} \quad (6)$$

where $[Ca^{2+}]_{x \% limed}$ is the concentration of Ca^{2+} (or correspondingly Mg^{2+}) at x % of lime additions, $[Ca^{2+}]_{meas}$ is the measured Ca concentration in the limed lake, $[Ca^{2+}]_{unlimed}$ is the calculated concentration after termination of liming according to Eq. 5 and x is in %.

To obtain evidence for the applicability of the model, the six lakes with monitored termination of liming were studied. The month with the highest Ca/Mg ratio after liming was chosen as the start month and simulated for pH and Al_i (for L. Skifsen the Ca concentration was estimated from previous years just after liming, Table A1). Then the “unlimed” Ca and Mg concentrations were calculated in the same way as for the larger data set and the pH and Al_i were predicted with 75 %, 50 %, 25 % and 0 % lime. The month when the Ca and Mg concentrations would reach these ratios was calculated based upon lake retention time according to:

$$\left(\frac{[Ca^{2+}]}{[Mg^{2+}]}\right)_{x\% \text{ limed}}(t) = \left(\frac{[Ca^{2+}]}{[Mg^{2+}]}\right)_{\text{ref}} + \left(\left(\frac{[Ca^{2+}]}{[Mg^{2+}]}\right)_{\text{meas}} - \left(\frac{[Ca^{2+}]}{[Mg^{2+}]}\right)_{\text{ref}} \right) \cdot \exp\left(\frac{-t}{t_{\text{ret}}}\right) \quad (7)$$

where $([Ca^{2+}]/[Mg^{2+}])_{\text{ref}}$ is the concentration ratio in the unlimed reference lake, t is the time after liming, t_{ret} is the retention time of the lake in years and $(Ca/Mg)_{\text{meas}}$ is the largest measured ratio in the limed lake (i.e., during the start month). The lakes were assumed to have reached the x % lime level when both sides of Eq. 7 were equal. A comparison was then made between the predicted and analysed values of pH and Al_i for that month. It is important to note that Eq. 7 assumes that the influent water will have a consistent composition of $([Ca^{2+}]/[Mg^{2+}])_{\text{ref}}$. This may be incorrect when the wetlands and upstream lakes in the catchments have been limed. Also potential residues of undissolved lime in the sediment may result in higher Ca/Mg ratios in the lake than predicted by Eq. 7 (Wällstedt et al., 2009).

It should be noted that for a small number of lakes of the larger data set sampled in 2007/2008 the calculated “unlimed” concentrations for Ca (2007: $n = 6$, 2008: $n = 66$) and Mg (2007: $n = 7$, 2008: $n = 69$) were higher than the measured values.

The pH value was simulated for all lakes at limed conditions and also for the unlimed reference lakes (excluding the calibration data set) to validate the model. The Al_i was also predicted with analysed pH data for all 4 850 lakes at present conditions; Al_i was also predicted with simulated pH values, to be able to compare the predictions of Al_i using both analysed and simulated pH values.

3. Results

Initially, the model of Sjöstedt et al. (2010) was tested to see how well the water chemistry in the six monitored lakes with terminated liming could be simulated. For the initial limed situation, there was a very good correspondence between simulated and analysed

pH (mean error 0.07 pH units, $r^2 = 0.95$, $P < 0.001$, $n = 6$) (Table A1). Unfortunately, there was only one lake with analytical results for Al_i available before liming was discontinued. The simulated Ca and Mg concentrations (based on Eq. 7) generally agreed with analysed concentrations for the 75, 50, and 25 % lime additions in lakes limed on the lake surface for the previous 10 years (Fig. 1a and b). More importantly, pH and Al_i were simulated very well (mean error 0.19 pH units, $r^2 = 0.66$, $P = 0.01$, $n = 8$; mean error Al_i 10.6 $\mu\text{g L}^{-1}$, $r^2 = 0.81$, $P = 0.006$, $n = 7$) (Fig. 1c and d, Table A1). However, for lakes with recent upstream liming; predicted Ca and Mg concentrations were too low for the 75, 50, 25 and 0 % of the lime additions (Fig. 1a and b; Table A1). This was not surprising since the inflowing water probably had a higher Ca to Mg ratio than the unlimed reference value. Consequently, the model often produced pH that was too low and Al_i that was too high (mean error 0.66 pH units, $r^2 = 0.41$, $P = 0.03$, $n = 11$; mean error Al_i 20.5 $\mu\text{g L}^{-1}$, if excluding one outlier: $r^2 = 0.94$, $P < 0.001$, $n = 8$) (Fig. 1c and d, Table A1).

Then the model of Sjöstedt et al. (2010) was applied to the 3 043 presently limed lakes as well as the 1 485 unlimed reference lakes (excluding the calibration data set for spring 2008). There was a close relationship for the limed lakes (2007: $r^2 = 0.80$ $P < 0.001$, 2008 $r^2 = 0.82$, $P < 0.001$) and the unlimed lakes (2007: $r^2 = 0.93$, $P < 0.001$, 2008: $r^2 = 0.94$, $P < 0.001$) between analysed and simulated pH values for all lakes (spring 2008, Fig. 2) and a total mean error of 0.17 pH units (Table 1). The simulations of Al_i were of similar quality for the limed lakes, regardless of whether analysed pH or simulated pH were used in the model (Table 1). However, there was a small difference for the unlimed reference lakes, where for simulations with analysed pH the mean Al_i concentration was about 5 $\mu\text{g L}^{-1}$ higher than with simulated pH (Table 1). This indicates that modelled pH can be used together with estimated Ca and Mg concentrations to predict Al_i . The predicted average value of Al_i with analysed pH for the limed lakes was around 14 $\mu\text{g L}^{-1}$, i.e. just above the model's lowest simulation limit at 12.4 $\mu\text{g L}^{-1}$ (Table 1). One to 3% of the limed lakes had predicted Al_i concentrations exceeding 30 $\mu\text{g L}^{-1}$.

When using the predictions of the calculated “unlimed” concentrations of Ca and Mg (i.e., the steady-state concentrations after simulated terminated liming) for all the limed lakes to predict pH; pH was lowered by, on average, 1.02 units (2007) and 0.92 units (2008) compared to the simulated original situation (Table 3 and Fig. 3a and e). The predictions were very similar for both samplings regarding how many lakes had a pH above 6.0: 1 101 lakes in 2007 and 1 202 in 2008 and out of them 968 lakes had a pH above 6.0 in both

samplings. For 39 % of the lakes, the pH was calculated to be below 5.6. The Al_i was increased by on average $17 \mu g L^{-1}$ up to an average of $32 \mu g L^{-1}$. Thirty-six per cent of the lakes had Al_i concentrations above $30 \mu g L^{-1}$.

The decrease in pH and the associated increase in Al_i were very different for different lakes, as the range of individual pH and Al_i changes was 3 pH units and $450 \mu g L^{-1} Al_i$, respectively. There was a clear geographical pattern, with lower pH in south-western Sweden, corresponding largely to the S deposition patterns (Fig. 4a, b and c) whereas Al_i was higher in the south (Fig. 4d).

The predicted pH decrease was not strongly correlated to any single water chemical variable. Low concentrations of the calculated Ca concentrations after termination of liming ($<0.05 mmol L^{-1}$) were associated with the largest reductions of pH, as would be expected. However, there was a relationship between the pH decrease and the ratio of the decrease of Ca and Mg (in charge equivalents) to the acid neutralising capacity (ANC) of the limed lakes in spring 2008 (Fig. 5). ANC was calculated here as the difference between cations to strong bases and anions to strong acids according to the equation:

$$ANC = (2 \cdot Ca^{2+} + 2 \cdot Mg^{2+} + Na^+ \text{ and } K^+) - (Cl^- + 2 \cdot SO_4^{2-} + NO_3^-) \quad (8)$$

To decrease pH by more than 0.4 pH units, the decrease of Ca and Mg must be more than 25 % of ANC. To decrease pH by 1 pH unit, the decrease of Ca and Mg must be more than 50 % of ANC.

The increase in Al_i was mostly determined by the pH value, and not by total Al; there was only a weak relationship between total Al and the increase of Al_i ($r^2 = 0.15$, data not shown).

The 1 807 unlimed reference lakes had average pH values and predicted Al_i concentrations that were similar to those of the 3 043 limed lakes after termination of liming (Table 1 and 3, Fig. 3e and f). Also the geographical variations in pH and Al_i were similar for the reference lakes and for the limed lakes after termination of liming (data not shown).

Values of pH and Al_i were also predicted for partially reduced lime doses in the limed lakes in spring 2008, where the predictions at a lime dose of 75 % lime were very similar to the present condition at 100 % liming (Table 3 and Fig. 3b). The pH was lowered by an average of 0.11 pH units compared with the simulated values for the 100 % limed situation (Table 3). The average value for Al_i was $13.7 \mu g L^{-1}$ which is an increase of an average of $0.5 \mu g L^{-1}$ compared to the original situation. Only 2% of the lakes had more than $30 \mu g L^{-1} Al_i$.

Likewise, with a 50 % lime dose most lakes still had values of pH and Al_i that were similar to those of the 100 % limed condition (Table 3 and Fig. 3c). The pH was lowered

with, on average, 0.27 pH units and Al_i was increased with $1.8 \mu g L^{-1}$ compared to the simulated original situation. However, for 3% per cent of the lakes, located mainly in southern Sweden, the pH decreased below 5.6.

In contrast, with only 25 % lime dose there was a much larger difference compared to the 100 % limed situation (Table 3 and Fig. 3d). The pH was lowered by, on average, 0.51 pH units and Al_i increased with $5.5 \mu g L^{-1}$. Ten per cent of the lakes now had a pH below 5.6 and Al_i concentrations above $30 \mu g L^{-1}$. There was a regional pattern where the southern third of Sweden had the highest percentages of lakes with low pH and high Al_i .

4. Discussion

The pH and Al_i were simulated well in the three monitored lakes in which liming had been terminated and where liming was performed directly in the lake during the ten previous years. The other three lakes with more recent upstream liming occasionally had simulated pH which was too low and Al_i which was too high, mainly due to too low calculated Ca concentrations compared to the measured ones. They had probably not reached the ratios predicted by the simple model of Eq. 7, since Ca and Mg from upstream liming might still be transported into the lake and/or lime was still present as lime residues in the sediments (Wällstedt et al., 2009).

Additionally, where low Al_i concentrations were determined the model generally simulated Al_i concentrations which were too high, due to the large intercept of $12.4 \mu g L^{-1} Al_i$ in the model of Sjöstedt et al. (2010; Eq. 2). However, this deficiency of the model is probably not of any significance when predicting lakes in which Al_i will be potentially toxic and exceed $30 \mu g L^{-1} Al_i$. For the combined data set of all limed and unlimed reference lakes in both samplings, the pH could be simulated with a mean error of 0.17 units ($n = 9\ 160$). There was a small bias for limed lakes, where a lower average pH (2007: 6.7, 2008: 6.6) was simulated compared to measured pH (2007: 6.8, 2008: 6.8), but the aim of the paper was to be able to predict pH in unlimed lakes, therefore the unlimed conditions are more important to be able to model correctly. The method is, therefore, sufficiently accurate to be used for predicting pH and Al_i at termination of liming.

Although prediction of the effect of a complete termination of liming showed a substantial average pH decrease (around 1 pH unit for all 3 043 limed lakes) there was a large variation between lakes and regions. Lakes in south-western Sweden were generally predicted to reach a low pH probably due to a historically higher S deposition. Southern

Sweden was predicted to reach the highest Al_i where the difference in pH might be caused by differences in soil or bedrock. In coastal areas of the northern half of Sweden around 35 % of the lakes had a pH below 5.6, while in the northern inner regions only a few lakes (less than 3 %) were predicted to have a pH of under 5.6. The effect of partial reductions of liming for the whole of Sweden was much smaller when the lime dose was set to 75 % and 50 % of the current one. Larger effects appeared when the lime dose was 25 %.

The results suggest the potential for a decrease in liming at several locations and a possibility of terminating liming in some areas. Around a third of the limed lakes would have a pH above 6.0 if liming was terminated, when both the autumn 2007 and spring 2008 data sets are evaluated, which is above the policy targets for liming. For many of these lakes it would, therefore, be possible to terminate liming. Lime doses have also been reduced since 2007.

The regional similarity between the predicted values of pH and Al_i in the limed lakes after modelled termination of liming and the observed values in the unlimed reference lakes is encouraging and indicates that the model is well suited to estimate the required lime dose to reach the water quality targets. It should also be possible to apply the method in other areas of the world with deposition of acidifying compounds, but possibly with some regional adaptations, e.g. % active DOM.

Some lakes had increased Ca and Mg concentrations after calculated liming termination, which is unreasonable. One explanation could be that reference lakes used for them were unsuitable due to different geology, catchment area or land use compared to the limed lake. It was sometimes difficult to find a suitable reference lake (Fölster et al., 2011a). Other errors could be reference lakes that are limed without proper documentation, or errors in the chemical analyses. These lakes, therefore, increased in pH with the calculated “unlimed” concentrations.

Of course there are a number of uncertainties involved in the kind of modelling that is employed in this paper. For example, the calculated concentration of inorganic C used in the model is uncertain, but it worked surprisingly well for the data as judged from the close correspondence between measured and simulated pH values. The relationship of Eq. 1 is based upon studies of 33 low-productivity lakes from three areas in Sweden, with pH values between 3.6 and 6.8 (Sobek et al., 2003), so it may be less relevant for limed lakes. The pH simulation worked better for the pH values below pH 6 in the study (Fig. 2). This might be due to the pH analysis technique used here, with air contact before the actual determination in

an open beaker immediately before the alkalinity measurement. This procedure increased the pH by on average 0.1 pH units ($n = 116$) compared to non-aired samples, especially for pH values above 6 (Fölster et al., 2011b). Another explanation could be the fact that the exact $p\text{ CO}_2$ is less important at low pH.

Additionally, there is a possibility that parameters other than Ca and Mg will change with reduced liming, such as TOC, F and SO_4 , which will influence pH and Al_i . Also, future lower S and N deposition may also change the water chemistry in lakes in ways not handled by the model. Parameters important for pH and Al_i modelling are total Al, F⁻, TOC, SO_4^{2-} , major ions and Fe. The parameter with the largest effects and which is most likely to change in the future is probably the TOC concentration. The TOC concentration has been increasing in surface water for the last 25 a in Scandinavia (Skjelkvåle et al., 2005) and other areas of Europe and North America (e.g. Driscoll et al., 2003; Hejzlar et al., 2003; Evans et al., 2005). The mechanism is under debate, but climate change and less S atmospheric deposition are possible explanations (Evans et al., 2006). Neither is it clear if termination of liming will cause a further increase or a decrease of TOC in lakes (Lydersen et al., 2002). The TOC concentration also has an intricate effect upon pH and Al_i since the pH decreases with more organic acids but at the same time Al_i decreases at higher concentrations of organic acids.

5. Conclusions

- A geochemical model for simulation of pH was tested for the 3 043 limed lakes in Sweden and for 1 485 unlimed reference lakes on two sampling occasions (2007 and 2008). The model was able to calculate the pH well in all cases; limed lakes were simulated with a mean error of 0.18 pH units and the unlimed lakes with 0.16 pH units.
- The model was used to predict pH and Al_i for reductions in liming with lower Ca and Mg concentrations calculated from Ca/Mg ratios in nearby unlimed reference lakes. The predictions were generally well correlated with results for three monitored lakes where liming had been terminated and with no recent upstream liming.
- If liming was terminated completely for the 3 043 presently limed lakes, pH was predicted to decrease by, on average, 0.97 pH units to pH 5.7. Al_i was predicted to increase by $17\text{ }\mu\text{g L}^{-1}$ to $32\text{ }\mu\text{g L}^{-1}$.
- If liming was reduced by 50 %, the pH was reduced by, on average, 0.3 pH units and Al_i was increased by $2\text{ }\mu\text{g L}^{-1}$.

- This implies that liming probably can be terminated in approximately a third of the lakes according to the modelling.

Acknowledgements

The Swedish Environmental Protection Agency funded this study within the ISELAW program. We thank Frida Edberg, Stephan Köhler, Estelle Lerceteau-Köhler, Marcus Sundbom and Teresia Wällstedt for help in gathering data. Tobias Vrede and Joakim Riml have given helpful suggestions on the text.

References

- Andrén, C. , Rydin, E., 2009. Which aluminium fractionation method will give true inorganic monomeric Al results in fresh waters (not including colloidal Al)? *J. Environ. Monitor.* 11, 1639-1646.
- Driscoll, C. T., 1984. A procedure for the fractionation of aqueous aluminum in dilute acidic waters. *Internat. J. Environ. Anal. Chem.* 16, 267–283.
- Driscoll, C.T., Driscoll, K.M., Roy, K.M., Mitchell, M., 2003. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environ. Sci. Technol.* 37, 2036-2042.
- Driscoll, C. T., Lehtinen, M.D., Sullivan, T.J., 1994. Modeling the acid-base chemistry of organic solutes in Adirondack, New York, lakes. *Water Resour. Res.* 30, 297-306.
- Evans, C.D., Monteith, D.T., Cooper, D.M., 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environ. Pollut.* 137, 55-71.
- Evans, C.D., Chapman, P.J., Clark, J.M., Monteith, D.T., Cresser, M.S., 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biol.* 12, 2044-2053.
- Fölster, J., Köhler, S., von Brömsen, C., Akselsson, C., Rönnback, P., 2011a. Korrigering av vattenkemi för kalkningspåverkan: Val av referenser och beräkning av osäkerheter. Report 2011:1 Department of Aquatic Sciences and Assessment, SLU (Swedish University of Agricultural Sciences), SE-750 07 Uppsala, Sweden (in Swedish).
- Fölster, J., Moldan, F., Stadmark, J., 2011b. Målsjöundersökningen 2007-2008. Report 6412. June 2011. Swedish Environmental Protection Agency, Stockholm, Sweden. (in Swedish with English summary).

422 Gadmar, T.C., Vogt, R.D., Østerhus, B., 2002. The merits of the high temperature
 423 combustion method for determining the amount of natural organic carbon in surface
 424 freshwater samples. *Internat. J. Environ. Anal. Chem.* 82, 451-461.

425 Gensemer, R.W., Playle, R.C., 1999. The bioavailability and toxicity of aluminium in aquatic
 426 environments. *Crit. Rev. Environ. Sci. Technol.* 29, 315-450.

427 Göransson E., Bringmark, E., Rapp, L., Wilander, A., 2006. Modeling the effect of liming on
 428 calcium concentration in Swedish lakes. *Environ. Monit. Assess.* 119, 331-348.

429 Granier, C., Bessagnet, B., Bond, T., D'Angiola, A., Denier van der Gon, H., Frost, G.J.,
 430 Heil, A., Kaiser, J.W., Kinne, S., Klimont, Z., Kloster, S., Lamarque, J.-F., Liousse, C.,
 431 Masui, T., Meleux, F., Mieville, A., Ohara, T., Raut, J.-C., Riahi, K., Schultz, M.G.,
 432 Smith, S.J., Thompson, A., van Ardenne, J., van der Werf, G.R., van Vuuren, D.P., 2011.
 433 Evolution of anthropogenic and biomass burning emissions of air pollutants at global and
 434 regional scales during the 1980-2010 period. *Clim. Change* 109, 163-190.

435 Gustafsson J. P., 2001. Modeling the acid-base properties and metal complexation of humic
 436 substances with the Stockholm Humic Model. *J. Colloid Interface Sci.* 244, 102-112.

437 Gustafsson J.P., 2012. Visual MINTEQ 3.0 program.
 438 <http://www.lwr.kth.se/english/OurSoftWare/Vminteq/index.html>

439 Hejzlar, J., Dubrovský, M., Buchtele, J., Růžička, M., 2003. The apparent and potential
 440 effects of climate change on the inferred concentration of dissolved organic matter in a
 441 temperate stream (the Malše River, South Bohemia). *Sci. Total Environ.* 310, 143-152.

442 Hruška, J., Köhler, S., Laudon, H., Bishop, K., 2003. Is a universal model of organic acidity
 443 possible: Comparison of the acid/base properties of dissolved organic carbon in the boreal
 444 and temperate zones. *Environ. Sci. Technol.* 37, 1726-1730.

445 Larssen, T., Lydersen, E., Tang, D. G., He, Y., Gao, J. X., Liu, H. Y., Duan, L., Seip, H. M.,
 446 Vogt, R. D., Mulder, J., Shao, M., Wang, Y. H., Shang, H., Zhang, X. S., Solberg, S. Aas,
 447 W., Okland, T., Eilertsen, O., Angell, V., Liu, Q. R., Zhao, D. W., Xiang, R. J., Xiao, J. S.,
 448 Luo J. H., 2006. Acid rain in China. *Environ. Sci. Technol.* 40, 418-425.

449 Lydersen, E., Löfgren, S., Arnesen, R. T., 2002. Metals in Scandinavian Surface Waters:
 450 Effects of acidification, liming, and potential reacidification. *Crit. Rev. Environ. Sci.*
 451 *Technol.* 32, 73-295.

452 Schecher, W.D., Driscoll, C. T., 1995. ALCHEMI: A chemical equilibrium model to assess
 453 the acid-base chemistry and speciation of aluminium in dilute solutions. In: Loeppert, R.,

454 Schwab, A.P., Goldberg, S. (Eds), Chemical Equilibrium and Reaction Models. Soil
 455 Science of America, Madison, Wisconsin, 325-356.
 456 Sjöstedt C., Köhler S., Gustafsson J.P., 2010. Chemical equilibrium modeling of organic
 457 acids, pH, aluminium and iron in Swedish surface waters. Environ. Sci. Technol. 44,
 458 8587–8593.
 459 Skjelkvåle, B.L., Mannio, J., Wilander, A., Johansson, K., Jensen, J.P., Moiseenko, T., Fjeld,
 460 E., Andersen, T., Vuorenmaa, J., Røyset, O. , 1999. Heavy metal surveys in Nordic lakes;
 461 harmonised data for regional assessment of critical limits. Report No. O-98024. Serial No.
 462 4039-99. Norwegian Institute for Water Research.
 463 Skjelkvåle, B.L., Stoddard, J.L., Jeffries, D.S., Torseth, K., Hogasen, T., Bowman, J., Mannio,
 464 J., Monteith, D.T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J.,
 465 Wilander, A., Worsztynowicz, A., 2005. Regional scale evidence for improvements in
 466 surface water chemistry 1990-2001. Environ. Pollut. 137, 165-176.
 467 SMHI (Swedish Meteorological and Hydrological Institute), 2012. National survey of
 468 atmospheric chemical data for Sweden's environmental monitoring, version
 469 Atmosfärskemi 2011.1, published by SMHI on commission of the Swedish EPA.
 470 Available at the website www.smhi.se March 2012.
 471 Sobek, S., Algesten, G., Bergström, A.-K., Jansson, M., Tranvik L.J., 2003. The catchment
 472 and climate regulation of $p\text{CO}_2$ in boreal lakes. Global Change Biol. 9, 630-641.
 473 Stoddard, J.L., Jeffries, D.S., Lukewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius,
 474 M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T.,
 475 Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvåle, B.L., Stainton, M.P., Traaen, T., Van
 476 Dam, H., Webster, K.E., Wieting, J., Wilander, A., 1999. Regional trends in aquatic
 477 recovery from acidification in North America and Europe. Nature 401, 575-578.
 478 Swedish Environmental Protection Agency., 2010. Handbok för kalkning av sjöar och
 479 vattendrag. Handbok 2010:2. Utgåva 1. March 2010. SE-106 48 Stockholm. 90 pp. (In
 480 Swedish)
 481 Swedish Environmental Protection Agency., 2011. Naturvårdsverkets årsredovisning 2011.
 482 Tipping, E., 1994. WHAM-a chemical equilibrium model and computer code for waters,
 483 sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by
 484 humic substances. Comput. Geosci. 20, 973-1023.
 485 Tipping, E., 1998. Humic ion-binding Model VI: an improved description of the interactions
 486 of protons and metal ions with humic substances. Aquat. Geochem. 4, 3-48.

487 Tipping, E., Carter, H.T., 2011. Aluminium speciation in streams and lakes of the UK Acid
488 Waters Monitoring Network, modelled with WHAM. *Sci. Total Environ.* 409, 1550-1558.
489 Wällstedt T., Edberg F., Borg H., 2009. Long-term water chemical trends in two Swedish
490 lakes after termination of liming. *Sci. Total Environ.* 407, 3554-3562.
491 Wilander, A., 2003. Riksinventering 2000. Report 2003:1 Institutionen för miljöanalys, SLU
492 (Swedish University of Agricultural Sciences), SE-750 07 Uppsala. (In Swedish).

Table 1. Averaged measured and simulated chemical and physical parameters for all lakes divided into unlimed reference and limed lakes during autumn 2007 and spring 2008. Standard deviations within parenthesis.

	2007 unlimed	2008 unlimed	2007 limed	2008 limed
<i>n</i>	1 737	1 807	2 894	3 043
Measured values				
pH	5.9 (± 0.9)	6.0 (± 0.8)	6.8 (± 0.5)	6.8 (± 0.3)
Temp/ ° C	2.9 (± 2.6)	12.4 (± 5.9)	2.7 (± 2.5)	11.3 (± 6.0)
Alkalinity/acidity/ mekv L ⁻¹	0.060 (± 0.139)	0.057 (± 0.124)	0.173 (0.103)	0.138 (± 0.084)
Ca/ mmol L ⁻¹	0.068 (± 0.065)	0.063 (± 0.060)	0.132 (± 0.054)	0.111 (± 0.049)
Mg/ mmol L ⁻¹	0.033 (± 0.019)	0.031 (± 0.020)	0.034 (± 0.014)	0.032 (± 0.014)
Na/ mmol L ⁻¹	0.13 (± 0.10)	0.13 (± 0.10)	0.14 (± 0.09)	0.14 (± 0.09)
K/ mmol L ⁻¹	0.013 (± 0.010)	0.014 (± 0.010)	0.015 (± 0.011)	0.015 (± 0.011)
Fe/ µg L ⁻¹	857 (± 857)	618 (± 583)	716 (± 816)	482 (± 507)
Mn/ µg L ⁻¹	46 (± 70)	43 (± 49)	41 (155)	32 (± 29)
Al/ µg L ⁻¹	231 (± 175)	220 (± 141)	178 (± 141)	183 (± 116)
SO ₄ ²⁻ / mmol L ⁻¹	0.033 (± 0.022)	0.035 (± 0.023)	0.036 (± 0.020)	0.037 (± 0.020)
Cl ⁻ / mmol L ⁻¹	0.12 (±0.11)	0.12 (± 0.12)	0.13 (± 0.10)	0.13 (± 0.10)
F/ mg L ⁻¹	0.094 (± 0.078)	0.093 (± 0.073)	0.093 (± 0.072)	0.090 (± 0.066)
TOC/ mg L ⁻¹	15.0 (± 9.4)	12.7 (± 7.0)	13.6 (± 7.4)	11.9 (± 5.8)
Simulated values				
pCO ₂ according to Eq. 1/ µatm	1 850 (± 1010)	1600 (± 750)	1 700 (± 800)	1520 (± 620)
pH	6.0 (± 0.8)	6.0 (± 0.7)	6.7 (± 0.4)	6.6 (± 0.3)
rmse / pH units	0.24	0.20	0.25	0.20
Mean error/ pH units	0.18	0.14	0.19	0.17
Al _i sim. with measured pH/ µg L ⁻¹	34.3 (± 35.9)	32.6 (± 35.5)	14.2 (± 10.3)	13.0 (± 3.9)
Al _i sim. with simulated pH/ µg L ⁻¹	29.5 (± 29.1)	28.6 (± 28.9)	13.8 (± 7.6)	13.2 (± 3.6)
Lakes with > 30 µg L ⁻¹ Al _i (in percentage)	589 (33.9 %)	565 (31.3 %)	81 (2.8 %)	21 (0.7 %)
Lakes with > 50 µg L ⁻¹ Al _i (in percentage)	395 (22.7 %)	338 (18.7 %)	46 (1.6 %)	13 (0.4 %)

Table 2. Geographical, physical and liming data of the six lakes with monitored termination of liming.

Lake name	Coordinates*	Area/ km ²	Retention time/ yrs	Last limed directly in lake	Last limed in an upstream lake	Last limed wetland
Skifsen	666268-142230	0.35	1.16	Oct 2004	1988	1988
Rädsjön	674570-141911	0.50	3.56	Sept 2005	Never	Never
Geten	649314-149514	0.20	1.9	Oct 2006	Never	Never
Tre- hörningen	656664-164238	0.034	0.42	March 1991	Never	1986
Långsjön (Tyresta)	656590-164240	0.10	0.87	March 1995	1991	1986
Långsjön (Örebro)	652412-143738	0.67	1.5	Aug 2006	2006	1987

* according to RT90 25 gon V.

Table 3. Calcium and magnesium concentrations for the different predictions as well as results for pH and Al_i for the limed lakes spring 2008 (n =3 043).

	100 % Limed	75 % Ca and Mg from lime	50 % Ca and Mg from lime	25 % Ca and Mg from lime	0 % Ca and Mg from lime
Ca/ mmol L⁻¹	0.111	0.095	0.079	0.063	0.047
(± standard deviation)	(± 0.049)	(± 0.040)	(± 0.032)	(± 0.027)	(± 0.027)
Mg/ mmol L⁻¹	0.032	0.031	0.030	0.029	0.028
(± standard deviation)	(± 0.014)	(± 0.014)	(± 0.014)	(± 0.015)	(± 0.016)
pH					
Predicted pH mean	6.65	6.54	6.38	6.14	5.73
(±standard deviation)	(± 0.31)	(± 0.31)	(± 0.34)	(± 0.42)	(± 0.63)
Predicted pH- change compared to "100 % Limed"		- 0.11	- 0.27	- 0.51	- 0.92
(±standard deviation)		(± 0.06)	(± 0.15)	(± 0.32)	(± 0.65)
Number of lakes with pH under 6.0	71	139	376	976	1 841
(in percentage)	(2.3 %)	(4.6 %)	(12.4 %)	(22.3 %)	(60.5 %)
Number of lakes with pH under 5.6	17	22	76	318	1 196
(in percentage)	(0.6 %)	(0.7 %)	(2.5 %)	(10.5 %)	(39.3 %)
Al_i					
Predicted Al_i mean/ $\mu\text{g L}^{-1} Al$	13.2	13.7	14.9	18.7	31.1
(± standard dev)	(± 3.6)	(± 5.2)	(± 8.6)	(± 15.0)	(± 27.3)
Predicted change of Al_i compared to "100 % Limed"		+ 0.5	+ 1.8	+ 5.5	+ 17.9
		(± 2.2)	(± 6.1)	(± 13.1)	(± 26.2)
Number of lakes with Al_i larger than 30 $\mu\text{g L}^{-1}$	28	46	89	305	1 046
(in percentage)	(0.9 %)	(1.5 %)	(2.9 %)	(10.1 %)	(34.4 %)
Number of lakes with Al_i larger than 50 $\mu\text{g L}^{-1}$	6	16	33	97	542
(in percentage)	(0.2 %)	(0.5 %)	(1.1 %)	(3.2 %)	(17.8 %)

Fig 1. Results of predictions at 75, 50, 25 and 0 % lime effect for the six lakes with monitored termination of liming (only L. Trehörningen and L. Långsjön (Tyresta) had results for 0 % lime). Filled triangles: Lakes limed directly at the lake surface for the previous 10 years. Open diamonds: Lakes that were also limed upstream for the previous 10 years.

- (a) Comparison of calculated Ca concentrations according to Eq. 7 and analysed Ca.
- (b) Comparison of calculated Mg concentrations according to Eq. 7 and analysed Mg.
- (c) Comparison of simulated pH versus analysed pH.
- (d) Comparison of simulated Al_i versus analysed Al_i.

Fig. 2. (a) The relationship between analysed pH and simulated pH for the 3 043 limed lakes 2008. Mean error = 0.17 pH units, $r^2 = 0.82$. (b) The relationship between analysed pH and simulated pH for the 1 485 unlimed reference lakes 2008. Mean error = 0.14 pH units, $r^2 = 0.94$.

Fig. 3. (a-e) Al_i predicted at the different predicted pH values for the limed lakes spring 2008 ($n = 3043$). (a) Original water data. (b) 75 % lime. (c) 50 % lime. (d) 25 % lime. (e) 0 % lime (one sample is out of scale). (f) Simulated Al_i and analysed pH of the unlimed reference lakes ($n = 1\,807$). A few samples have pH above 8 not shown.

Fig. 4. (a) Total S deposition in Sweden 1998 (SMHI, 2012). (b) Total S deposition in Sweden 2009 (SMHI, 2012). (c) Percentages of limed lakes in the counties that had predicted pH values below 5.6 for the no-lime scenario. (d) Percentages of limed lakes in the counties that had predicted Al_i concentrations above $30 \mu\text{g L}^{-1}$ Al for the no-lime scenario.

Fig. 5. The predicted change of pH from simulated present limed situation to predicted terminated liming as compared to the decrease of ($\text{Ca}^{2+} + \text{Mg}^{2+}$) as charge percentages of ANC for spring 2008. Some points with large increases of pH and ANC are out of scale. Smaller dashed lines indicate a reduction of pH with 0.4 units, and larger dashed lines a reduction of 1 pH units. Where the Ca and Mg decreases are lower than 0 % an increase of Ca and Mg has been calculated, and where the percentages are higher than 100 % the ANC has become lower than 0.

Electronic Annex. Table A1. Analysed and simulated values for the six lakes with monitored termination of liming. The dates are chosen according to predicted Ca/Mg ratios calculated with Eq. 7.

	% limed	Year	Month	pH		Al _i / µg L ⁻¹		Ca/ mmol L ⁻¹		Mg/ mmol L ⁻¹		SO ₄ ²⁻ / mmol L ⁻¹	Al tot/ µg L ⁻¹
				Analysed	Simulated	Analysed	Simulated	Analysed	Input model	Analysed	Input model	Analysed	Analysed
Skifsen	Limed	2005	5	6.7	6.81		12.5	0.118*		0.015#		0.020#	116#
	75 %	2005	9		6.66		12.5		0.095		0.014		
	50 %	2006	5	6.6	6.46		12.7		0.073		0.013		
	25 %	2007	4	6.3	6.12	5.3	13.5	0.060	0.050	0.015	0.012	0.019	135
	0 %	2012	11		5.37		27.7		0.028		0.011		
Rädsjön	Limed	2005	10	6.98	7.12		l.s	0.098		0.012		0.019	43.2#
	75 %	2007	4	7	7.02	3.7	l.s	0.103	0.080	0.013	0.011	0.019	51
	50 %	2008	4	6.51	6.90	< 3	l.s	0.052	0.062	0.007	0.011	0.016	30
	25 %	2010	9	6.75	6.73	< 3	12.5	0.054	0.043	0.011	0.011	0.016	64
	0 %	2030	9		6.46		12.5		0.025		0.010		
Geten	Limed	2007	5	6.2	6.20	9.4	20.2	0.121		0.049		0.070	315
	75 %	2007	10	6.4	6.15	5.3	22.7	0.132	0.115	0.052	0.048	0.070	208
	50 %	2008	9	6.29	6.08	14.6	25.4	0.131	0.109	0.051	0.048	0.075	294
	25 %	2010	4	5.72	6.01	22	29.2	0.098	0.104	0.046	0.048	0.063	348
	0 %	2015	1		5.94		34.2		0.098		0.047		
Trehörningen	Limed	1991	8	7.0	7.02		l.s	0.355		0.035		0.080	165
	75 %	1991	9	7.0	6.84		12.5	0.360	0.277	0.040	0.032	0.050	170
	50 %	1991	11	7.3	6.52		12.6	0.295	0.199	0.035	0.029	0.045	212
	25 %	1992	3	6.6	5.58		20.4	0.210	0.121	0.030	0.026	0.045	177
	0 %	1994	8	6.7	4.07	< 3	98.0	0.120	0.042	0.027	0.022	0.057	130
Långsjön (Tyresta)	Limed	1995	11	7.5	7.42		l.s	0.408		0.034		0.065	73
	75 %	1996	3	7.1	7.28	8.0	l.s	0.417	0.314	0.039	0.030	0.071	87
	50 %	1996	5	7.3	7.08	4.1	l.s	0.388	0.220	0.033	0.026	0.059	89
	25 %	1997	3	6.5	6.68	< 3	12.5	0.179	0.126	0.030	0.022	0.068	240
	0 %	2004	4	5.8	4.53	31.0	46.3	0.082	0.032	0.028	0.018	0.059	305
Långsjön (Örebro)	Limed	2006	8	6.76	6.67		12.5	0.125		0.032		0.047	86
	75 %	2007	2	6.61	6.54	< 3	12.5	0.122	0.105	0.033	0.030	0.052	154
	50 %	2007	8	6.8	6.36	< 3	12.7	0.104	0.086	0.031	0.027	0.043	133
	25 %	2008	9	6.42	6.08	6.3	13.2	0.092	0.066	0.031	0.025	0.045	141
	0 %	2014	10		5.56		17.6		0.047		0.023		

l.s.= lowest simulation (12.4 µg L⁻¹ Al) * Estimated from previous years. # Estimated from following years.

For L. Skifsen and L. Rädsjön measured data used in the study was between 1978-2010, for L. Geten 2007-2010, L. Trehörningen and L. Långsjön (Tyresta) 1983-2010, and Långsjön (Örebro) 1989-2011.