



# report

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## Geochemical modelling of acidification and recovery in forest soils and runoff waters

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<p><b>Sammanfattning/Summary</b></p> <p>The Model of Acidification of Groundwaters in Catchments (MAGIC) was used to simulate the impact of acidifying deposition and future recovery at the Gårdsjön Covered Catchment Experiment, at a number of hypothetical stations defined by statistical variation of the Gårdsjön data and at 20 forest monitoring sites in Southern Sweden. For the future predictions a decrease of sulphur deposition of more than 70% was assumed. This assumption is based on a full implementation of the agreements made under the second sulphur protocol from 1994. The modelled impact of reduced deposition on the soils and on the runoff waters was discussed. To complement the discussion on long-term trends in future run-off chemistry, data from Gårdsjön has been used to asses the risk for short-term acid runoff episodes.</p> <p><b>Nyckelord samt ev. anknytning till geografiskt område, näringsgren eller vattendrag/Keywords</b>  acidification, recovery, modelling, forest, soil, runoff, Västra Götaland, Sweden</p>	
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## **1. Preface**

This is the final report of the project “Geokemisk modellering av försurnings- och återhämtningsförlopp” (Geochemical modelling of acidification and recovery processes) which was initiated in 1996. Two status reports (Moldan et al., 1997; 1998a) have been presented earlier.

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## **Summary**

The overall aim of this project was to develop and apply model tools for the simulation of the future development of forest soil acidification and the recovery process. The model should be able to take into account different types of land use, deposition scenarios, regional differences in soil status and degree of acidification. This project is a continuation of earlier projects aimed at modelling the recovery process in the Gårdsjön Covered Catchment Project. In this phase, the work has focused on developing a model tool for generalisation and future predictions on a regional scale representing south Sweden.

The Model of Acidification of Groundwaters in Catchments (MAGIC) was used to simulate the impact of acidifying deposition and future recovery in the initial work at the Gårdsjön Covered Catchment Experiment. Here, we report the results from the second phase where MAGIC was applied to simulate conditions representing other regions in south Sweden. Two approaches have been used:

1. To simulate the recovery process at a number of hypothetical stations defined by statistical variation of the Gårdsjön data.
2. To apply the model to 20 specific monitoring sites using data from the forest monitoring network and a future scenario of acid deposition.

### ***Monte Carlo simulations***

The hypothetical stations were created by varying key soil and deposition parameters of the Gårdsjön site within reasonable limits using the so called Monte Carlo technique. The basis of the Monte Carlo technique is the random selection of a set of environmental parameters and variables. These random numbers are then combined in data sets representing hypothetical stations. The model is used to select those data sets which are realistic in terms of basic equilibrium chemistry relations and mass balances and that also are representative of the environmental conditions in the region of interest.

In this study, the acidification history of the hypothetical sites were simulated for the period 1850 to 1990. The results give a general picture of the acidification of forest soils in the region of southern Sweden derived from Gårdsjön data. The range of Acid Neutralising Capacity (ANC) in stream water has shifted from values in the range -20 to + 200  $\mu\text{eq/l}$  in 1850 to -430 to 0  $\mu\text{eq/l}$  in 1990. Aluminium has increased from an average value of less than 20  $\mu\text{eq/l}$  to around 200  $\mu\text{eq/l}$ . Although these results are derived from a hypothetical data set, they clearly demonstrate the severe damage that has occurred in forest soils in the region during the last century.

### ***Model application to 20 forest sites***

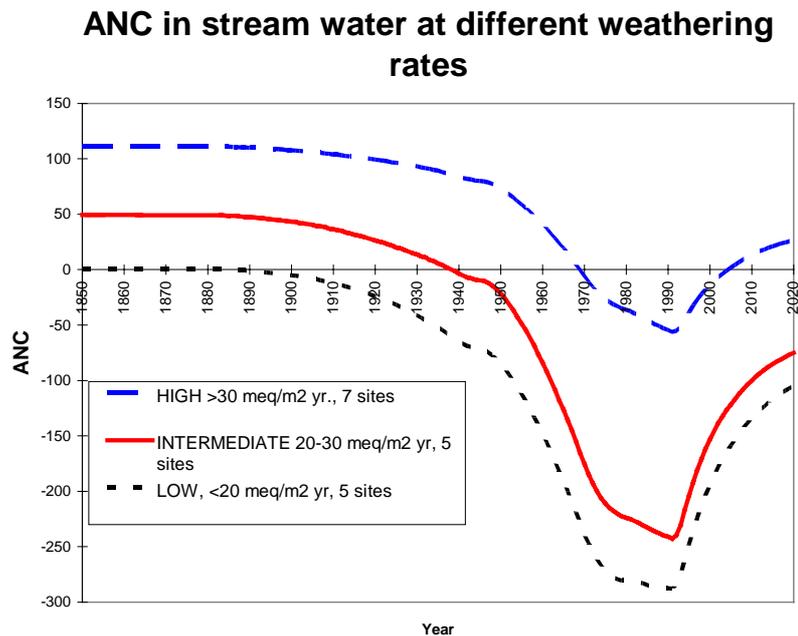
The 20 monitoring plots, having a wide range of soil and deposition parameters, are located in S Sweden. MAGIC was used to describe the historical development of acidification and to simulate the future development until year 2020.

A decrease of sulphur deposition of more than 70% was assumed for the future predictions. This assumption is based on a full implementation of the agreements made under the second sulphur protocol. A second major assumption was that no change occurred in present land use; forests at all sites were left unharvested even

after reaching maturity. We consider this future scenario as a relative optimistic interpretation of the expected future; the soils are not depleted by harvesting the forest and replanting next rotation, and emission cuts are followed by an equally strong decline in sulphur deposition with no delays.

With a few exceptions, the above described scenario leads to a certain improvement of the modelled run-off quality at all sites. However, at the same time the scenario resulted in continuation of the lowering of the soil base saturation at a majority of the modelled sites. The modelled improvement should be seen as a shift towards a new balance between acidifying deposition and the state of the ecosystem rather than a complete recovery in terms of improvement of the soil base saturation.

The achieved run-off quality in the year 2020 was not satisfactory at any of the sites which were heavily acidified. At none of the sites the acid neutralising capacity (ANC) of the run-off reached pre-industrial levels by the year 2020. The strongest recovery in terms of run-off pH and ANC was predicted at the sites with well-buffered soils and higher weathering rates. The outcome was much less positive for the more sensitive sites. The modelled scenario leads to a break in the acidification trend at most of the sites. However, the forecast represents a recovery only up to a certain degree at which point the positive trends will level off and the previously acidified sites will remain acidified for a very long time even beyond the year 2020. This can be illustrated by the simulated results for ANC in the Figure below.



There was a general agreement in model calibrations to hypothetical sites and to the 20 real sites. The Monte Carlo technique is a viable option in generalising modelling results from one intensely studied site to a region where data are sparse.

**Acid episodes**

MAGIC is based on equilibrium calculations with time steps of one month or one year and is thus not capable of predicting short term incidents such as acid episodes. In

order to address this problem, ten years (1988 - 1997) of run-off data from control site F1 at Gårdsjön were evaluated. During this period, the complete chemical composition in 225 run-off samples was analysed. In addition to the chemical composition of the run-off samples, daily information on run-off flow as well as precipitation amount was available for the evaluation.

A statistical treatment of the data using Principal Component Analysis (PCA) reveals that acid episodes (identified by extreme levels of  $H^+$  and  $Al^{3+}$ ) occur after prolonged dry periods. Snow-melt had only a minor effect for the Gårdsjön area. Only 3 episodes with both elevated  $H^+$  and  $Al^{3+}$  occurred (concentrations values above the 90%-ile of the total data set) during the ten years period.

The representativity of these results should be treated with some care. The run-off from the F1 catchment is acidified at all times with pH of around 4.1 to 4.2. Thus, only extreme acid episodes will be seen. In other areas where the soil acidification is not so pronounced or when the soil has partially recovered, acid episodes will be more distinct and may cause greater damage in downstream lakes.

## **Svensk sammanfattning**

Den övergripande målsättningen med projektet var att utveckla och tillämpa modellverktyg för simulering av framtida utvecklingen och återhämtning i försurad skogsmark. Kravet på modellen var att den skulle kunna behandla olika markanvändning, olika nedfallsscenarioer, regionala skillnader i markstatus och försurningsnivå. Projektet är en fortsättning på tidigare studier där arbetet främst fokuserats på att simulera återhämtningsprocessen i takprojektet vid Gårdsjön. I denna fas har arbetet fokuserats på anpassning av modellen för generalisering och framtidsförutsägelser i en regional skala representativ för södra Sverige.

Modellen "Model of Acidification of Groundwaters in Catchments" (MAGIC) användes i det tidigare arbetena med att simulera resultat från takprojektet i Gårdsjön. I denna rapport presenteras resultaten från arbetet med att anpassa modellen och genomföra simuleringar av förhållandena i södra Sverige. Två olika angreppssätt har använts:

1. Simulering av försurningsprocessen i ett antal hypotetiska avrinningsområden definierade efter en statistisk variation av mätdata från takprojektet, och,
2. Anpassning av modellen till 20 utvalda skogsytor från den skogliga miljöövervakningen i södra Sverige och simulering av det historiska försurningförloppet och ett framtidsscenario.

### ***Monte Carlo simuleringar***

De hypotetiska stationerna skapades genom att variera vissa mark- och depositionsparametrar, uppmätta i Gårdsjöområdet, med den s.k. Monte Carlo metoden. Monte Carlo metoden baseras på ett slumpmässigt urval av värden på indetifierade parametrar och variabler. Uppsättningen av det slumpmässigt urvalet kombineras därefter till datamängder som får representera ett stort antal hypotetiska avrinningsområden. Modellen (MAGIC) används därefter för att sortera ut de datamängder som är realistiska med avseende på grundläggande kemiska jämvikter och massbalanser och som är representativa för förhållanden i den region som är av intresse.

I denna studie har den historiska utvecklingen av försurningen i de hypotetiska avrinningsområdena simulerats för perioden 1850-1990. Resultaten ger en generell bild av hur skogsmarken försurats i södra Sverige under denna period. Avrinningsvattnets förmåga att neutraliserande ämnen (beräknat som ANC; Acid Neutralising Capacity) har förändrats från att ligga inom intervallet -10 till 200  $\mu\text{eq/l}$  år 1850 till mellan -430 och ca 0  $\mu\text{eq/l}$  år 1990. Aluminium har ökat från medelvärdet kring ca 20  $\mu\text{eq/l}$  till ca 200  $\mu\text{eq/l}$  under samma period.

### ***Modellering av 20 avrinningsområden***

De utvalda 20 ytorna ligger i södra Sverige och markegenskaper och nedfallet varierar inom ett brett intervall. MAGIC har använts för att beskriva den historiska utvecklingen av försurningen och för att simulera framtidsutvecklingen till år 2020.

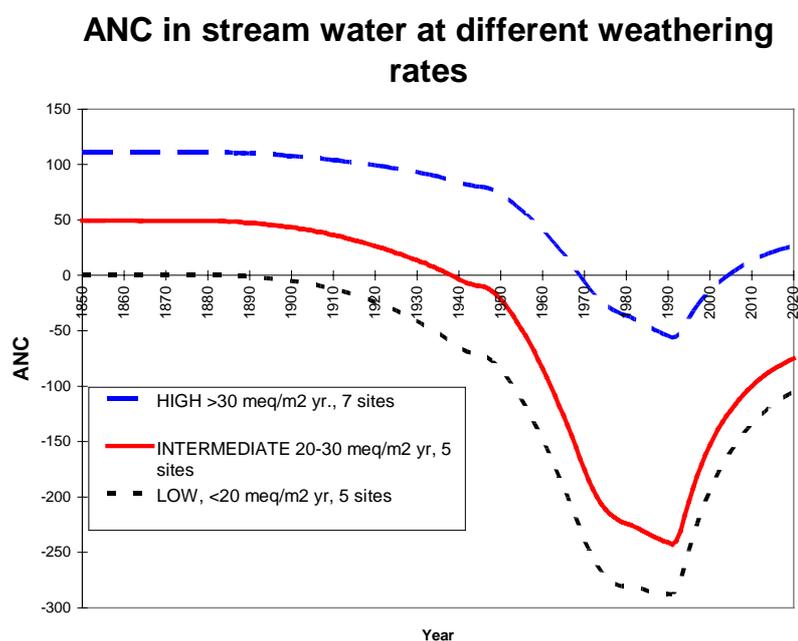
För framtida nedfall av svavel har antagits en minskning med ca 70% vilket baseras

på en fullständig implementering av det andra svavelprotokollet. För skogen har antagits att ingen avverkning sker även om beståndet är fullvuxet. Scenarier får anses vara optimistiskt ur försurningssynpunkt eftersom minskningar i svavelutsläpp ger en linjär minskning i nedfall och att ingen avverkning eller återplantering av skog sker, vilket skulle leda till en förhöjd förbrukning av markens baskatjoner.

Med få undantag ger det ovan beskrivna scenariet som resultat att en viss förbättring av vattenkvaliten i avrinning från de 20 skogsytorna sker. En fortsatt minskning av markens basmättnadsgrad sker dock vid de flesta ytorna. Den förutspådda förbättringen ska därför betraktas som ett nytt jämviktsläge mellan nedfall och tillståndet i skogsekosystemet och inte som en fullständig återhämtning av skogsmarkens basmättnadsgrad.

Avrinningsvattnet kommer inte i något av de mest försurade fallen uppnå en acceptabel kvalite före år 2020. ANC kommer inte att nå för-industriella nivåer i någon av de modellerade ytorna. Den största återhämtningen vad gäller pH och ANC sker i mark med relativt hög buffringskapacitet och hög vittringshastighet. I de mer känsliga områdena är resultaten än mer negativa. Det antagna scenariet leder till ett avbrott i försurningstrenden men den positiva trenden kommer att plana ut och de tidigare försurade områdena kommer att förbli försurade under lång tid, även efter år 2020.

Resultaten sammanfattas väl av modellerad ANC som presenteras i figuren nedan.



I ett generellt betraktelsesätt stämmer resultaten från de 20 verkliga områdena väl överens med resultaten från Monte Carlo simuleringarna baserade på hypotetiska avrinningsområden. Monte Carlo metoden kan därför sägas vara ett användbart verktyg för att överföra resultat från ett intensivt studerat område till regioner där mätdata inte är tillgängliga.

## **Surstötter**

MAGIC baseras på tidssteg om en månad eller ett år och kan därför inte användas för att simulera eller förutsäga surstötter. För att utreda möjligheterna att finna samband mellan förekomsten av surstötter och andra faktorer har mätdata från referensområde F1 vid Gårdsjön från perioden 1988 till 1997 utvärderats. Under denna tidsperiod har fullständig kemi uppmätts i 225 avrinningsprov och information om flöden regnmängder m.m. finns också tillgängliga.

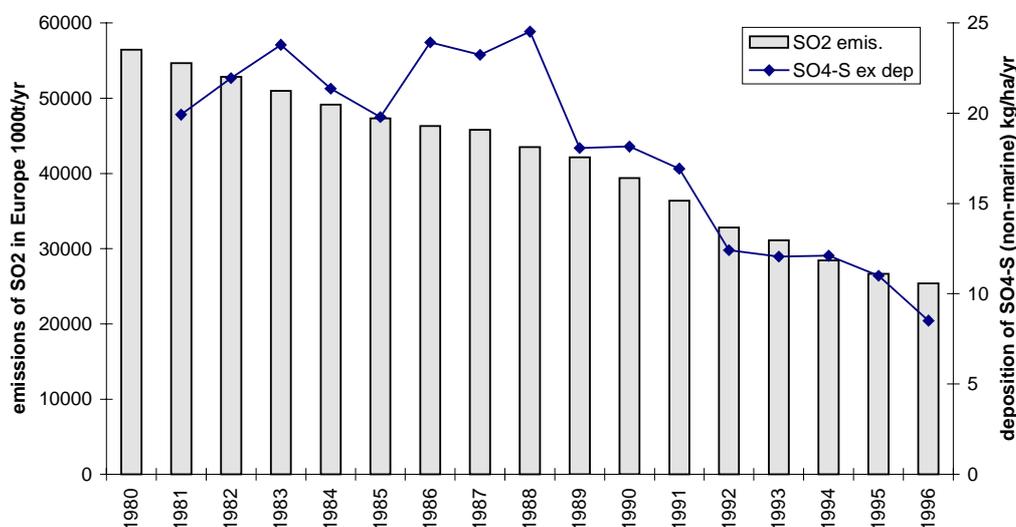
En statistisk bearbetning av mätdata med PCA (Principal Component Analysis) visar att kraftiga surstötter (definierade som extremvärden av  $H^+$  och  $Al^{3+}$ ) inträffar efter längre torrperioder. Snösmältning har mindre effekt i detta område. Under tidsperioden inträffade endast 3 perioder med såväl förhöjda  $H^+$  som  $Al^{3+}$  koncentrationer (definieras som perioder med koncentrationer över 90%-ilen).

Utvärderingen av surstötter ska betraktas med viss försiktighet. Avrinningen från område F1 är ständigt försurat med årsmedelvärden för pH mellan 4.1 och 4.2. Av denna anledning kommer endast extrema surstötar att synas. I andra områden med mindre omfattande markförsurning eller i områden där en återhämtning delvis skett, kommer surstötter att vara mer distinkta och även orsaka större skador i nedströms vattensystem.

## 2. Introduction

Acidification of forest soils and freshwater is one of the major environmental problems in many areas in the northern hemisphere. In Europe, the most serious damage has been observed in the coniferous forest areas in central Europe and Scandinavia. Acidification is mainly caused by atmospheric deposition of sulphuric acid originating from anthropogenic emissions of sulphur from energy production and other combustion activities. The environmental response to acid deposition is highly variable and is dependent of the capacity of the ecosystem to counteract the acidity. In large areas of Scandinavia, forest soils and lakes have a very low capacity to buffer the acid deposition and the worst damage is mainly found in these regions.

Today, international agreements have already led to drastic reductions in emissions of sulphur in Europe. About 70 % of non-marine S deposition in Sweden is directly attributable to emissions abroad, with Germany, Poland and Great Britain as the largest contributors (average 1985 - 1996 inclusive) (EMEP 1998). Sulphur deposition from Swedish S emissions contributes only less than 10% of the total deposition while the remaining 20% is mostly from unattributable sources with a small contribution from sea traffic. Therefore the S deposition in Sweden is probably from up to ca 90% imported. Due to the emission cuts (Figure 1), deposition of sulphur has decreased since 1980 by at least 40% at many locations in southern Scandinavia. Further agreements on reductions within the European Union may also be signed in the near future.



**Figure 1.** Emissions of SO<sub>2</sub> in Europe (natural emissions from sea and volcanic emissions excluded) and deposition of non-marine SO<sub>4</sub>-S measured at Gårdsjön, SW Sweden. The Gårdsjön deposition declined from 1981 to 1996 by about 50% which is very similar to a decline of total European emissions.

In Sweden, after a referendum in 1980 about the future of nuclear energy production, the Swedish parliament decided that all Swedish nuclear power plants should be closed by the year 2010. So far there has been a political inter-party decision in

February 1997 to close only two reactors (located in Barsebäck nuclear power plant) of the total of twelve existing nuclear reactors in Sweden.

If the Swedish nuclear power production is to be eventually phased out, it is vital to develop alternative sources of energy along with means to generally lower the energy consumption. Much of the focus has been put on biomass burning. Replacing a part of the energy potential of nuclear power in Sweden with non-fossil fuels would necessarily involve an intense utilisation of forest resources which has led to concern for the environmental effects, such as increased soil acidification. This is of special concern at high sulphur deposition areas in SW Sweden, where nutrients such as  $\text{Ca}^{2+}$  or  $\text{K}^+$  continue to be leached from the soil as a direct consequence of historical and present acidifying deposition.

### **3. Aims and scope of project**

This project is a continuation of earlier modelling projects mainly focused on simulating the recovery process in the covered catchment experiment (Moldan et al., 1998a).

The overall aim of this project is to develop a model tool for predictions of forest soil and stream water response to changing loads of acid deposition, geographical variations of this response, and the effects of land-use such as forestry, fertilisation and liming.

The major task has been to adapt the model to allow calculations of forest soil response in different catchments in southern Sweden and to evaluate the future recovery process in this region.

### **4. Model description**

#### **4.1 Selection of model**

Models can be used for evaluation of results from field experiments and for extrapolation of results to other scenarios and to other time scales. However, mathematical descriptions of processes in different compartments of the environment can never be exact and simplifications are necessary. Two different types of models can be used; *process models* are based on descriptions of a limited number of governing processes in the system to be investigated. They require a firm knowledge of the governing processes and how they interact with each other. *Statistical models* on the other hand are based on statistical relationships between measurable parameters and are often based on regression analysis of measured parameters. Both model types can be either dynamic i.e. with a defined time scale, or static in which case only the final end point is predicted.

In this project, the model MAGIC (Model of Acidification of Groundwater in Catchments) has been used (Cosby et al., 1985a,b). This model can be characterised as a dynamic model with mathematical descriptions of key soil processes. MAGIC was chosen because of its general usefulness and its capability to generate results without unrealistic demands on input data. This was specially important for the generalisation since detailed information may not be available for sites in the geographical region to be investigated.

MAGIC has been applied to data from the Roof project (Moldan et al., 1998c). It has also been compared with other well-known acidification models; SAFE (Warfvinge et al., 1993) and SMART (de Wries et al., 1989). The results of these comparisons show that all three models can reproduce the changes in run-off after the construction of the roof (Beier et al., 1996).

#### **4.2 Description of MAGIC**

MAGIC is based on the theory of mobile anions in which deposition of sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and to some extent chloride ( $\text{Cl}^-$ ) with hydrogen as counter-ion leads to acidification. The hydrogen ions are exchanged on soil particles in an ion-exchange reaction with base cations which leave the system together with the mobile anions in run-off.

MAGIC is based on a simple mathematical model developed by Reuss (1983) describing the chemical equilibrium between ions in soil solution and adsorbed on soil solid phase. The Reuss model has been expanded to take into account the effect of carbonic acid ( $\text{H}_2\text{CO}_3$ ) on the  $\text{Ca}^{2+}$  -  $\text{SO}_4^{2-}$  system (Reuss and Johnsson, 1985).

MAGIC reduces the natural variability in soil chemical properties to an average soil with a maximum of two layers which are assumed to represent the whole investigated area. The model is not area-specific and all calculations are made per unit area,  $1 \text{ m}^2$ . The time steps can be set to one month or one year.

In the model water from precipitation can be channelled directly to the run-off, through one or both soil layers (which can be arranged vertically or horizontally) or as any combination of these. Using these options is meaningful at sites where information about water flow and chemistry in the different soil compartments is available.

The model contains 3 main parts; equilibrium chemistry, mass-balance and a part which links the two former via a set of definitions relating the equilibrium equations to different parts of the mass-balance expressions. The equilibrium chemistry part contains equations quantitatively describing the soil chemistry processes and processes occurring in the transition from soil water to stream water. The mass-balance part consists of quantitative descriptions of input-output relationships for base cations and strong acid anions.

#### **4.3 Calibration procedure**

Our current understanding of forest ecosystems is not sufficient to quantitatively describe substance flows and time-dependent processes. Thus, experimentally derived information on soil chemistry and microbiology, interactions with vegetation and hydrology etc. are not sufficient for model calculations. Models used for predictions of acidification and recovery must be calibrated i.e. a model calibration of governing parameters to real measured fluxes and concentrations must be made.

In MAGIC, the calibration procedure is based on measured chemistry in run-off, deposition to open field and throughfall, the physical and chemical properties of the soil, historic land use and vegetation uptake, and estimated historic deposition.

The calibration is made in steps. First,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are adjusted so that the modelled  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations match those in run-off. This is done by changing the input, the hydrology and parameters of sulphur adsorption in the soil. In the covered catchment at Gårdsjön, no adjustment to data is needed for  $\text{Cl}^-$  since the throughfall input is in balance with the run-off output. This is generally not the case in other areas where especially the dry deposition can be difficult to determine exactly and has to be calibrated. For  $\text{NO}_3^-$  and for ammonium ( $\text{NH}_4^+$ ), MAGIC contains a very simplified description used for both reduced and oxidised forms of nitrogen. The only adjustment that can be made is the first-order uptake of nitrogen by vegetation to balance the input with the output. In the case of the Gårdsjön catchments, the uptake is calibrated to 99% since there is practically no output of  $\text{NO}_3^-$ . After adjusting  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , base cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  are calibrated by adjusting initial (historical) base saturation of the individual base cations and weathering rates. This can be done using an automated optimisation procedure based on the Rosenbrock algorithm (1960).

MAGIC is calibrated to target values corresponding to the observed concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  in run-off and the exchangeable fractions of base cations in the soil. When applying the optimisation procedure to the base cations, a choice can be made between a calibration to the exact target values or a "fuzzy calibration" where some uncertainty is allowed. In the latter case, the model is calibrated to target windows defined around the target values. Using the exact calibration is meaningful only in cases when exact values of target variables are known. If the annual run-off chemistry is calculated from a few samples per year or if there is not a detailed soil study allowing an exact determination of the soil base saturation, the fuzzy calibration is more appropriate. In all MAGIC simulations described below, the fuzzy calibration method was used.

The physical and chemical properties of soil and surface water for which data are available (e.g. the cation exchange capacity of the soil, bulk density) are set as fixed parameters which are not changed during the calibration procedure. More uncertain parameters such as weathering rates, historic base saturation and selectivity coefficients for individual base cations and aluminium are used as variables in the calibration. Calibration is performed by running a hindcast-simulation of the historic development of soil and surface water chemistry from up to 140 years back in time up to the target year where measurement results are available. After each hindcast simulation, the variables are changed to obtain a better fit to the measured data. This procedure is repeated until the modelling results are acceptable or no further improvement can be reached.

## **5. Modelling the covered catchment**

Although the main purpose of this project is to simulate the acidification and recovery in catchments in representative areas of southern Sweden, a brief summary of the results of modelling efforts on the covered catchment is given here. The covered catchment experiment is unique and provides real data on the effects of reduced atmospheric deposition on the chemistry of soil water and run-off. The results from the first 4 years of covered catchment experiment have been presented elsewhere (Hultberg and Skeffington, 1997) and only the modelling is discussed here.

The roof construction was completed in April 1991, providing a unique experimental

facility for investigating the effects of reducing the anthropogenic component of the atmospheric input of sulphur by nearly 100%. The covered catchment is irrigated with water with a chemical composition corresponding to pre-industrial times. The catchment is representative of a forest ecosystem with a high sensitivity to acid deposition; the soil thickness is low and weathering rates are low.

MAGIC was calibrated to measured results from the period 1988-1989 i.e. 2 years before the completion of the roof construction. The model was then used to forecast the response in run-off using the actual input scenario of the experiment. The model could successfully reproduce all observed trends in chemical composition.

### **5.1 Effects of sea-salt**

Since Gårdsjön is situated near the coast, the deposition of sea-salt is large and highly variable. Large variations in sea-salt deposition has a significant short-term effect on the chemistry of the run-off water. MAGIC is not suitable for simulating these short term effects since  $\text{Cl}^-$  is treated as a conservative element in the simulations i.e. it is transported through the catchment to run-off within the same time step as it is deposited (one month or one year). In reality, a  $\text{Cl}^-$  retention of a few weeks up to a few years occurs depending on hydrology and other factors. This leads to time shifts between simulated and observed ups and downs of the  $\text{Cl}^-$  in run-off. Since MAGIC is based on calculations of ion balances in run-off, an agreement between modelled and observed concentrations of all other elements may be affected by these shifts. An example of this was during the first year after the construction of the roof when the input of sea salt was large and MAGIC overestimated the output of many components. This can be seen clearly in Figure 2. Although the inability of the model to predict short-term chemical changes does not affect its capability for long-term predictions of recovery, it can lead to erroneous results for individual years.

### **5.2 Sulphur dynamics**

Apart from the effects of sea salt, the dynamics of sulphur is the main governing parameter for the chemistry of run-off in the covered catchment. After the completion of the roof construction, the output of  $\text{SO}_4^{2-}$  started to decline fast. This rapid change continued for several years but at a reduced rate. The governing parameter for the sulphur output is desorption of  $\text{SO}_4^{2-}$  previously adsorbed in the soil. MAGIC simulates this process using a Langmuir isotherm for the distribution of  $\text{SO}_4^{2-}$  between soil water and the adsorbed phase.

The total soil store of sulphur consists of two different parts; organic sulphur and adsorbed sulphur. In the Gårdsjö area, 90% of the soil sulphur is in the organic form (Mörth et al., 1995). This sulphur is tightly bound in the soil and there is no experimental evidence that a net mineralisation occurs where the organic sulphur is transformed to the leachable  $\text{SO}_4^{2-}$  form. Thus, all  $\text{SO}_4^{2-}$  that was leached out of the soil after the roof construction originated in the adsorbed fraction. However, net mineralisation of organic sulphur cannot be disregarded as an unimportant process. The currently large store of adsorbed  $\text{SO}_4^{2-}$  will slowly be depleted and other processes such as a net mineralisation of organic sulphur can become relatively more important. In this case, model descriptions based on adsorption/desorption will not be sufficient for simulations of long-term recovery processes in acidified soils. Based on the output rates of today, the current stores of adsorbed sulphur will be depleted in about 20 years.

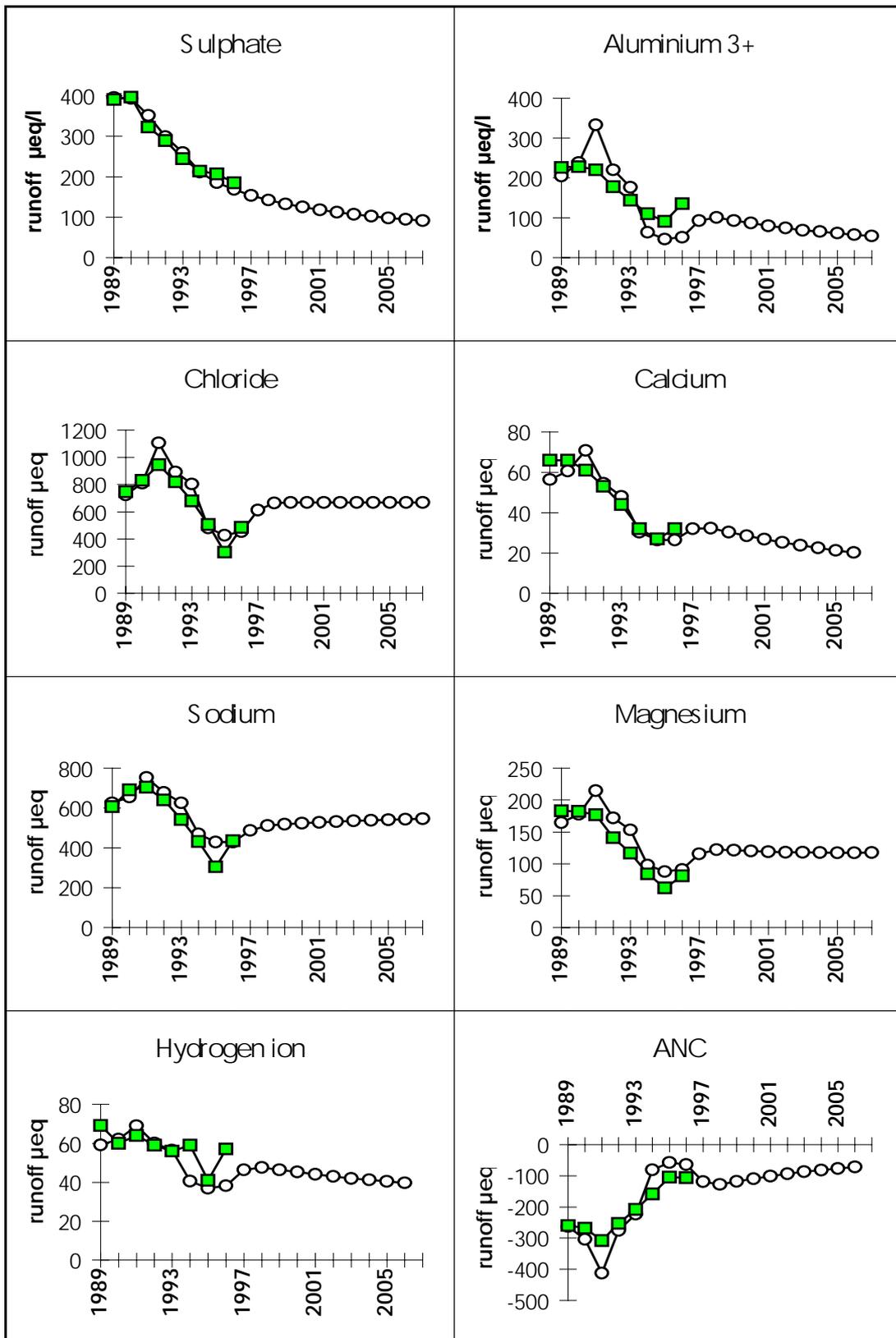
### 5.3 Recovery in the covered catchment

In a severely acidified forest soil at Gårdsjön, large sulphur deposition leads directly to high concentrations of  $\text{SO}_4^{2-}$  in the run-off water, since little retention of sulphur occurs in the soil. Thus changes in sulphur input will directly lead to changes in the overall chemical composition in run-off.

The recovery process can be regarded as a two-phase process. In the first phase, the reductions in input of sulphur and acidity leads to a decrease in run-off concentrations of  $\text{SO}_4^{2-}$ . This leads to corresponding changes in the output of cations with run-off. In the covered catchment, the decrease in  $\text{SO}_4^{2-}$  has led to a decrease in aluminium and base cations (roughly corresponding to 50% each of the  $\text{SO}_4^{2-}$  decrease) whereas output of  $\text{H}^+$  is more or less unchanged. In the second phase, when leaching of adsorbed  $\text{SO}_4^{2-}$  has reached an equilibrium with the input, the recovery will mainly be determined by three processes; weathering of minerals, input of base cations and nutrient uptake by vegetation. If acceptable improvement of run-off water quality is not reached during the first phase (due to high degree of depletion of base cation stores in combination with slow weathering or insufficient reductions of acid input) the recovery may take decades or centuries, if it is at all achievable.

The covered catchment simulates a scenario with a nearly complete reduction of the anthropogenic contribution to the sulphur input and a large reduction of the nitrogen input. The reduction in base cations is moderate but is still of importance for the recovery. At the Roof catchment, the run-off water quality will not reach acceptable levels even after a very long time (>100 years), according to model simulations. To some extent, the unsatisfactory recovery is an artefact of the covered catchment experiment which slightly reduced inputs of base cations along with reducing the S and N (Moldan et al., 1998 b). This, in turn, is caused by practical difficulties in generating artificial throughfall. In short, the deficiency in base cations is caused by difficulties in compensating for the tree root uptake of calcium. In a natural forest stand, the root uptake of calcium is compensated by an internal circulation in the trees yielding an input via throughfall of calcium ions bound to organic ligands. These organic ligands are difficult to characterise which makes it exceedingly difficult to compensate for this flux experimentally. Thus, the covered catchment receives a lower input of calcium than a naturally recovering forest soil. This effect can, however, be compensated for in the modelling so that an ideal scenario of reduced input can be simulated. In Figure 2, results of a simulated ideal case of Gårdsjön forest soil recovery is presented. The simulations are performed after calibrating the model to the covered catchment results and using an ideal scenario of atmospheric input i.e. with “natural” levels of calcium.

The results of simulations over long time periods should always be considered with some care. This is especially true for the predicted absolute concentrations in run-off towards the end of the simulated period. The main conclusion of the Gårdsjön model simulations is that the recovery of severely acidified forest soils will take several decades even if deposition of S and N is practically eliminated in one step. In areas with a low weathering rate and nutrient-poor soils, very small changes in net input of acidifying compounds and base cations will determine the quality of the run-off water for many years into the future.



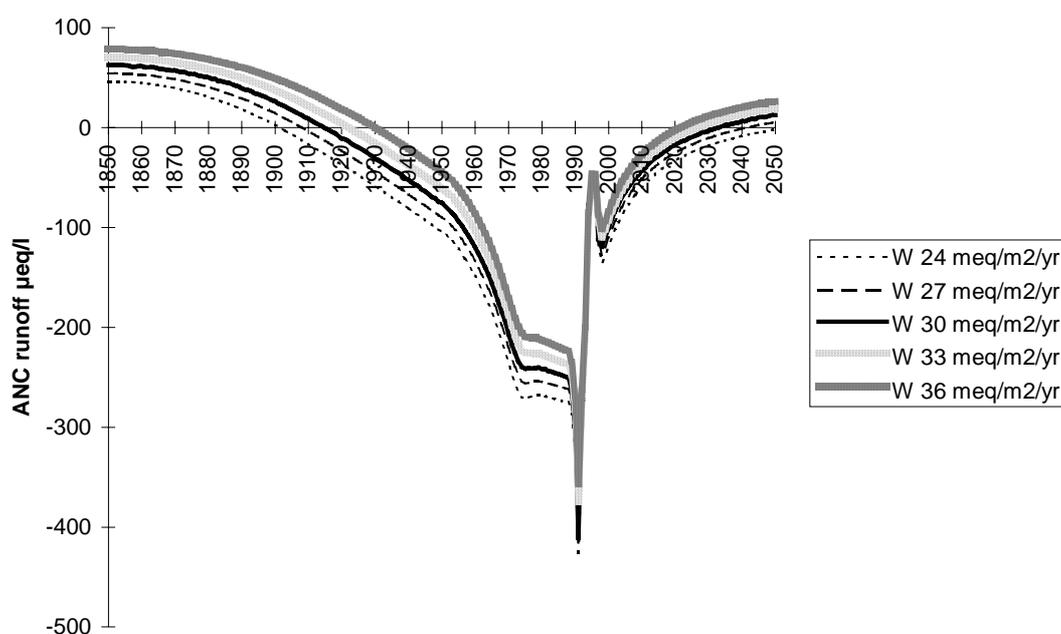
**Figure 2.** Measured (filled squares) and modelled (opened circles) run-off chemistry in the covered catchment experiment. The roof eliminates acidifying deposition from 1991. The run-off became less aluminium rich and slightly less acidic. However, even after 20 years with no acidifying deposition the ANC remained negative.

## 6. Generalisation of MAGIC results - single parameter variation and Monte Carlo simulations

One of the main objectives of modelling acidification and recovery is to generalise results from field measurements and experimental manipulations. This generalisation can be made either over geographical regions where soil properties and degree of acidification varies or by predicting the recovery process for different deposition scenarios. The most informative results are obtained if the generalisation is performed by calibrating the model to measurement results from a wide range of sites in the region of interest. This is the main approach used in this study and the results are presented in section 8. In preparing for this work, two other approaches were used for initial simulations of the variability of recovery: the single parameter variation and Monte Carlo simulations. The results of this work was presented in previous reports (Moldan et al., 1997; 1998a) and only a brief summary is given here.

### 6.1 Single parameter variation

In this approach, MAGIC was first calibrated to the data from the covered catchment. Then, individual parameters were varied and the future recovery process simulated with a deposition scenario corresponding to a complete reduction of anthropogenic contribution to the acid deposition. Here, the results of the simulations where the weathering rate was varied are presented. In Sweden, weathering rates are typically in the range 20 - 150  $\text{meq m}^{-2} \text{ yr}^{-1}$  (Sandén and Warfvinge, 1992). In order to investigate the sensitivity of the predicted recovery, model calculations were performed at weathering rates of 24, 27, 30, 33 and 36  $\text{meq m}^{-2} \text{ yr}^{-1}$ , where the rate of 30  $\text{meq m}^{-2} \text{ yr}^{-1}$  corresponds to the actual rate at Gårdsjön. The predicted ANC was used as an indicator of the overall recovery. The results of these simulations are presented in Figure 3.



**Figure 3.** Predicted recovery of ANC at different weathering rates (24 - 36  $\text{meq m}^{-2} \text{ yr}^{-1}$ ).

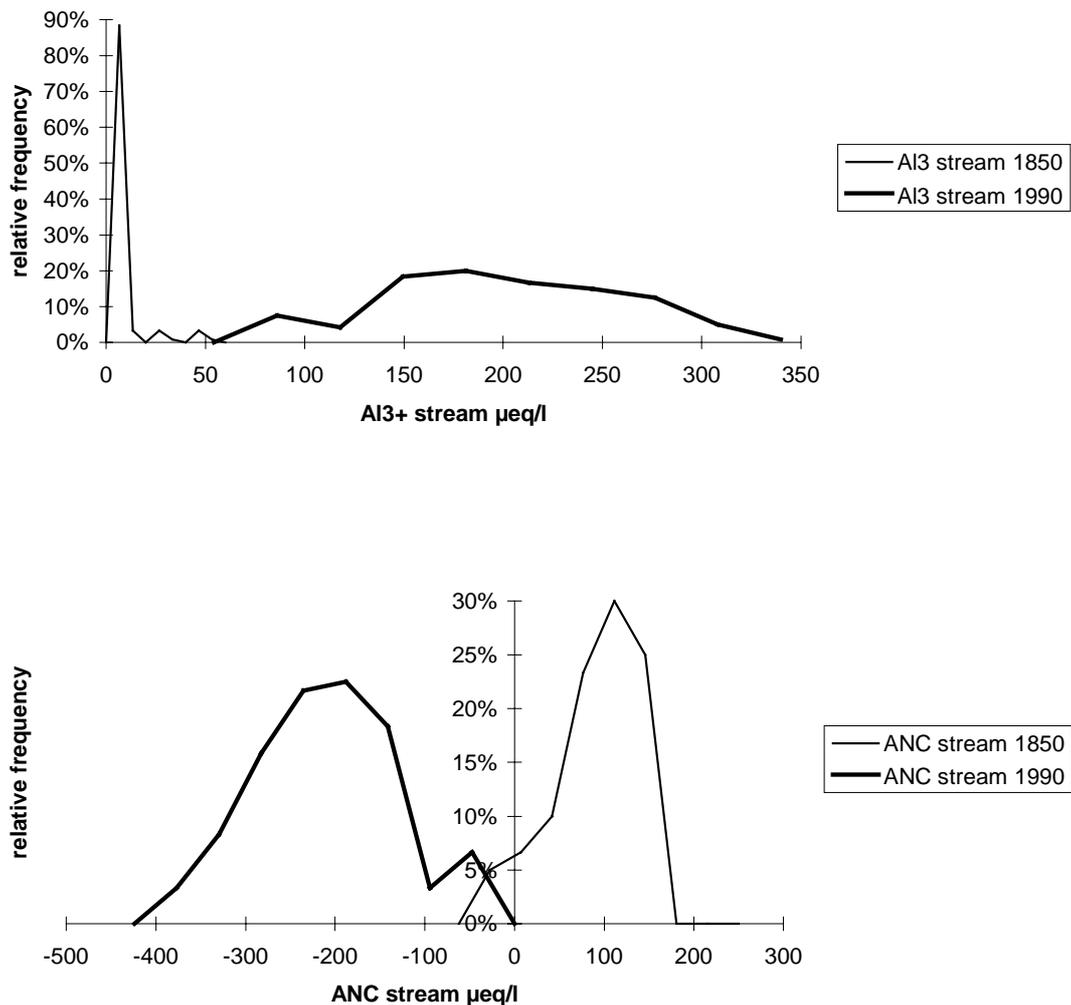
Although the weathering rate was varied within a relatively narrow range compared to the natural variability, the time for recovery (here defined as  $ANC > 0$ ) differs by over 20 years. At a first glance, the curves representing the different weathering rates show a very similar response to the decreased acid input in year 1991 (corresponding to the construction of the roof). However, if  $ANC > 0$  is used as an indicator of recovery, the slope of the curves has decreased so that even these small changes in weathering rates result in predicted times to reach  $ANC = 0$  ranging from year 2020 to 2050 i.e. a difference of around 30 years. This illustrates a general difficulty in predicting the forest soil recovery during the second phase (see section 5.3) for which measurement data are not available for model calibration. Similar, if not equally dramatic, differences are obtained when varying several other parameters such as soil thickness or soil cation exchange capacity.

## **6.2 Monte Carlo simulations**

The Monte Carlo method is a mathematical procedure for random selection and combination of a population of parameters. In this application it is used to create hypothetical sites where the variability in the randomly selected parameters represent the natural variability in the investigated region. Model simulations are then performed on these hypothetical sites to produce a picture of the recovery process in the region. In this project, this method was used to calculate the variability of some basic soil parameters and input/output chemistry in SW Sweden (Moldan et al., 1997).

The initial random selection and combination of parameters is complemented by a test to ensure that all known correlations between parameters are still valid even at hypothetical sites, so that unrealistic sites are rejected. An example of this is the correlation of  $Na^+$  and  $Cl^-$  in wet deposition. These two species are well correlated all over southern Sweden and thus all random selections where this correlation is not present can be discarded.

In this study, Monte Carlo simulations were performed with MAGIC calibrated to the covered catchment. Twenty-two parameters describing deposition and soil properties were varied with the values around the values from the covered catchment ( $\pm 50\%$ ). A total of 1 000 hypothetical sites were created of which 122 were found to be potentially realistic. Hindcast simulations of these sites provide a useful picture of the variability of the response to acidification in this region. In Figure 4, distributions of stream water aluminium and ANC at the years 1850 (representing the start of the hindcast simulation) and 1990 are presented.



**Figure 4.** Aluminium and ANC in stream water in 1850 and 1990 in hypothetical sites in southern Sweden. Calculated using Monte Carlo simulations with MAGIC.

Although these calculations provide a useful picture of the degree and variability of the acidification of forest soils and stream water in region similar to Gårdsjön, this approach was not pursued further to predict future recover scenarios. Instead, the work was focused on calibrating MAGIC to data sets from 20 different forested areas in Götaland region. The results of the Monte Carlo simulations does, however, provide a useful tool for generalisation in areas where measurement results are not available.

## 7. MAGIC simulations at 20 sites in Southern Sweden

### 7.1 Description of the 20 sites

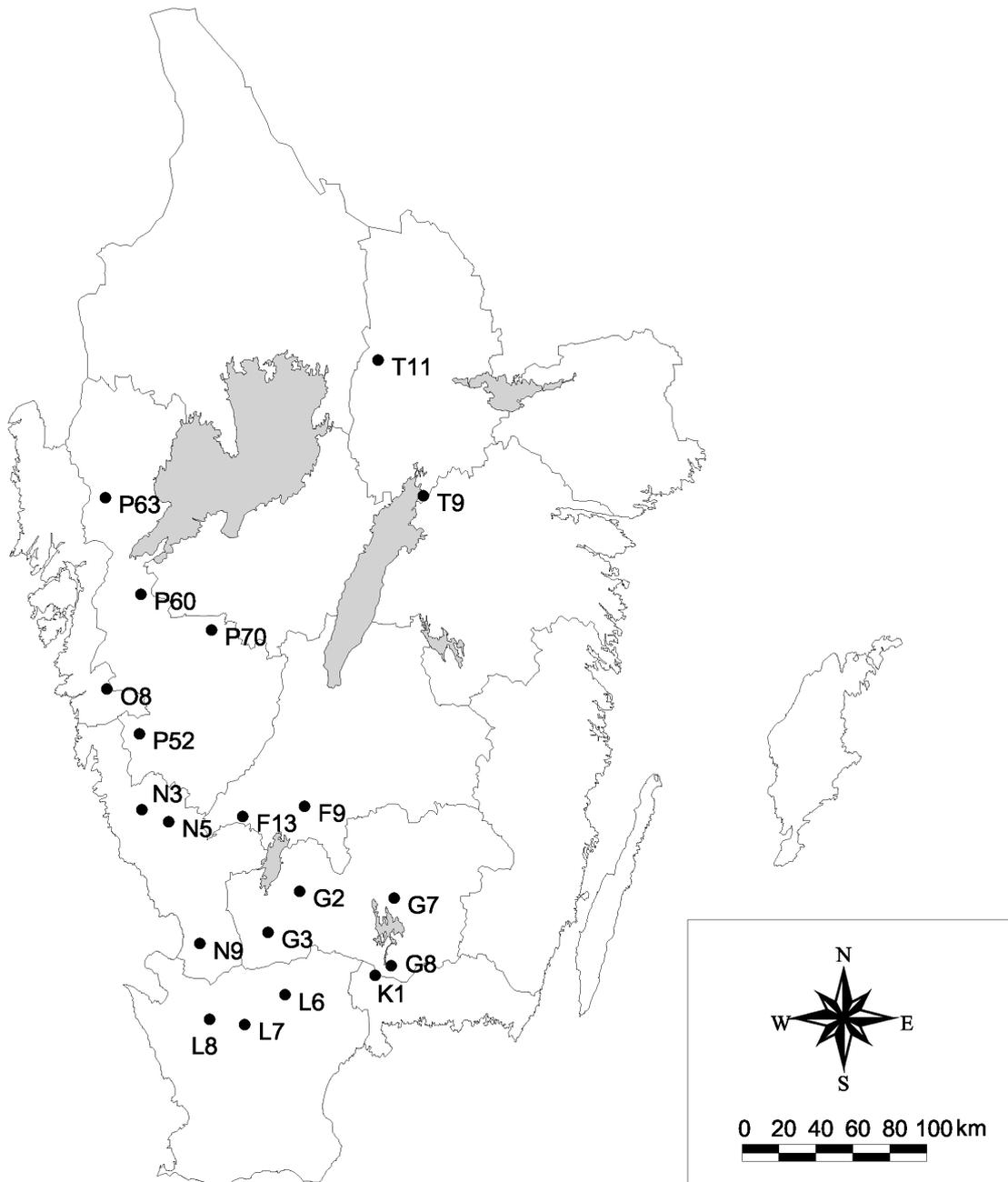
In order to model the acidification and recovery in the southern region of Sweden, MAGIC was calibrated to results of field measurements at 20 representative sites. The sites are all part of the forest monitoring network operated by IVL and SLU, Asa field

station, (Hallgren Larsson et al., 1995). Throughfall and soil water measurements have been performed at the selected sites since at least 1989. A general description of the site characteristics is given in Table 1.

**Table 1.** Description of selected sites, deposition of sulphur (S) in throughfall and nitrogen (N) in throughfall and open field. Soil characteristics are given using the following abbreviations: Sa = coarse sand; Sm = coarse - fine sand; Fm=fine sand; m=morain; s=sediment; Pod=Podsol; Br=Brown soil. The mixture of tree species (Trsl.bl.) is given as 1/10-fractions for pine, spruce and deciduous trees, where X indicates 10/10. Site index (SI) is given in meters. SI=27 m corresponds to an ideal production of ca 8 m<sup>3</sup> biomass ha<sup>-1</sup> yr<sup>-1</sup> and SI=35 ca 15 m<sup>3</sup> biomass ha<sup>-1</sup> yr<sup>-1</sup> TF=throughfall, OPF=open field. Data from Örlander et al., (1994).

Site	Name	Height asl, m	Textu re	Soil type	Tre e spec ies	Tree heig ht, m	Age bh., yr	Ground area, m <sup>2</sup> /ha	SI, m	S dep., TF kg/ha, yr	N dep., TF kg/ha yr	N dep., OPF kg/ha yr
F9	Alandsryd	225	Sm m	Pod	0X0	25	62	36,6	31	16	5	10
F13	Fällinge	230	Sm m	Pod	0X0	27	71	37	50	23	10	16
G2	Orberg	175	Sm m	Pod	0X0	27	55	35,8	34	16	5	8
G3	Beterås	175	Sm m	Pod	0X0	24	62	33,3	30	24	8	11
G7	Osaby	165	Sm m	Pod/Br	280	26	88	35,7	27	12	4	7
G8	Krokshult	140	Sm m	Pod	190	26	89	35	28	19	8	7
K1	Dalanshult	125	Sm m	Pod	0X0	28	66	36	33	18	9	9
L6	Lur	100	Sm m	Br/ Pod	0X0	19	28	49,4	37	17	13	9
L7	Västra Torup	120	Sa m	Br/ Pod	0X0	21	43	37,4	32	20	9	10
L8	Klippan	50	Sa m	Br/ Pod	0X0	25	46	43,2	34	21	13	10
N3	Brännhult	100	Sm m	Br/ Pod	0X0	31	67	38,4	35	24	19	15
N5	Normanstorp	125	Sm m	Br/ Pod	0X0	27	63	34,1	33	20	12	15
N9	Ahla	50	Sa sed	Pod	0X0	24	533	41,9	32	20	21	11
O8	Jonsered	125	Sm m	Pod	190	21	41	25,5	322	23	19	15
P52	Ösjö	100	Fm m	Br/Pod	0X0	26	55	37,3	33	24	15	12
P60	Koberg	75	Fm m	Pod	190	26	86	38,8	28	15	8	8
P63	Högsäter	100	Fm sed	Pod	0X0	22	48	30,4	31	14	7	9
P70	Hudene	150	Fm m	Pod	0X0	24	54	30,1	31	10	4	6
T9	Hammar	125	Sm m	Br	0X0	30	75	29,8	33	10	6	9
T11	Karlskoga	150	Sm m	Pod	280	24	50	46,5	33	11	4	6

The sites were selected to represent a gradient in sulphur deposition and soil properties. In addition to this, they were also selected to give a good geographical distribution in the region of interest. The location of the selected sites is shown in Figure 5.



**Figure 5.** Geographical location of the selected sites.

## **7.2 Model parameters and driving variables**

Data from field investigations have been used to create a set of parameters for each location. The data can be classified in three categories:

- i) fixed parameters describing the soil and its properties such as cation exchange capacity (CEC), base saturation and weathering;
- ii) driving variables such as time series of deposition and the net uptake of nutrients by the vegetation;
- iii) data used for calibration, in this case soil water chemistry.

### **7.2.1 Fixed parameters**

Information on soil properties at different depths has been at each site weighted to one representative average value. A one-box approach has been used, i.e. the soil down to a certain depth (Table 2) was represented by one set of parameters, since the available data on soil water chemistry was measured at one depth (50 cm). Data of the fixed soil parameters is presented in Table 2.

Using a one-box approach also means that the water flow through the soil is treated in a very simplistic way, i.e. no lateral flow is modelled. This assumption might be close to reality in recharge areas which typically make up most of any catchment area. In the recharge areas (slopes) the water from precipitation is transported through the unsaturated zone vertically for most of the time. However it is less realistic for discharge areas (valley bottom) or generally for areas with shallow groundwater, where the lateral flow from the upper soil to the stream is more important. At the 20 modelled sites the only information about the soil water chemistry is from 50 cm depth. Separate modelling of chemistry of soil waters at other soil depths, which would eventually form run-off, is therefore not possible since measurement data for verification is not available.

**Table 2.** Summary of fixed soil parameters at the selected sites.

Parameter	units	Ålandsr yd	Fälling e	Örber g	Beter ås	Osab y	Krokshul t	Dalanshul t	Lur	V. Torup	Klippa n	Brännh ult	Normanst orp	Ahla	Jonser ed	Ösjö	Kober g	Högsät er	Huden e	Hamm ar	Kariskog a
		<b>F 9</b>	<b>F13</b>	<b>G 2</b>	<b>G 3</b>	<b>G 7</b>	<b>G 8</b>	<b>K 1</b>	<b>L 6</b>	<b>L 7</b>	<b>L 8</b>	<b>N 3</b>	<b>N 5</b>	<b>N 9</b>	<b>O 8</b>	<b>P 52</b>	<b>P 60</b>	<b>P 63</b>	<b>P 70</b>	<b>T 9</b>	<b>T11</b>
soil thickness	cm	67	66	65	55	67	69	60	63	66	68	64	67	68	56	65	70	73	64	63	55
bulk.dens.	g/cm3	1.15	1.16	1.18	1.13	0.96	1.12	1.05	1.21	1.17	1.13	1.19	1.15	1.13	1.10	1.17	1.11	1.06	1.19	1.21	1.13
soil mass	kg/m2	768	767	765	618	640	772	627	761	766	770	764	769	771	621	766	774	780	764	761	619
CEC	meq/kg	24	24	17	19	47	36	52	19	27	28	28	24	26	14	20	43	47	16	32	21
CEC*	eq/m2	18	18	13	11	30	28	32	15	21	21	22	19	20	9	15	33	37	12	24	13
BSat	%	11%	12%	13%	12%	15%	17%	20%	43%	10%	9%	15%	10%	17%	9%	27%	7%	13%	15%	38%	14%
ECa	%	4.8%	6.0%	7.5%	5.3%	7.5%	11.5%	12.6%	36.5%	5.2%	3.6%	8.2%	4.3%	10.0%	2.6%	15.8%	2.1%	7.2%	6.0%	28.4%	8.5%
EMg	%	2.8%	2.6%	2.2%	3.0%	4.5%	2.1%	4.1%	2.0%	2.1%	2.1%	3.1%	2.9%	3.6%	1.6%	5.1%	1.5%	3.5%	3.8%	6.0%	2.5%
ENa	%	2.1%	2.1%	1.1%	1.1%	1.8%	1.6%	1.6%	2.8%	1.0%	1.4%	2.4%	1.4%	2.0%	3.7%	3.0%	2.0%	1.8%	2.5%	2.4%	1.0%
EK	%	1.7%	1.6%	1.8%	2.4%	1.4%	1.9%	2.0%	1.2%	1.8%	1.6%	1.3%	1.9%	1.3%	1.3%	3.3%	1.2%	1.0%	1.4%	2.1%	2.1%
Ca weathering	meq/m2 /yr	12	14	16	15	20	15	17	18	14	13	23	16	9	17	29	14	14	11	9	10
Mg weathering	meq/m2 /yr	5	3	5	5	7	6	8	6	3	4	10	4	1	9	15	7	6	3	3	4
Na weathering	meq/m2 /yr	4	6	7	6	8	5	6	7	6	6	6	7	4	6	10	5	6	4	4	5
K weathering	meq/m2 /yr	3	3	4	3	4	3	3	4	4	4	3	3	3	2	3	3	3	3	2	4
Ca uptake	meq/m2 /yr	44	30	44	38	36	31	40	124	59	80	39	45	62	62	51	41	60	47	54	61
Mg uptake	meq/m2 /yr	12	8	13	11	11	9	12	39	19	25	11	13	18	16	14	10	14	12	13	13
K uptake	meq/m2 /yr	14	9	14	12	12	10	13	43	21	27	12	14	20	18	15	11	16	13	14	16
Stand age (1993)	age yrs	68	76	62	63	88	99	66	33	48	58	85	69	64	55	77	92	57	61	79	53

CEC = Cation Exchange Capacity.

CEC\* = for given soil depth.

Bsat = Base saturation.

EMg, ECa, ENa, EK = Exchangeable magnesium, calcium, sodium, potassium.

For modelling purposes, information on soil capacity per unit surface area is needed whereas experimentally determined parameters are often given per unit weight. To transform different intensity parameters (concentration per kg) to capacity (concentration per m<sup>2</sup>), information on soil mass per unit surface is needed. This property can be calculated from the soil bulk density, although this has not been measured at the selected sites. In this work, we have used soil bulk density data from forest soil investigations (Karlton (ed), 1995), where soil bulk density measured at 10 sites in Götaland (South Sweden) and at 9 sites in Svealand (Central Sweden) is reported, see Table 3.

**Table 3.** Average soil bulk density in Götaland and Svealand (Karlton, 1995).

	<b>Götaland</b>	<b>Svealand</b>	<b>Average Göt+Svea</b>
Soil horizon	bulk density (g/cm <sup>3</sup> )	bulk density (g/cm <sup>3</sup> )	bulk density (g/cm <sup>3</sup> )
humus	0.24	0.12	0.18
mineral soil 0-10 cm	1.07	1.20	1.13
mineral soil 10-20 cm	1.14	1.01	1.08
mineral soil 20-30 cm	1.22	1.17	1.20
mineral soil 30-40 cm	1.32	1.27	1.29
mineral soil 40-50 cm	1.44	1.37	1.40
mineral soil 50-60 cm	1.47	1.45	1.46
mineral soil >60 cm	1.40	1.39	1.40

The soil bulk density at the sites in this study was calculated by weighting the soil density values from Table 3 with the measured thickness of the different soil layers at the selected sites. The resulting values for soil mass per unit area were then used to calculate the soil capacities given in Table 2.

### 7.2.2 Driving variables

The most important driving variable for MAGIC is the deposition. Two years (1989 - 1990) of data on throughfall, open field deposition and calculated total deposition has been used. The 20 selected plots represent a gradient in deposition of sulphur, nitrogen and sea-salt, see Figure 6 a-c.

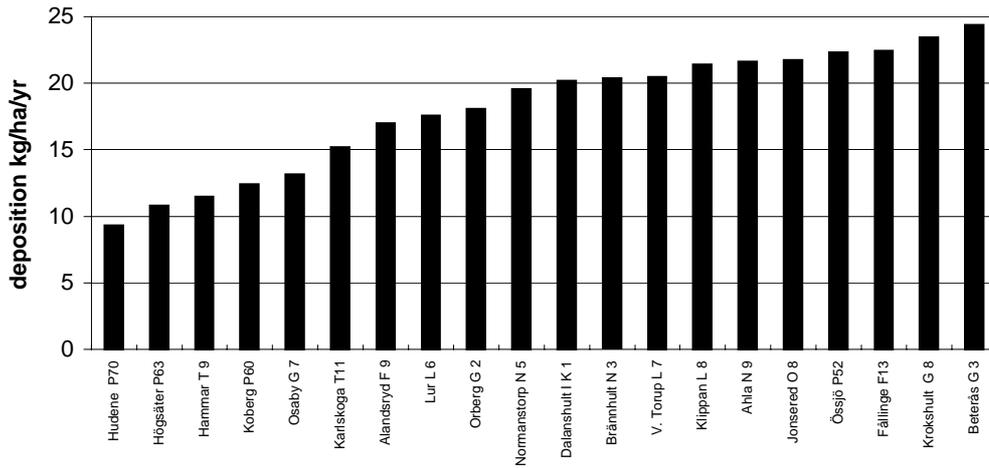


Figure 6a. Deposition of sulphur (SO<sub>4</sub>-S).

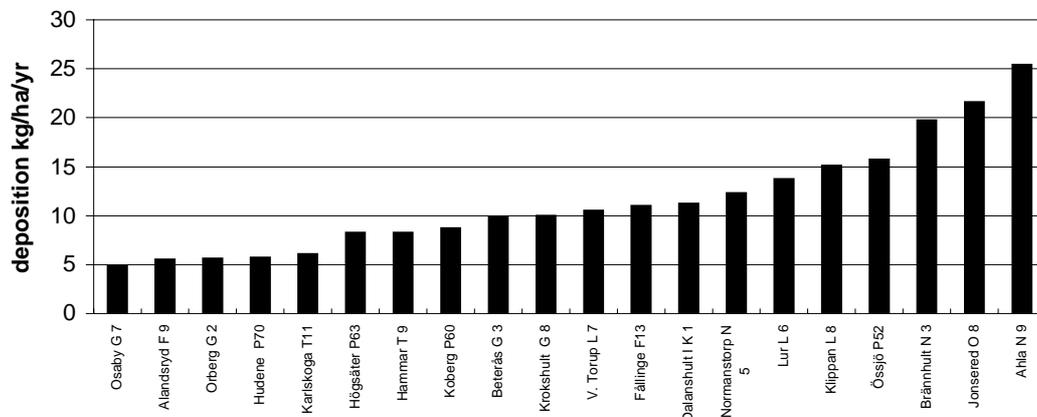


Figure 6b Deposition of nitrogen (NO<sub>3</sub>-N + NH<sub>4</sub>-N)

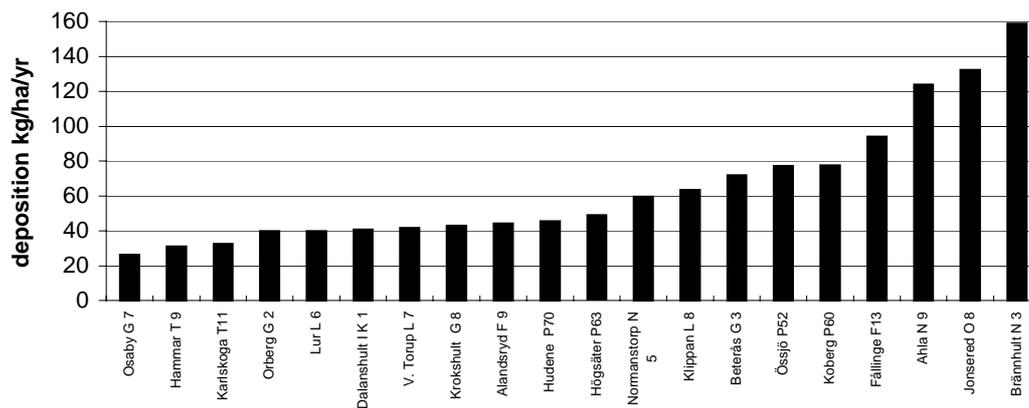
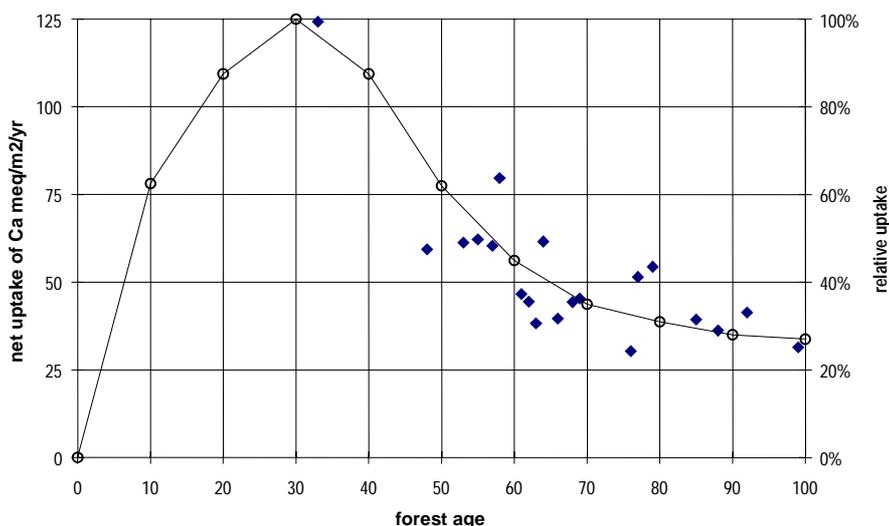


Figure 6c Deposition of chloride (Cl)

**Figure 6.** Deposition of non-marine sulphur (SO<sub>4</sub>-S) (a), total nitrogen (NO<sub>3</sub>-N + NH<sub>4</sub>-N) (b), and chloride (Cl) (c) at the 20 selected sites arranged from lowest to highest values.

The second most important driving variable is the tree uptake of nutrients. The net uptake of base cations was calculated by fitting the empirical data from the sites. Maximum uptake was assumed to take place at canopy closure i.e. when the projected canopy surface completely covers the ground surface, at a tree age of 30 years. The time series of base cation uptake was calculated from the empirical observations and information on forest stand age and latest rotation. The uptake model is presented in Figure 7.



**Figure 7.** Empirical model for calculating forest stand uptake of nutrients at the 20 selected sites. Opened circles are modelled uptake and closed squares are uptake of calcium at actual sites.

The absolute values given in Figure 7 were used in the initial phase of the MAGIC calibration. However, it was found that these values were too high and a recalculation of uptake was made for each individual site with a retained shape of the uptake curve. See further discussion in section 8.1.5.

### 7.2.3 Soil water chemistry

The general calibration procedure is presented in section 4.3. The first step is to enter all the fixed parameters and data on nutrient uptake and deposition. Then, parameters for which direct measurement results are not available are adjusted manually or with help of an automatic optimisation routine.

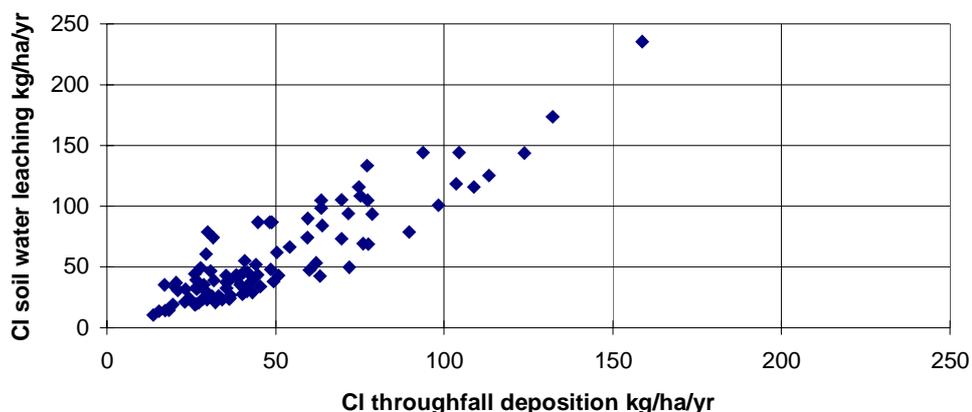
The aim of the calibration is to model from a specific point in the past up to the target year and to simulate the chemistry of the groundwater, run-off or, as in this case, soil water. The evaluation of model fit is made using the minimum of sum of squares of the standard deviation between the measured and modelled target variables such as run-off concentrations of individual ions and soil saturation with individual base cations.

Generally, the 20 sites fulfil the main requirements for modelling purposes. Measured

or calculated values for all important parameters and variables used in MAGIC are available with the exception of soil bulk density which was calculated as described above. Despite this, it was found that modelling the soil water chemistry as measured with lysimeters was not feasible. The explanation for this fact is that the calculated annual averages of chemical parameters in soil water could not be extrapolated to annual fluxes by multiplying with calculated water flows. The soil water investigations were not originally made for the purpose of calculating annual fluxes at the sites. Lysimeter sampling does not provide information on soil water flows and an estimate has to be made. This estimate was based on precipitation amounts and was adjusted to give the best flow estimate based on measured soil water concentrations. This is a compromise with regard to the conservative  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  budgets and means that these calculated fluxes are not directly applicable as input data to MAGIC which works after a mass balance principle.

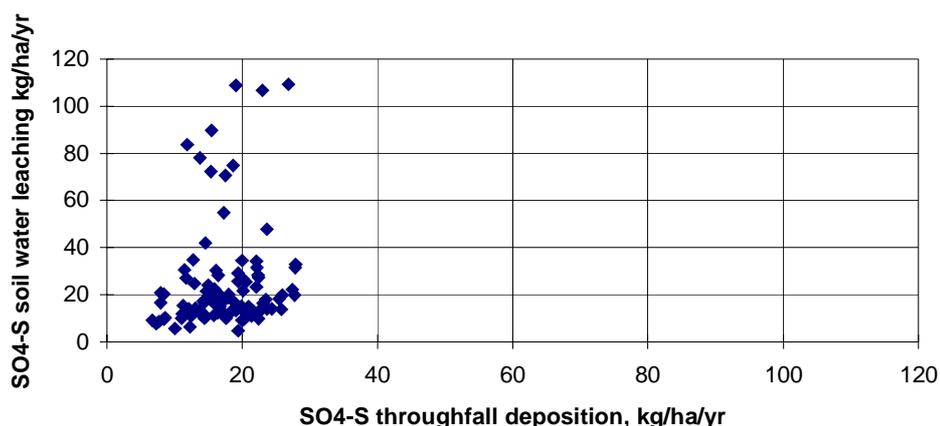
#### 7.2.4 Chloride and sulphate budget

Chloride is assumed to be a conservative element in deposition, and transport through the soil and run-off. During limited time periods, deviations between input and output of  $\text{Cl}^-$  can appear, i.e. during episodes of high sea salt concentrations in precipitation during storm events in coastal regions. The  $\text{Cl}^-$  budget can then take months or even years before it is in equilibrium. On average, however, the input and output of  $\text{Cl}^-$  should follow a 1:1 relationship. This is not the case when the  $\text{Cl}^-$  deposition is compared to the calculated  $\text{Cl}^-$  output at the 20 sites, (Figure 8).



**Figure 8.** Annual deposition and export of chloride during 1989-1993 at the 20 selected sites.

At most of the sites, the  $\text{Cl}^-$  output is higher than the input. This can be corrected for by increasing the evapotranspiration in the model by 40%. However, the third important mass balance factor apart from  $\text{Cl}^-$  and water, the sulphur budget, could not be adjusted at the same time. Irrespective if the water flow is corrected to balance the  $\text{Cl}^-$  budget or not, the annual sulphur export from most of the sites is overestimated in comparison to the input fluxes (Figure 9). This is difficult to explain as a release of previously deposited sulphur, because the sulphur deposition was relatively constant for about a decade preceding the start of measurements.

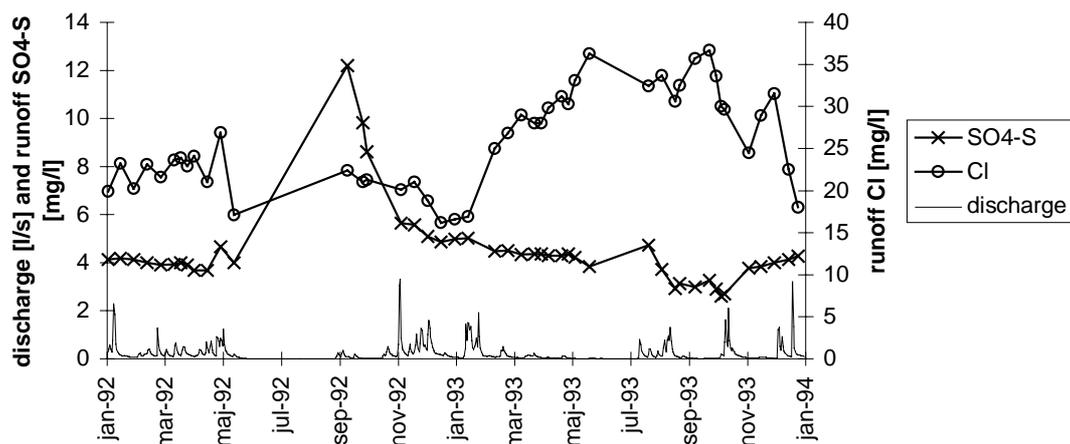


**Figure 9.** Annual deposition and export of sulphate during 1989-1993 at the 20 selected sites.

The sulphur budget at the 20 sites in question, should be more or less in balance. Some sulphur may be bound to growing biomass and deviations from balanced inputs and outputs may occur during fast changes in sulphur input, as seen in the covered catchment data. These factors can only explain part of the deviation observed at the sites. At some of the sites, the calculated export exceeds the input by more than a factor of 5.

MAGIC cannot be used to model these improbable phenomena since there is no mechanism for retention or internal production of  $\text{Cl}^-$  and the parameterisation for  $\text{SO}_4^{2-}$  does not allow for such large variations.

As an illustration of the difficulties in using lysimeter data for flux estimates, run-off data from the Gårdsjön measurements can be used. In Figure 10, a time series of run-off flow,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  from the reference area F1, is shown. Both  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  show large fluctuations but at different times and for different reasons. Sulphate concentrations were extremely high after the long dry period during the summer of 1992. This was mainly caused by oxidation of soil sulphur to  $\text{SO}_4^{2-}$  which was flushed out of the soil during precipitation events in August and September. The high  $\text{SO}_4^{2-}$  concentrations decrease rapidly as higher precipitation leads to higher run-off amounts later in the year. The extreme concentration values in early September have very little effect on the annual fluxes since the water flow was very limited. The  $\text{Cl}^-$  concentrations, on the other hand, did not show any increase during this period. High  $\text{Cl}^-$  concentrations were instead observed in the spring of 1993 when the meteorological conditions prevailing in early 1993 led to high deposition of sea salt.



**Figure 10.** Water flow,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations in run-off from the F1 reference catchment at Gårdsjön.

Since different mechanisms lead to increases in  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , the arithmetic mean of soil water concentrations will be affected differently depending on when the lysimeter sampling is made. For the same reason, an adjustment of water flows to fit the  $\text{Cl}^-$  budget will not necessarily give a correct estimate of the sulphur budget.

The measurements of soil water chemistry at the selected sites are not made with the intention of calculating fluxes. The aim is to investigate the risk for damage to vegetation caused by high concentrations in the soil water. Sample collection has been made during periods of a few days at 3-4 occasions in a year and primarily during situations of high water flows. Estimates of leaching losses per unit area have been made as a control of the plausibility of the results despite the infrequent sampling. This implies that differences in the annual input and output of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  within the ranges of a few tens of percent have been judged as acceptable. It cannot completely be disregarded that some errors in deposition estimates further enhance the deviations. A few tens of percent difference in  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  represents a large part of the ion balance in comparison to the size of weathering, deposition and tree uptake of base cations. For modelling, this means that average values of soil water concentrations cannot be judged as a fully acceptable replacement for run-off data.

### 7.2.5 Estimating run-off chemistry from soil water data

The most critical information for modelling purposes concerning soil water chemistry are not the absolute concentrations but the ratio between the components, mainly non-marine  $\text{SO}_4^{2-}$  and cations. Thus a procedure for calculating a hypothetical run-off chemistry from soil water data has been employed. The basic steps in this procedure are:

1. Estimate the evapotranspiration and calculate the run-off amount as throughfall volume minus the evapotranspiration.
2. Calculate  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations in run-off assuming their conservative budgets and using estimated run-off amounts.
3. Use the composition of the sea-salt to calculate the marine part of the base cations from  $\text{Cl}^-$  concentrations and the relationship between non-marine  $\text{SO}_4^{2-}$  and base cations to calculate the non-marine fraction of the individual base cations.

4. For sites with available  $\text{NO}_3^-$  or  $\text{NH}_4^+$  concentrations, use these values as a basis for the calculations.

The main advantage of this data treatment is that inconsistent data could still be used for modelling purposes because the relationship between concentrations of non-marine  $\text{SO}_4^{2-}$  and non-marine base cations and aluminium is in the recalculated data preserved.

## **8. Modelling of the 20 sites**

### **8.1 Parameterisation of the 20 stations - Driving variables**

#### **8.1.1 Hindcast scenarios**

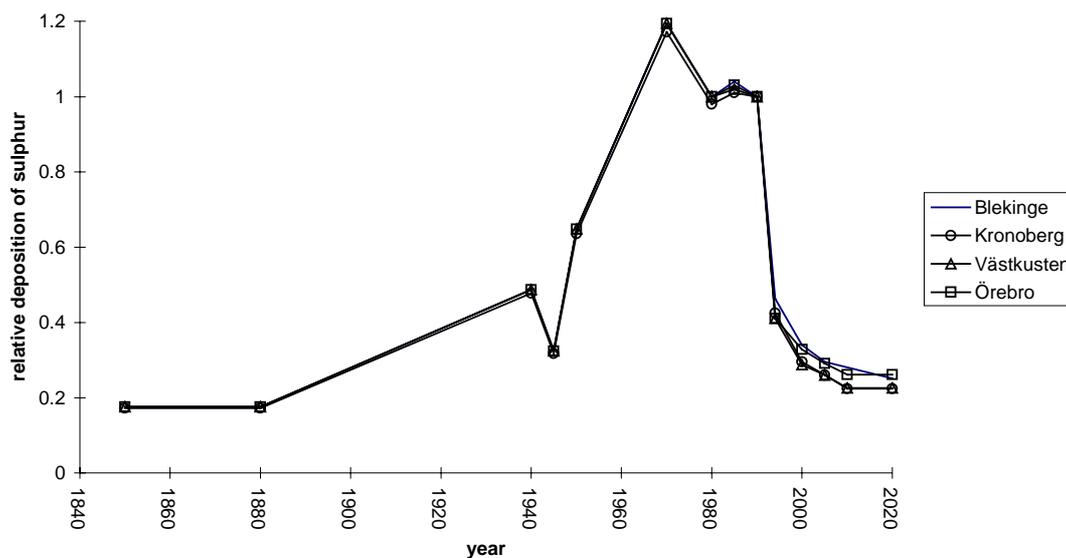
In contrast to test runs described in a previous progress report (Moldan et al., 1998a), separate scenarios for sulphur, nitrogen and base cation deposition, both at historical times in hindcast runs and for the future, have been modelled.

#### **8.1.2 Sulphur**

To obtain the general pattern of historical development of the S deposition during 1850 - 1980, results from the EMEP model calculations were used (Mylona, 1993) at the EMEP square 20, 21 covering large parts of the Götaland region. For the years 1980 - 1990 the temporal pattern of deposition measured at Gårdsjön was used and for the future 1990 - 2010, the EMEP calculations were used assuming full implementation of the Second Sulphur Protocol signed in Oslo in 1994. As a result of these measures, the EMEP model predicts reductions of deposition of non-marine sulphur by 74 - 77% of the 1980 values, by the year 2010. The relative reduction in deposition was scaled for each station to obtain absolute values using the 1989/1990 deposition measured at the sites as reference. For the last modelled decade, 2010 - 2020, the S deposition was set as constant.

The effect of the proposed EU's Strategy Against Acidification has not been included in these modelling studies. If implemented, it would cause a further deposition decline. According to EMEP model calculations (G. Lövblad, pers. comm.), a deposition reduction by a further 4 - 7 % of the 1980 values could be expected for Götaland. The deposition would thus be reduced in 2010 by 78 - 84% from the 1980 values.

In this investigation, the present and future deposition was calculated for four areas denoted as Blekinge (stations G8, K1, L6), Kronoberg (F9, F13, G2, G3, G7), Västskusten (P63, P60, P70, O8, P52, N3, N5, N9, L7, L8) and Örebro (T9, T11). As shown in Figure 11, the differences in deposition reduction between the areas were small.



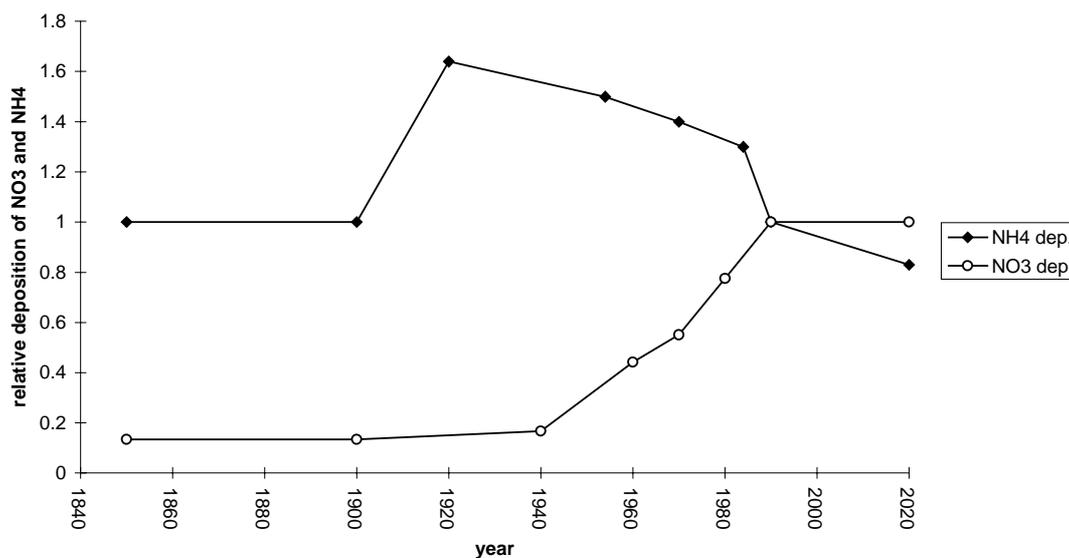
**Figure 11.** Relative scaling factors of sulphur deposition used to calculate historical and future deposition. For each station measured, deposition during 1989/90 was used as a reference to calculate an absolute value.

It should be noted that the above described sulphur deposition scenario is a relatively optimistic interpretation of measured deposition data and agreed emission cuts, where it is assumed that all emissions will be reduced according to the existing agreements and that the relationship between emissions and deposition is linear. The latter assumption is not necessarily correct. A non-linear relationship was observed in Gårdjön (Figure 1) and other sites in southern Sweden during the 1980's when the sulphur deposition was more or less constant (Lövsblad, 1990) whereas the EMEP model predicted declines of nearly 40%. Possible explanations of this non-linearity include unpredictable weather conditions (Lövsblad, 1990) and unusually high levels of ozone and other oxidants in the troposphere (Fricke, 1993). Such time lags between emission reductions and resulting deposition will change the dynamics of the recovery of soils from acidification towards slower improvement.

### 8.1.3 Nitrogen deposition

Historical deposition of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were scaled with regard to estimates of historical emissions of  $\text{NO}_x$  and  $\text{NH}_x$  in Sweden during 1900 - 1960 (Kindbom et al., 1993). Due to the lack of data, the deposition was held constant during 1850 - 1900, at the 1900 level. From 1960 to 1990, the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition were scaled to match the measured deposition at each plot using 1989/1990 as a reference (Figure 12).

With an exception of three stations, Brännhult N3, Ahla N9 and Jonsered O8, there is very little  $\text{NO}_3^-$  leaching at the modelled plots. The deposition of the N is of little importance for the model outcome, since it does not cause direct soil or surface water acidification, with exception of the three above mentioned stations.



**Figure 12.** Relative scaling factors of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition used to calculate historical and future deposition. For each of the stations, measured deposition during 1989/90 were used to calculate an absolute value.

#### 8.1.4 Base cations.

Deposition of base cations (BC) is a notoriously uncertain factor. It is relatively difficult to measure directly or to calculate from throughfall and bulk precipitation monitoring. Historical estimates are also a lot more uncertain than those of deposition of sulphur. Bulk precipitation collectors (which are generally used for deposition monitoring networks) might be biased by collecting an uncertain amount of dry deposition. In addition, throughfall measurements give the sum of deposited BC and BC leached from the canopy where the two are difficult to separate without additional information about a dry deposition of BC e.g. from a particle collector (Ferm and Hultberg, 1995).

The deposition of BC during 1989/1990 at the 20 plots was calculated as a sum of marine BC in throughfall, (assuming all Cl in throughfall originates from sea salt), plus a non-sea salt part of BC in the bulk precipitation (Table 4).

According to an estimate of historical emissions of alkaline particles in Sweden (Kindbom et al., 1993), a dramatic decline of BC emissions occurred throughout most of the 20th century. Thus from a peak emission of  $3 \cdot 10^9$  equivalents/year in the 1920s, emissions have decreased to present values, which are estimated to be about 10-20 times lower. The underlying reasons are mainly the declining use of local scale wood burning for household energy needs, improvements of industrial processes, increased use of oil for energy production from the 1950s onwards, and the introduction of electrostatic particle filters since the 1970s. However, if this decrease in Swedish emissions is used to scale up historical BC deposition, unrealistic results are obtained. This is probably due to uncertainties in historical European emissions; the decrease may be substantially lower during this period. Furthermore the local scale wood burning leads to emissions of relatively large particles which are consequently deposited near their sources. Scaling the BC deposition up by factors

deduced from historical Swedish BC emissions results in strongly alkaline deposition, soil and surface waters over the first half of this century.

Consequently, much lower historical deposition of BC was assumed for the MAGIC modelling. In the simulations a constant sea salt deposition throughout the modelled period has been assumed. The deposition of non marine BC was assumed to be 50 % higher in 1850 than at present and the difference was linearly decreased down to 1990 values.

**Table 4.** Deposition (mean values for 1989/90) at the 20 modelled stations.

meq/m <sup>2</sup> /yr																
Name	Code	year	precip.	Ca	Ca ex	Mg	Mg ex	Na	Na ex	K	K ex	NH <sub>4</sub>	SO <sub>4</sub>	SO <sub>4</sub> ex	Cl	NO <sub>3</sub>
Alandsryd	F 9	89/90	871	8.9	5.1	23.6	2.9	89	10.4	3.6	1.7	18	113	103	104	20
Fällinge	F13	89/90	981	14.3	6.1	46.1	2.2	190	6.6	5.7	1.8	30	158	135	222	46
Orberg	G 2	89/90	799	11.8	8.3	18.9	0.5	80	0	3.4	1.7	15	110	101	93	17
Beterås	G 3	89/90	927	12.7	6.7	33.3	1.1	139	1.5	5.1	2.2	21	167	150	162	37
Osaby	G 7	89/90	645	7.3	5.0	13.5	0.8	55	0	2.9	1.8	13	90	83	64	24
Krokshult	G 8	89/90	681	9.6	5.7	21.5	0.5	91	0	4.0	2.1	19	150	139	106	43
Dalanshult I	K 1	89/90	728	8.8	5.0	20.2	0.2	87	0	3.8	2.0	30	133	123	101	41
Lur	L 6	89/90	627	9.0	5.5	20.2	1.5	81	2.1	5.5	3.8	48	119	109	94	48
V. Torup	L 7	89/90	779	10.1	6.4	21.4	0	86	0.8	5.7	3.9	36	137	126	101	36
Klippan	L 8	89/90	640	11.7	6.5	29.3	0	121	0	5.7	3.2	55	136	122	141	47
Brännhult	N 3	89/90	968	18.6	4.9	74.7	0	317	0	8.2	1.5	53	161	123	370	72
Normanstorp	N 5	89/90	1058	10.5	5.3	29.5	0	121	0	4.1	1.5	37	132	117	141	34
Ahla	N 9	89/90	666	25.4	15.3	55.4	0	234	0	8.3	3.4	104	149	121	273	65
Jonsered	O 8	89/90	1200	21.3	7.6	75.3	1.5	320	4.1	11.9	5.2	68	174	136	373	86
Ösjö	P52	89/90	1240	17.0	9.0	44.6	0	187	1.8	7.1	3.2	49	162	139	218	63
Koberg	P60	89/90	840	13.2	5.1	44.7	0	188	0	6.1	2.1	21	100	78	219	41
Högsäter	P63	89/90	978	20.0	14.9	29.0	1.7	118	0	4.2	1.8	27	82	67	138	32
Hudene	P70	89/90	823	10.4	5.7	26.8	0	110	3.1	7.0	4.7	15	71	58	128	26
Hammar	T 9	89/90	667	10.2	7.4	18.0	3.0	65	6.2	3.7	2.3	18	76	68	76	40
Karlskoga	T11	89/90	668	9.0	6.3	15.7	1.5	62	1.1	3.2	1.9	14	84	76	72	21

### 8.1.5 Uptake sequences

Net uptake of calcium, magnesium, potassium and nitrogen from the soil to the biomass has been simulated in the following way. The year to year variation of the net uptake of base cations by the trees was scaled from the shape of uptake curve (Figure 7) and from forest age at each plot. The total amount of base cations accumulated in biomass above ground was as reported by Rosèn (1988) for a 70-year old spruce forest in Southern Sweden; 1991 meq/m<sup>2</sup> Ca<sup>2+</sup>, 715 meq/m<sup>2</sup> of Mg<sup>2+</sup> and 532 meq/m<sup>2</sup> of K<sup>+</sup>. These values were scaled from the year of planting the trees to year 2020 according to actual forest age at the respective plots (Table 5). For the forest preceding present stand, a constant low net uptake corresponding to 50 % of a net uptake of 100 year old spruce forest was assumed, suggesting an extensive land use. The uptake values used were 5 meq/m<sup>2</sup>/yr of Ca<sup>2+</sup>, 2 meq/m<sup>2</sup>/yr of Mg<sup>2+</sup> and 1.5 meq/m<sup>2</sup>/yr of K<sup>+</sup>.

The significant leaching of NO<sub>3</sub><sup>-</sup> at the plots N3 Brännhult, N9 Ahla and O8 Jonsered was modelled by incomplete nitrogen uptake at these three stations. At the rest of the sites, the nitrogen uptake was set to 99.5 % of atmospheric nitrogen deposition.

**Table 5.** The net uptake of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  to the above ground part of a spruce forest in S Sweden used in the simulations.

forest age	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$
	meq/m <sup>2</sup> /yr	meq/m <sup>2</sup> /yr	meq/m <sup>2</sup> /yr
0			
10	26.0	9.3	6.9
20	36.3	13.0	9.7
30	41.5	14.9	11.1
40	36.3	13.0	9.7
50	25.7	9.2	6.9
60	18.7	6.7	5.0
70	14.5	5.2	3.9
80	12.9	4.6	3.4
90	11.6	4.2	3.1
100	11.2	4.0	3.0

### 8.1.6 Run-off chemistry targets

The soil water sampling at the 20 plots was designed to monitor changes in chemical conditions at the 50 cm depth. The soil water was sampled four times a year. Calculations of volume-weighted average soil water chemistry is not possible because the volumes of water, which should be assigned to each sample, are unknown. The soil water chemistry is not constant. Therefore using a simple average of measured soil water concentrations instead of a volume-weighted average, leads to errors when calculating leaching per unit area. Furthermore, since the ratios between the solutes are concentration-dependent, the differences between simple average and volume-weighted average vary from solute to solute. This has been demonstrated by observed discrepancies in budgets of sulphur and  $\text{Cl}^-$ , Figures 8 and 9, where run-off volume calculated to maintain a conservative budget for  $\text{Cl}^-$  resulted in a clearly unrealistic budget for  $\text{SO}_4^{2-}$  and vice versa. Therefore the average concentrations in the soil water samples could not be used as an estimate of run-off.

As an alternative, soil water chemistry data were recalculated based on a hypothetical run-off. The data were treated as described in a previous report (Moldan et al., 1998a) and in section 7.2.5. The calculated run-off in years 1989/90 (Table 6) was then used as target chemistry for the model calibrations. At the three stations where the  $\text{NO}_3^-$  was present in soil water in significant quantities, the run-off  $\text{NO}_3^-$  was assumed to be the same as in soil water.

**Table 6.** Target run-off chemistry (averages 1989/90) derived from soil water sampling at the 20 sites.

Calculated run-off			mm	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	
Name	Code	year	discharge	SO4	SO4 ex	Cl	NO3	Ca	Ca ex	Mg	Mg ex	Na	Na ex	K	K ex
Alandsryd	F 9	89/90	321	353	320	325	0	36	24	91	26	298	20	7	1
Fällinge	F13	89/90	444	355	303	499	0	20	1	99	0	428	0	9	0
Orberg	G 2	89/90	314	352	322	297	0	36	25	79	21	277	22	11	5
Beterås	G 3	89/90	360	465	418	451	0	34	17	89	0	405	18	15	6
Osaby	G 7	89/90	226	397	368	285	0	15	4	70	14	380	136	5	0
Krokshult	G 8	89/90	185	811	752	572	0	342	320	190	77	494	3	79	68
Dalanshult I	K 1	89/90	306	435	400	330	0	144	132	166	101	324	40	21	16
Lur	L 6	89/90	197	604	554	479	0	695	678	95	0	419	7	9	0
V. Torup	L 7	89/90	330	414	383	306	0	83	71	61	0	262	0	24	18
Klippan	L 8	89/90	227	602	538	620	0	81	58	123	0	532	0	17	6
Brännhult	N 3	89/90	435	370	282	851	149	93	62	169	0	730	0	20	5
Normanstop	N 5	89/90	513	257	229	276	0	17	7	55	0	237	0	5	0
Ahla	N 9	89/90	293	509	413	932	313	65	31	185	0	800	0	45	28
Jonsered	O 8	89/90	723	241	188	516	24	37	18	102	0	442	0	9	0
Ösjö	P52	89/90	632	256	221	345	0	194	181	211	142	296	0	6	0
Koberg	P60	89/90	364	275	214	601	0	45	23	119	0	515	0	11	0
Högsäter	P63	89/90	535	153	126	258	0	18	8	56	5	221	0	5	0
Hudene	P70	89/90	298	240	195	431	0	86	70	138	53	465	95	25	17
Hammar	T 9	89/90	179	423	379	424	0	311	296	162	78	364	0	8	0
Karlskoga	T11	89/90	291	288	262	247	0	79	70	77	28	212	0	50	46

The H<sup>+</sup> and inorganic Al were calculated by the MAGIC model, using Gibbsite solubility constant pK<sub>Al</sub> equal to 8.4 and partial pressure of CO<sub>2</sub> in the soil of 0.5 kPa. The partial pressure of CO<sub>2</sub> in the stream was assumed to be 0.1 kPa i.e. about three times the atmospheric partial pressure of 0.035 kPa.

## 9. Model results

### 9.1 Calibration to targets and hindcast simulations

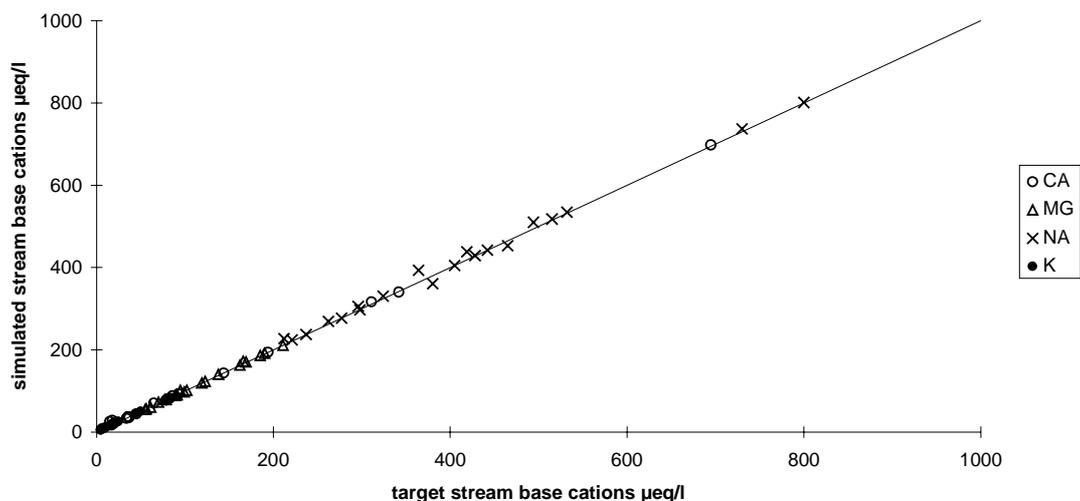
The MAGIC model was calibrated with data from all 20 stations. Target variables to which the model was optimised were soil base saturation with Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> (Table 2) and major ions in target water chemistry (Table 6). At three stations, Osaby G7, Högsäter P63 and Ahla N9 the calibration was unsatisfactory. No reasonable combination of model parameters reproduced target variables in the reference year 1990 well. At G7, the calculated target run-off contained a very high amount of non-marine Na<sup>+</sup> (Table 6) and at the same time the soil saturation with Na<sup>+</sup> was relatively low (Table 2). The high Na<sup>+</sup> in run-off could only be modelled if a high input of Na<sup>+</sup> occurred either from weathering or from deposition. That would, however, result in relatively higher amounts of Na<sup>+</sup> ions at the soil cation exchange sites.

The problem at the P63 station was of similar nature. In this case, the targets had high Ca<sup>2+</sup> saturation of the soil (and to a lesser extent Mg<sup>2+</sup> saturation) and at the same time

the concentrations of these cations in the run-off were low. These discrepancies probably result from the estimates of average soil properties at the two stations. Both stations have fine-grained sedimentary bedrock, in contrast to all other 18 stations where the soils are developed on moraine (Table 1). An estimate of average soil parameters could thus be biased when the soil was sampled and analysed in the same manner as all other soils without special care to their nature.

Monitoring of the G7 station was recently terminated because of the unclear relationship between moderate deposition and high degree of soil acidification, and because of generally inconsistent data. The station Ahla N9 has among the 20 investigated plots an unusually high leaching of nitrate (Table 6). At N9, the target run-off concentration was 313  $\mu\text{eq NO}_3^-/\text{l}$ . The  $\text{NO}_3^-$  leaching at this station exceeds the  $\text{NO}_3^-$  deposition. MAGIC treats the nitrogen cycle in a very simplistic way, which is satisfactory when modelling stations with little or no  $\text{NO}_3^-$  leaching. However, a model describing the specific behaviour of nitrogen is needed if sites with high  $\text{NO}_3^-$  leaching such as N9 are to be modelled with more accuracy.

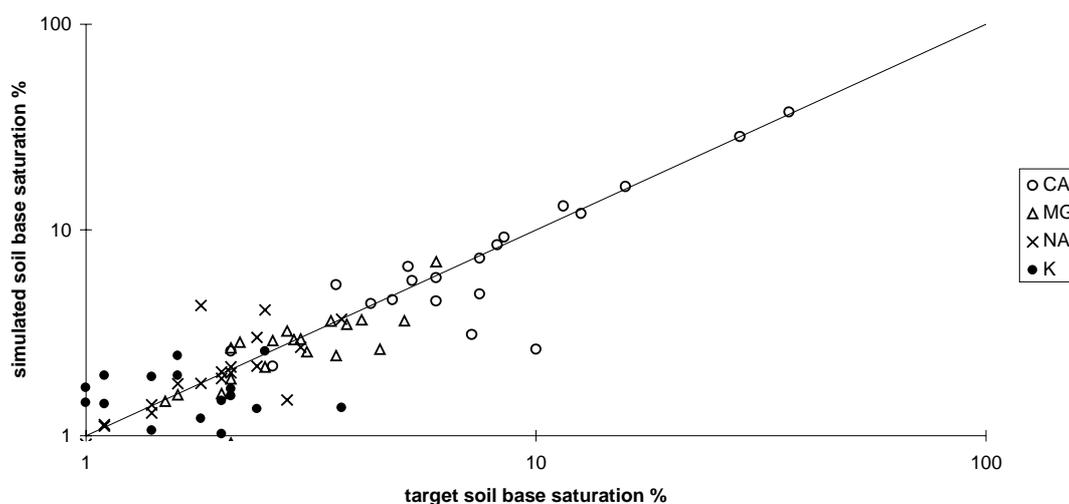
At all remaining stations, modelled concentrations of base cations were within  $\pm 10\%$  error margins from target values. With very few exceptions, the general fit was even closer (Figure 13).



**Figure 13.** Target concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ , (year 1990) plotted against simulated values at the 20 modelled stations.

As discussed above, it was necessary to recalculate the soil water data based on a hypothetical run-off, since the mass balance part of the model could not reconstruct the annual mean concentrations calculated from the soil water measurements. The calculated target run-off chemistry is consequently hypothetical and not measured run-off. This uncertainty needs to be borne in mind. The calculated run-off at the 20 stations covers a rather wide range of run-off chemistry. Perhaps the best way to interpret the results is not only to pinpoint results from each station to its geographical location, but to look at the ranges in model simulations and consider them as valid for ranges of input variables. The uncertainty in predictions should be minimised by such an interpretation.

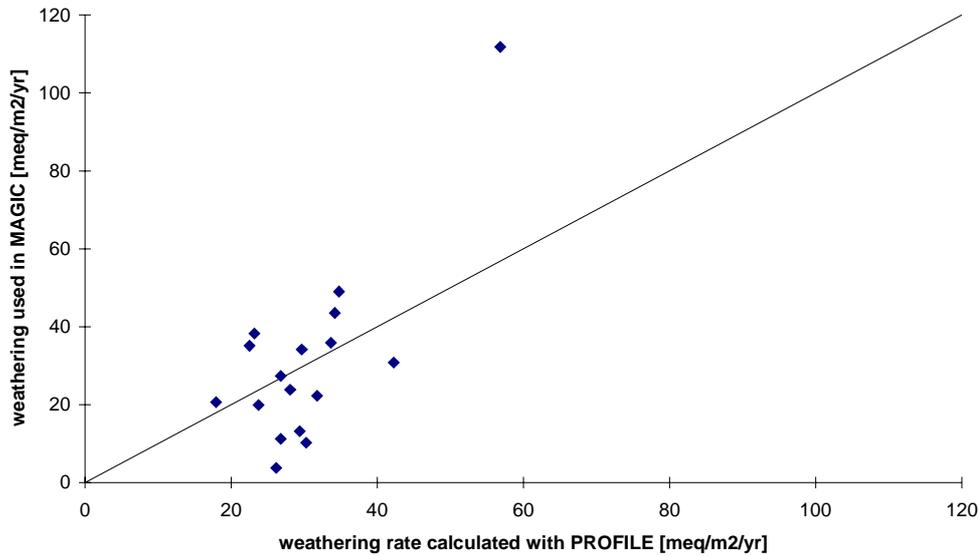
Measured individual base cations saturation in soil was used four additional target variables. Due to spatial variability of soil properties, the uncertainty in the measured values is assumed to be larger than that of run-off measurements. Therefore a larger scatter was allowed in the calibration (Figure 14). Calibration to a  $K^+$  saturation proved particularly difficult. Saturation with  $K^+$  is low relative to other base cations. Thus the simulation of  $K^+$  is particularly sensitive to accuracy of available information on deposition, uptake and weathering. Small relative errors in any of the three factors will have a relatively large impact on the accuracy of the soil  $K^+$  saturation.



**Figure 14.** Target soil saturation with  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$ , (in the reference year 1990), plotted against simulated values at the 20 modelled stations. Note the logarithmic scale.

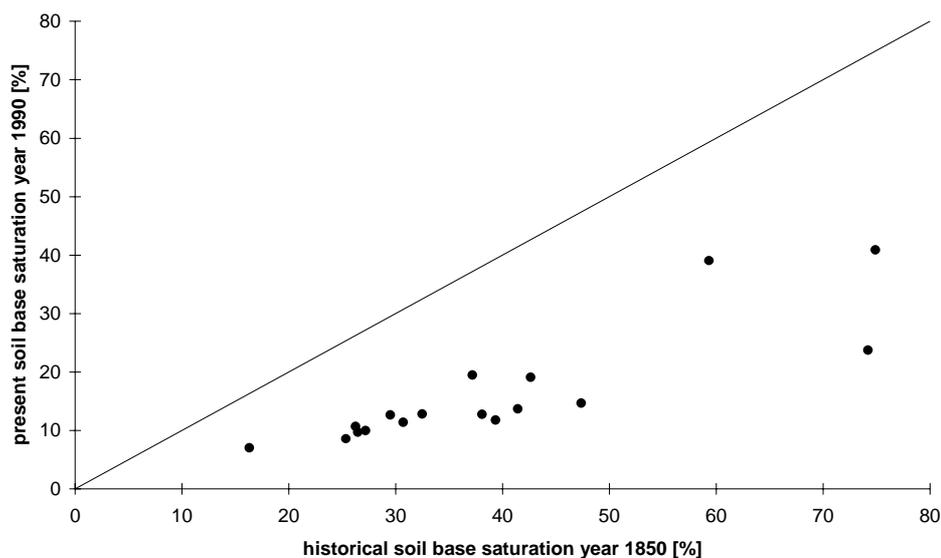
In the MAGIC model, the rate of mineral weathering is one of the parameters which can be set in order to obtain the best fit with target chemistry data. The allowed degree of freedom is defined by the width of the target window within which the weathering rate is varied during the optimising procedure. There are two main reasons for treating the weathering rates in this way. The first one is that, even if weathering rate data, obtained by some independent method, are available at the modelled stations, there exists a spatial variability which causes uncertainty in assuming these values as valid averages for the whole modelled area. The other reason is, that in MAGIC, weathering is treated as a source of base cations together with deposition of base cations while the sinks are net uptakes to biota and leaching. The deposition and net uptake are driving variables while the leaching is calculated by MAGIC. In MAGIC, there is no principal difference between the weathering and the deposition; both are treated as net sources. Together with the sink represented by the net uptake, the combination of these three variables set the conditions for leaching. Since both deposition of the base cations and the net uptake are given, any deviations in these variables from reality will offset the rate of weathering needed in MAGIC for the best fit to be obtained. As mentioned above, deposition of non-marine base cations is often rather difficult to estimate.

The optimised weathering rates used in the MAGIC simulations at the 20 stations were in the same range as the weathering rates calculated from mineralogy of soils at the 20 sites by the PROFILE model. However, at individual stations, the weathering which produced the best fit to the target variables often differed from the PROFILE calculation (Figure 15). The general agreement in ranges of the weathering rates used in MAGIC simulations and from PROFILE calculations was for the above mentioned reasons accepted as satisfactory.



**Figure 15.** Weathering rates calculated by the PROFILE model and the weathering rates used in MAGIC model simulations. In the MAGIC model the weathering rates used gave the best fit between the MAGIC model predictions and the target variables (run-off water chemistry and soil base saturation) in the reference year 1990.

The MAGIC model reconstructed the decline in soil base saturation in hindcast runs from the beginning of the modelled period in 1850 to 1990 (Figure 16). The largest decline was modelled at the stations where the initial base saturation was highest. Relative decline was, however, similar at all stations.

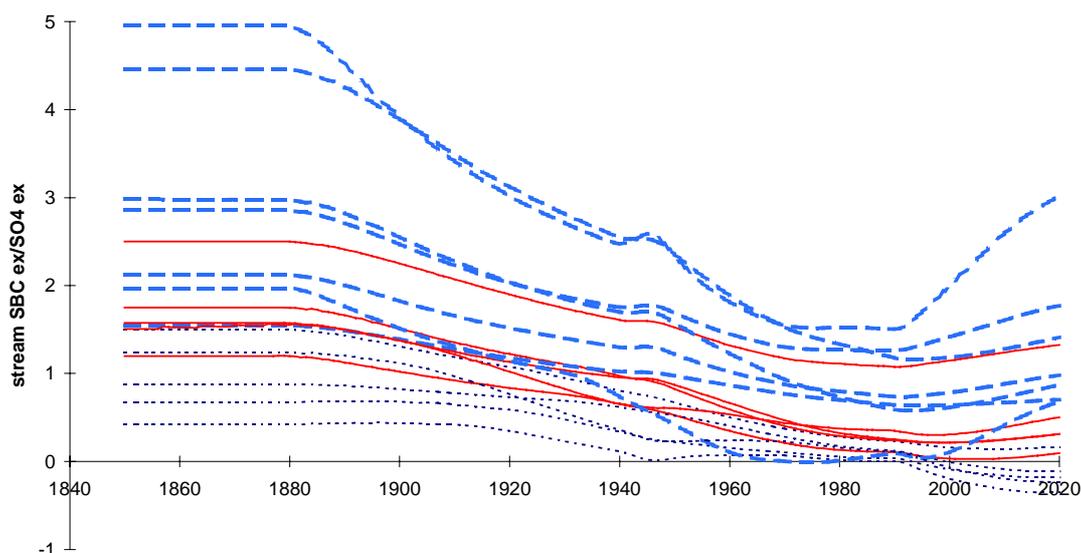


**Figure 16.** Change in the soil base saturation from 1850 to 1990 at the 20 modelled sites.

The soil base saturation has declined as a consequence of the acidifying deposition, primarily of sulphur. Elevated  $\text{SO}_4^{2-}$  in run-off causes leaching of base cations which together with a net uptake of base cations to the vegetation exceeds the sum of deposition of base cations and weathering. Already for year 1850, the simulations assumed a certain amount of non-marine  $\text{SO}_4^{2-}$  in deposition and in run-off. However, at most of the stations, the non-marine  $\text{SO}_4^{2-}$  in run-off was fully balanced by non-marine base cations.

## 9.2 Forecast simulations

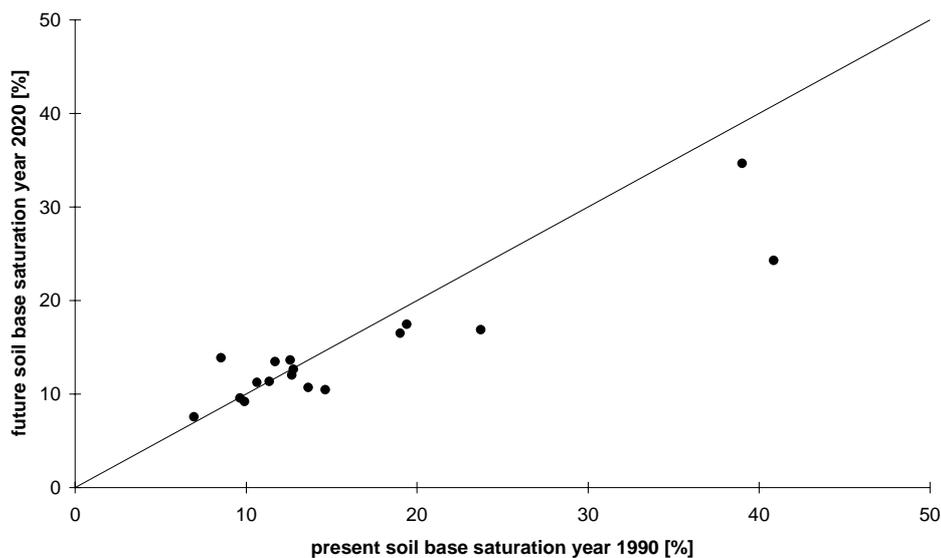
In Figure 17, the results of future predictions of non-marine base cations (SBC ex) and non-marine  $\text{SO}_4^{2-}$  ( $\text{SO}_4^{2-}$  ex) have been divided into three categories according to the weathering rates assumed for the MAGIC simulations at the individual stations. At the stations with the highest weathering, there was up to five times more SBC ex in the run-off than there was  $\text{SO}_4^{2-}$  ex (on an equivalent basis). However, that ratio declined successively at all stations as the deposition of sulphur continued to increase up to 1980. At poorly buffered stations the run-off was completely depleted of non-marine base cations. At the given pH, the soils were practically depleted from base cations and the  $\text{H}^+$  from deposition was exchanged at the soil only with  $\text{Al}^{n+}$ . Declining deposition of non-marine base cations and increased uptake of base cations after planting forest at all stations increased the depletion of bases from the soil. According to this simulation, at the most sensitive sites with the lowest weathering rates, the situation will not be very different for the next 30 years. The successively reduced sulphur deposition will still be high enough to cause further acidification of run-off. At the sites with highest weathering, there will be a certain recovery in SBC ex/ $\text{SO}_4^{2-}$  ex ratio towards pre-acidification values indicating increased availability of base cations in the soil. The sites with an intermediate weathering were with respect to SBC ex/ $\text{SO}_4^{2-}$  ex ratio in between the other two categories (Figure 17).



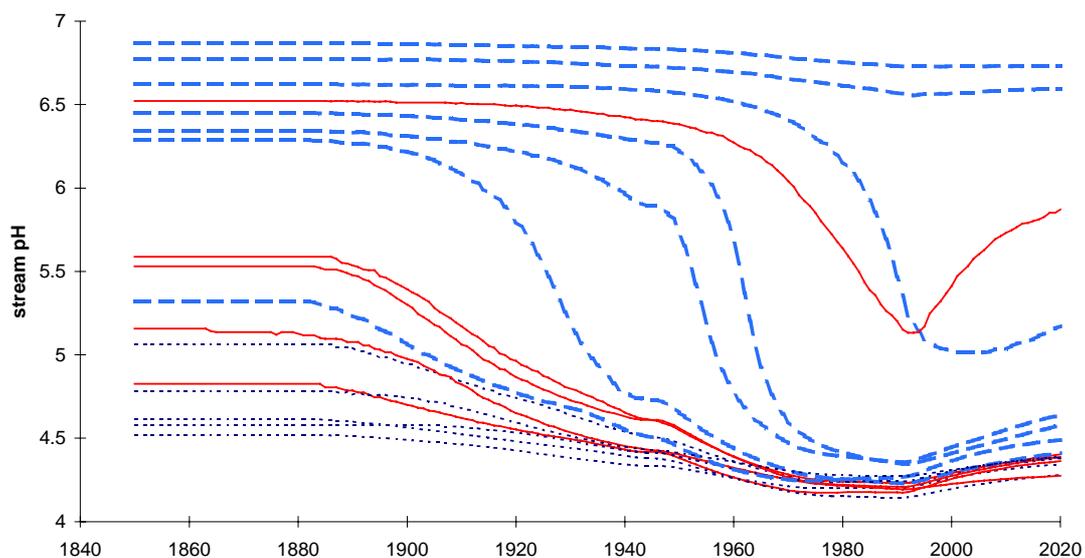
**Figure 17.** Time series of ratios between sum of non-marine base cations (SBC ex) and non-marine sulphate (SO<sub>4</sub> ex). Stations are divided into three categories according to the weathering rates used in the MAGIC simulations. Thin dashed line - low weathering below 20 meq/m<sup>2</sup>/yr (stations F9, F13, L8, N5 and P60); solid line - intermediate weathering between 20 and 30 meq/m<sup>2</sup>/yr (stations G2, G3, L7, N3 and T9) and thick dashed line - high weathering above 30 meq/m<sup>2</sup>/yr (stations G8, K1, L6, O8, P52, P70 and T11).

At seven of the 17 successfully calibrated sites, the modelled decline in deposition from 1990 to 2010 by ca 70% was not sufficient to stop further acidification of their soils. The SO<sub>4</sub><sup>2-</sup> leached caused further decrease in soil base saturation at these sites (Figure 18). Noticeably, these are the 7 sites with highest base saturation in the year 1990. Sites with lower soil base saturation either remained almost unchanged (7 sites, Figure 18) or in three cases increased.

During 1850 - 1990 the MAGIC model simulated pH decline of the run-off water at all 20 sites. However, the differences were large (Figure 19). At the two sites, L6 Lur and P52 Ösjö, (the uppermost two lines in Figure 19) the soils are Brown soils/podzols which were the best buffered at the beginning of the simulation period. Before planting the forest, the soils at L6 were agricultural fields which were ploughed, and very likely fertilised and probably limed. L6 and P52 are also the two sites with highest weathering rates calculated by the MAGIC model. The stations with the lowest weathering rates were more acid already at the beginning of the modelled period when the stations were assumed to be in approximate steady state with regard to deposition and soil and run-off chemistry. With the exceptions of four sites during the hindcast period 1850 - 1990, the run-off at all other sites was acidified to a pH between 4.2 to 4.4. Reduced deposition during the forecast period 1990 - 2020 caused a marked increase of the pH at several of the modelled sites. The pH increase was largest at the intermediately acidified sites. At the best buffered sites, which were never acidified, the pH remained about the same. The pH at the most acidified sites increased only slightly, since given the sensitivity of these sites, the deposition was not reduced sufficiently. These sites remained severely acidified.



**Figure 18.** Change in soil base saturation from 1990 to 2020 at the modelled sites.

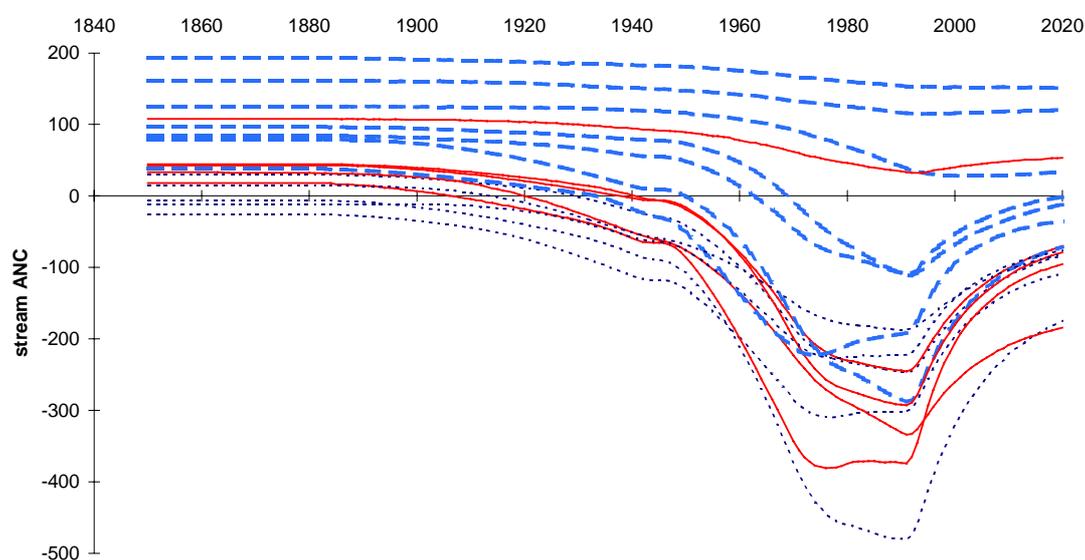


**Figure 19.** Time series of simulated pH in the stream. Stations are divided into three categories according to their weathering rates used in the MAGIC simulations: Thin dashed line - low weathering below  $20 \text{ meq/m}^2/\text{yr}$  (stations F9, F13, L8, N5 and P60); solid line - intermediate weathering between  $20$  and  $30 \text{ meq/m}^2/\text{yr}$  (stations G2, G3, L7, N3 and T9) and thick dashed line - high weathering above  $30 \text{ meq/m}^2/\text{yr}$  (stations G8, K1, L6, O8, P52, P70 and T11).

The MAGIC model simulated a general decrease of acid neutralising capacity (ANC) at all modelled stations during the hindcast period 1850 - 1990. After the sulphur deposition has peaked and started to decline in the 1980's, the ANC decline has generally slowed down and with the exception of the best buffered stations, the ANC

started to increase (Figure 20). Timing of the break of the trend varied among the stations, but for most of the stations, the ANC starts to increase before year 2000. The modelled reduction in acidifying deposition was, however, not sufficient to cause recovery back to pre-industrial levels or to desirable surface water quality, defined among other parameters by an ANC of no less than 50  $\mu\text{eq/l}$ . At the most sensitive sites, the run-off ANC was negative already from the beginning of the modelled period. This supports EMEP calculations, which indicate that the sulphur deposition in this part of Sweden exceeded the calculated critical load already at the beginning of the EMEP calculations in the 1880's (Mylona 1993).

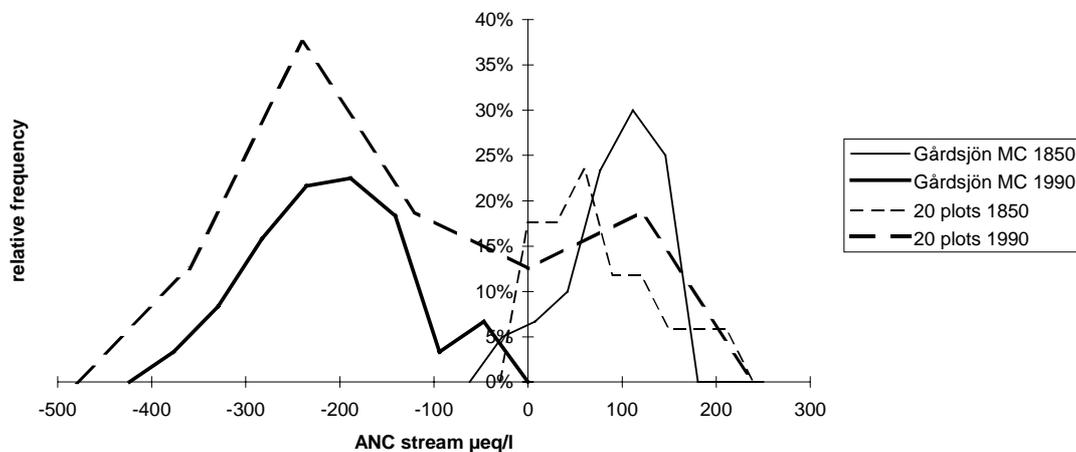
Modelled deposition in the year 2020 continues to cause acidification of the soils at the best buffered stations (Figure 18). In Figure 20, these stations are represented by the uppermost lines. The run-off at these stations was never acidified. However, even after the deposition was strongly reduced, the well buffered stations continued to gradually become more acidified. Severely acidified stations with the lowest ANC recovered only partly and their recovery in terms of ANC levelled off towards the end of the modelled period, when deposition was strongly reduced, but no longer declining. This could be attributed to a cumulative nature of the effect of the acidifying deposition on the soils. The deposition during 2010 - 2020 is still too high and caused further depletion of buffering capacity from the soils at most stations. The increased ANC occurs at most of the modelled sites (those where the soil base saturation did not increase from 1990 to 2020 - Figure 18) and is a result of the slower decline of buffering capacity of the soils rather than a build-up of base saturation and a more complete recovery.



**Figure 20.** Modelled acid neutralising capacity (ANC) of the run-off water at the 20 stations. Stations are divided into three categories according to their weathering rates used in the MAGIC simulations. Thin dashed line - low weathering below 20  $\text{meq/m}^2/\text{yr}$  (stations F9, F13, L8, N5 and P60); solid line - intermediate weathering between 20 and 30  $\text{meq/m}^2/\text{yr}$  (stations G2, G3, L7, N3 and T9) and thick dashed line - high weathering above 30  $\text{meq/m}^2/\text{yr}$  (stations G8, K1, L6, O8, P52, P70 and T11).

### 9.3 Discussion of the modelling results

The MAGIC model was used to extrapolate experimental results from the roof project at Gårdsjön (Figure 2), to model a hypothetical range of stations with the Monte Carlo technique using the Gårdsjön as a mid point (Figure 4) and to model 20 forest monitoring plots in S Sweden (Figures 18 - 20). The results of the Monte Carlo hindcast simulations were comparable to the results from modelling the 20 plots (Figure 21). The 20 stations covered a wider range of conditions than the ranges used in the Monte Carlo simulations. Therefore the simulations results also cover wider ranges of the modelled parameters. The general picture of the recovery process was the same in all simulations; decreased deposition resulted in certain improvement, but improvement to acceptable levels is unlikely to occur over the next few decades at the modelled sites under the presented future scenario.



**Figure 21.** Comparison of historical (1850) and reference (1990) year stream water ANC simulated at hypothetical stations modelled derived from Gårdsjön data by Monte Carlo technique and at the 20 forest monitoring plots.

When using a deposition scenario based on agreed emission abatements and their calculated impact on southern Sweden, there were no stations where the acidifying process would reverse completely. The positive effect of a strongly declined deposition from 1970's towards the end of century sooner or later levelled off at all sites which were previously acidified with negative ANC (Figure 20). Only in the case of a nearly 100% reduction of the acidifying deposition, as achieved experimentally by the roof at Gårdsjön, in combination with a high weathering rate and no large losses of base cations by e.g. harvesting the biomass, the results of the MAGIC simulations point towards a true recovery, where the soil regains lost alkalinity and run-off water reaches positive ANC before the year 2020.

Already achieved reductions in acidifying deposition will cause a certain improvement of soil status and water quality, but at most stations, the recovery will not lead to desirable conditions. On the contrary, at the sites presently unaffected by acidification, acidification may start to proceed further after temporary improvements (Figure 18). Only the stations with the most favourable conditions might possibly

recover in the next few decades without further cuts in emissions or other counter-measures. None of the acidified sites of the 20 modelled plots fall in this category.

Whether or not the soils and surface waters at any particular location will recover depends on a combination of factors as weathering of minerals in the soil, historical base saturation or atmospheric deposition. According to MAGIC simulations, answers to questions such as at what level the recovery from acidification will stop and how long time it will take, depend on relatively moderate differences in the input parameters. For instance, change in land use towards more intensive biomass harvesting could, if not compensated for by e.g. ash treatment or liming, change the effect of reduced deposition very significantly. Similarly the result of emission cuts might be dependent on small differences of how successful the implementation of the agreements is. This sensitivity also implies, that even moderate misjudgement of input variables in the model might offset the end result in the future. This might happen even if the prediction of development of the first phase of the recovery, when the deposition was strongly declining, was predicted correctly.

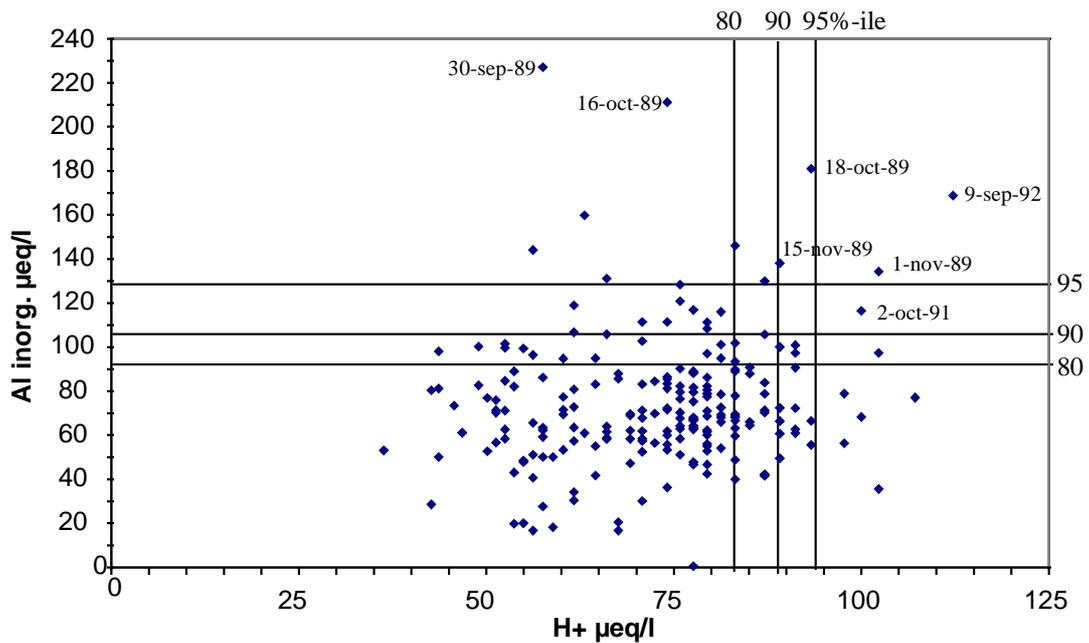
## 10. Acid episodes

The presented MAGIC model predictions are based on annual mean values. Before accepting results of any future scenario as satisfactory, questions of within-year variability of the run-off chemistry must be addressed. Average run-off quality might not, even when achieved, have a desirable effect on restoring populations of aquatic organisms. These might be damaged by a short acid episodes, when the run-off water will be of much worse quality than an annual mean would suggest.

To address the acid episodes problem, ten years (1988 - 1997) of run-off data from control site F1 at Gårdsjön were analysed. During that period 331 run-off samples were chemically analysed. In addition to the chemical composition of the run-off samples, daily information on run-off flow as well as precipitation amount was available.

To define and identify an acid episode, an approach of selecting samples with high concentrations of both  $H^+$  and inorganic Al was used. The 95-, 90- and 80 %-ile of the  $H^+$  concentration and of the inorganic Al concentration were determined separately. Two samples out of the available run-off samples met the criteria of both  $H^+$  and inorganic Al concentrations being above the 95%-ile. Investigating further, the samples meeting the criteria of the 90%-ile and 80%-ile were identified accordingly. Three additional samples met the 90%-ile limit while 10 additional samples showed concentrations of both  $H^+$  and inorganic Al above the 80%-ile (Figure 22).

All of the samples above the 90%-ile, and several of the reminder meeting the 80%-ile criteria, are from late summer or autumn, sampled after periods of no or very little run-off. The additional samples are either from events with heavy precipitation and/or from winter/early spring with large run-off, presumably melting of snow. In the description of the acid episodes below, primarily those with both  $H^+$  and  $Al^{3+}$  concentrations above the 90%-ile are included.



**Figure 22.** The concentration of inorganic  $\text{Al}^{3+}$  vs.  $\text{H}^+$  ( $\mu\text{eq/l}$ ) in the run-off samples, Oct. 1988-March 1997. The 95-, 90- and 80%-ile for inorg.  $\text{Al}^{3+}$  and  $\text{H}^+$  are indicated.

Of the five samples meeting the 90%-ile criteria, three are among the first samples collected on 18th October, 1st November and 15th November, after prolonged drought in the summer of 1989. The other two samples are from the 2nd October 1991 and from the 9th September 1992. Thus there are three separate events of acid episodes, in 1989, 1991 and 1992.

In Figure 22, the two samples with the highest concentrations of inorganic Al, which were not sufficiently acidic to be classed into the above criteria, are from 1989. The sampling dates were on the 30th September and the 16th October 1989, that is, immediately before the acid episode in 1989. These samples will also be included in the description of the event in 1989.

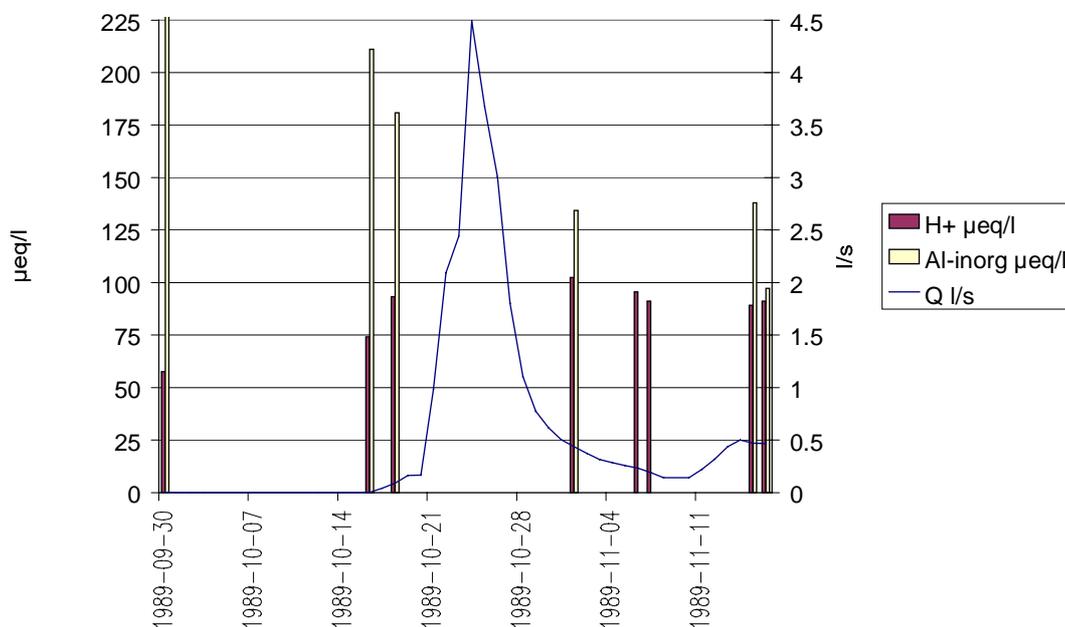
The selected samples, sorted into three events, are listed in Table 7.

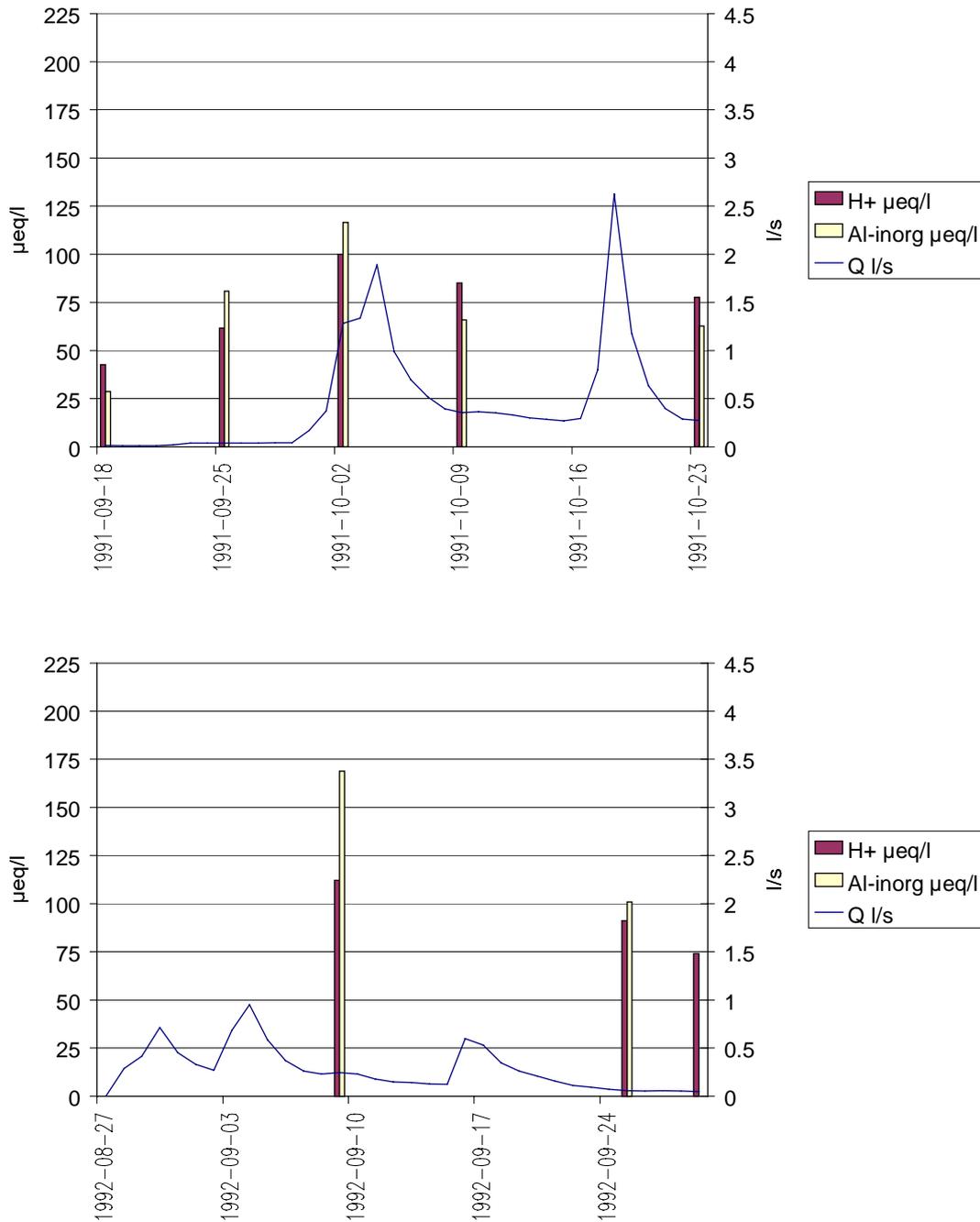
**Table 7.** The three acid episode events.

Sample	Date	criteria % ile	Preceding no. of days with run-off <0.1 mm	Run-off* mm	Precipitation* mm	pH units	Al <sup>n+</sup> (inorg) µeq/l	SO <sub>4</sub> <sup>2-</sup> ex µeq/l
89:0			131					
89:1	30-Sep	95(Al)		0.007	204	4.24	227	749
89:2	16-Oct	95(Al)		0.009	247.	4.13	211	790
89:3	18-Oct	90		0.32	256	4.03	181	644
89:4	1-Nov	95		52	325	3.99	134	385
89:5	15-Nov	90		62	350	4.05	138	329
91:0			61					
91:1	2-Oct	90		6	205	4.00	117	293
92:0			109					
92:1	9-Sep	95		14	310	3.95	169	761
92:2	25-Sep	80		22	338	4.04	101	na

\* sum from the beginning of the "dry" period until sampling date.  
na= not available.

Preceding the two episodes in 1989 and in 1992 were long dry periods (more than 100 days) with no or very little run-off. These two events were those above the 95%-ile. The event in 1991 was preceded by a period with relatively little run-off but the period was not as long and not as "dry" as in 1989 and 1992.





**Figure 23.** Time series of run-off (Q, l/s, daily average), H<sup>+</sup> and Al inorg. concentrations (scattered sampling dates) during the three identified acid events in 1989, 1991 and 1992.

A Principal Component Analysis (PCA) was made using the chemical composition of 225 run-off samples (after excluding samples with incomplete chemical analyses). The first principal component (PC) was dominated by the concentrations of Ca and Al inorg, with contributions also from Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and ANC, which explained 30% of the variation in the material. The second PC was dominated primarily by typical sea salt solutes Na<sup>+</sup> and Cl<sup>-</sup>, but also by non-marine K<sup>+</sup>. These two PCs together explained 51% of the variation. The samples that were separated from the larger mass of samples in the PCA were actually those included in the two acid events in 1989 and

1992, preceded by "dry" periods of more than 100 days. The concentration of  $H^+$  only became important when calculating the third PC, accounting for another 11% of the variation.

At present, the run-off from the F1 catchment at Gårdsjön is at all times acidic, rich in aluminium and therefore toxic to fish and other organisms. Annual volume weighted mean pH is typically between 4.1 and 4.2. In ten years, three events of even more severely acid run-off were identified. These three are examples of acid episodes after dry summers, when the groundwater table drops below the usual level allowing oxidation of reduced forms of sulphur to  $SO_4^{2-}$ , which is then flushed out from the soil, after saturating the soil again with rain water at the end of the summer. The flow of  $SO_4^{2-}$  in the acidified soil causes a pulse of  $H^+$  and of  $Al^{3+}$ . Acidic episodes caused by a snow-melt or by high precipitation events were less severe.

The three acidic events lasted from a few days to a few weeks. For aquatic organisms, such events have a potential to counteract even an improved run-off quality. At Gårdsjön F1, the run-off is generally so acidified, that the acid sensitive organisms have been extinct. Therefore the acid episodes might be more important for the streams, lakes and rivers downstream, rather than for the F1 stream itself. It is reasonable to assume, that if the soil recovers from acidification, the  $SO_4^{2-}$  pulses should be to a large extent balanced by higher concentrations of base rather than of acid cations. A similar phenomena, although in the opposite direction, has been described by Wright et al., (1988), where pulses of sea salt after storms resulted in acid episodes particularly at the acidified soils. To conceptualise future development of the acid episodes to a model for predictive purposes requires data to verify a model. Data from less acidified or from partly recovered areas should be analysed.

## **11. Proposed further work**

The aim of this project was to develop an approach for modelling the recovery from acidification in S Sweden based on the Gårdsjön Covered Catchment experiment and on data from 20 monitoring plots. The developed concept was then applied to one future scenario which consisted of our best estimate of the future deposition combined with no change in land use. The major task which is to be tackled in a follow up of this work, is to use the model approach described in this report (either the Monte Carlo simulations or the model calibrated to the 20 sites) to simulate a variety of different future scenarios such as changes in land use, land management, different deposition scenarios or combinations of these. The modelling concept was developed primarily with this task in mind. There are, however, several other possibilities for continuation. The modelling could be adapted to different monitoring data such as lake- or general surface-water chemistry and for modelling the impact on them. If regional predictions need to be complemented by forecasts done with higher temporal resolution (e.g. modelling of acid episodes) or spatial resolution (e.g. focus on discharge areas or other specific parts of catchments), the modelling should be complemented and broadened to include tools more suited for these tasks.

## 12. Acknowledgements

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