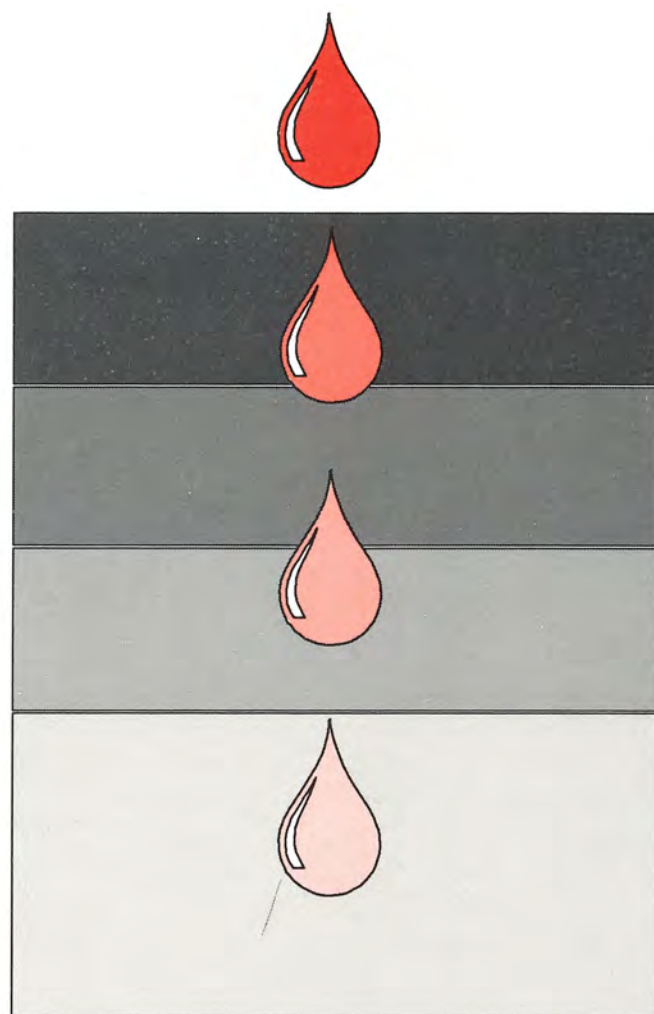




MODELLING GROUNDWATER RESPONSE TO ACIDIFICATION

Edited by Per Sandén and Per Warfvinge

MODELLING GROUNDWATER RESPONSE TO ACIDIFICATION

REPORT FROM THE SWEDISH INTEGRATED GROUNDWATER ACIDIFICATION PROJECT

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Title (and Subtitle) Modelling groundwater response to acidification		
Abstract The observed acidification of lakes and forest soils in Sweden has raised concern over the future of groundwater resources. Many of the processes which effect groundwater quality occur above the water table in the unsaturated soil. Models of the hydrology and chemistry in this zone were developed and the results of that work are presented in this report. The overall objective of this project was to obtain a better understanding of the chemical and hydrological processes involved in the acidification of soil and groundwater in order to estimate future changes due to changes in acid deposition in relation to other acidifying processes. This work concluded of this report is that the groundwater in Sweden is vulnerable to acid deposition and that drastic reductions in emissions are necessary to protect this water. The model development provides a set of tools which are generally applicable to the hydrochemistry of acidification. They demand limited calibration and the requirements for input data and parameter values can usually be met. This makes it possible to use the models for assessment of groundwater acidification. The spatial and climatic variabilities of parameters and driving variables, however, are large. The uncertainties introduced by this variability must be considered when the results are used for decision making.		
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PREFACE

This report presents the modelling subprojects of the Swedish Integrated Groundwater Acidification Project. The project was initiated and mainly financed by the Swedish Environmental Protection Agency. Ulf von Brömssen and Ulla Bertils have been the officers from the agency, while the scientific coordinator has been Gert Knutsson (Dept. of Land and Water Resources, Royal Institute of Technology). The project was divided into a number of subprojects, covering field work at different research areas, analytical quality control and method development, and hydrological and hydrochemical modelling.

The research areas were Masbyn and Risfallet in central Sweden (Responsible: Lars Lundin, Dept. of Forest Soil, Swedish University of Agricultural Science), a hillslope at Fårahall in the southwestern Sweden (Responsible: Gunnar Jacks, Dept. of Land and Water Resources, Royal Institute of Technology), and the Stubbetorp research basin in southeastern Sweden (Responsible: Sten Bergström, Swedish Meteorological and Hydrological Institute). Some springs in the Loftsdalen area was also studied in the early stages of this project (Responsible: Gert Knutsson, Dept. of Land and Water Resources, Royal Institute of Technology).

A separate subproject dealt with intercalibration, analytical quality control and development of a aluminum speciation method (Responsible: Folke Ingman and Lars Göran Danielsson, Dept. of Analytical Chemistry, Royal Institute of Technology).

The modelling was divided into two subprojects. One of these was responsible for the development of the hydrological model (Sten Bergström, Swedish Meteorological and Hydrological Institute), the other for the hydrochemical model (Harald Sverdrup, Dept. of Chemical Engineering II, Lund Institute of Technology).

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1 INTRODUCTION

The observed acidification of lakes and forest soils in Sweden has raised concern over the future of groundwater resources. In Sweden many households rely on groundwater from shallow aquifers for their water supply, either at their permanent residence or at their summer houses. Studies in the late 1980's revealed increased groundwater acidification and an understanding of the interaction between acidification and hydrology. This work ended with the recognition that there is a risk for groundwater acidification (Bertils *et al.*, 1989). The Swedish Integrated Groundwater Acidification Project was therefore initiated by the Swedish Environmental Protection Agency to provide information concerning soil and groundwater acidification as a basis for policy decisions.

The overall objective of the project is to obtain a better understanding of the chemical and hydrological processes involved in the acidification of soil and groundwater to be able to estimate future changes due to changes in acid deposition in relation to other acidifying processes.

This objective leads to the following tasks:

- Determine the quantitative characteristics of those aquifers that are vulnerable to acid deposition, and develop methods for mapping such groundwater regionally.
- Determine the time required to acidify groundwater aquifers of different sensitivity and at different geographical locations within Sweden.
- Quantify the response in the chemical composition of groundwater to different future acid deposition scenarios and estimate critical loads.

Stream, lake and groundwater acidification is here defined as a reduction in alkalinity over time. Soil acidification is the reduction of base saturation over time. It is termed acidification regardless of cause or origin of the acidity.

Research on the mass fluxes in boreal forested ecosystems of the temperate zone has modified and increased the understanding of the interaction between the factors contributing to soil and water acidification. It has been realized that there is no single cause of the acidification, but rather a number of factors.

Acidification is a problem that requires multi-disciplinary efforts. Therefore a modelling group was established with hydrologists from the Swedish Meteorological and Hydrological Institute (SMHI) and chemists from the Lund Institute of Technology. The group also received substantial scientific support from other participants in the Swedish Integrated Groundwater Acidification Project.

Several working hypotheses were formulated:

- The principal processes participating as sinks and sources of acidity in the soil are atmospheric deposition, base cation uptake, nitrification, ammonium uptake, nitrate uptake, biomass decomposition, chemical weathering and ion exchange. Soil processes either consume or produce alkalinity or are alkalinity neutral. Acidification is caused by net acidity input to the system after accounting for all sinks and sources inside the system boundary.

- Non-equilibrium phenomena play an important role in the formation of strongly acidic episodic events.
- Short term variations in concentrations of major constituents of soil water and runoff are dominated by hydrological fluxes and pathways.
- Aluminum dynamics are controlled by the interaction of ion exchange, primary production of aluminum from the weathering of soil minerals, and precipitation of metastable organic/silicious complexes.
- The field base cation release rates due to chemical weathering of soil minerals can be calculated with a model based on mineralogy, hydrology, soil texture and chemical conditions.

Acidification of groundwater is a problem that is so complex that numerical models are necessary to describe relevant physical and chemical processes.

The models developed in the project were subject to certain requirements:

- The models must be generally applicable. This means that the models must operate exclusively on input, which have a physico-chemical meaning and can be measured. Input data must also be generally available.
- The models shall be controlled by observations of water balance components, chemical weathering rate, soil profile chemistry and groundwater chemistry.

Early in the project it was decided to restrict the modelling study to processes during recharge of groundwater in order to keep the study within reasonable limits and to concentrate on the most critical part of groundwater acidification.

The Swedish Integrated Groundwater Acidification Project resulted in three vertically distributed models, the modified PULSE, PROFILE and SAFE. The modified PULSE model describes water content and flux in the unsaturated zone. PROFILE is a steady state soil chemistry model for acidification sensitivity assessments and calculation of base cation release due to chemical weathering of soil minerals. SAFE (Soil Acidification in Forested Ecosystems) is a dynamic version of the PROFILE model. The integrated dynamic model for groundwater acidification consists of PULSE and SAFE used in tandem. The flowchart in Figure 1.1 shows how the models are coupled.

The integration of a hydrological and a hydrochemical model and its extrapolation into the future entails many uncertainties (see, for example, Bergström, 1991). One is that the general overview is lost because of the specialization of the two groups. Another is related to the non-stationary conditions and lack of possibility for model validation. A third uncertainty is our lack of knowledge of the history of deposition, plant uptake and other relevant factors. These uncertainties are the reason for a strong emphasis on sensitivity analysis in model development. The individual sensitivity of each model is analysed as well as their interactive sensitivity and effects on the end results.

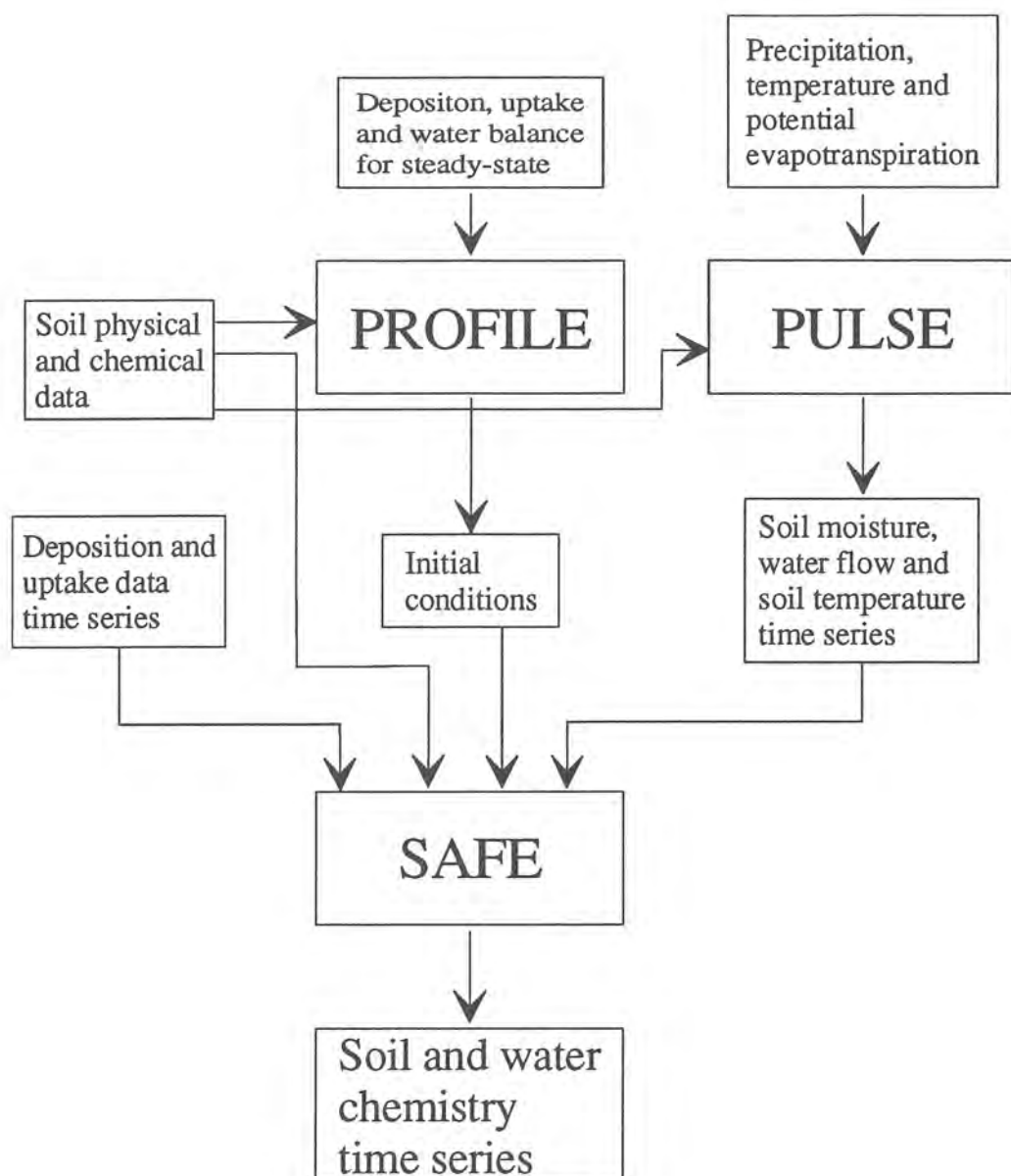


Figure 1.1. The internal structure of the integrated groundwater acidification model. The flowchart shows how input data, model outputs and the models PULSE, PROFILE and SAFE are coupled.

The modelling effort was initiated with a literature survey where earlier acidification models were evaluated. One objective of this was to identify where earlier models have succeeded as well as failed. Much valuable information was gained in that exercise. The main limitations found in the models can be summarized as follows:

- The hydrological models often have an insufficient description of water residence time in the system, which limits the possibilities to introduce more advanced chemical subroutines (Bergström and Lindström, 1989).

- Existing soil chemistry models had no weathering rate submodel. Instead they used this as a calibration parameter, either by fitting a polynomial or a constant, ignoring geochemical parameters and soil mineralogy. This was felt insufficient, as soil acidification sensitivity is strongly dependent on the soil weathering rate.
- Existing soil chemistry models use aluminum hydroxide (gibbsite) or more complex secondary aluminum-sulphate-hydroxides (jurbanite). However, no-one has ever been able to show the presence of gibbsite in any of the forest soils the models have been applied to, including Swedish forest soils.
- Existing soil chemistry models are based on the assumption that ion exchange equilibrium is instant in soils. However, experiences from soil liming modelling has clearly shown that this is not the case for short term variations. The kinetic ion exchange models developed for soil liming were refined and modified to be incorporated in the integrated soil chemistry model of the project.
- Existing soil chemistry models tend to be one-layer models. This implies simplifications concerning both geochemical and physical properties of the soil, as well as general hydrology. Most soils show a clear stratification, and that these layers have different chemical and hydrological properties.

The work on the geochemical model was sectioned into experimental work, mainly on chemical weathering and ion exchange kinetics, development of process submodels and integrated model development. The hydrological work was similarly divided into field studies and model development. The main part of the field work was organized and carried out by separate groups.

It was realized that several new field research catchments had to be established. Some research sites had to be under the control of the project in order to produce the full set of relevant data. It was also recognized that there is data available from other projects that can be used for validation of the models. Characteristics of the research sites and the data collected are briefly presented in this report and will be the subject of a separate report from the Swedish Integrated Groundwater Acidification Project (Lundin *et al.*, 1992).

The specifics of the PULSE, PROFILE and SAFE models are given in the following chapters together with sensitivity analyses and long term scenario simulations. Finally a discussion of the results and some conclusions are presented.

2 DATA BASE (M. Gardelin and P. Warfvinge)

Different aspects of the hydrological and hydrochemical model performance were tested using field measurements at several research sites in Sweden (Figure 2.1). Short descriptions are given of these sites together with a summary of the data base used for the different model simulations. More detailed site and research descriptions for the project's sites (Stubbetorp, Masbyn and Risfallet) are given in Lundin *et al.* (1992). Additional data was provided from the Gårdsjön, Linderödsåsen, Velen and Trysilvelva basins. Data used in the test of the weathering rate submodel are presented in connection to the results in Section 4.4.2.



Figure 2.1.
Geographical location of research sites and type of model application. The project's research basins are underlined.

Basin	Model application
Trysilvelva	PULSE (snow routine)
Velen	PULSE (soil moisture, soil temperature)
<u>Stubbetorp</u>	PULSE (groundwater levels, transit times in lysimeters, long-term simulation), PROFILE, SAFE, MAGIC
<u>Masbyn</u>	PULSE (soil moisture, long-term simulation), PROFILE, SAFE
<u>Risfallet</u>	PULSE (soil moisture, long-term simulation) PROFILE, SAFE
Gårdsjön	PROFILE
Linderödsåsen	PROFILE, SAFE

2.1 STUBBETORP

The Stubbetorp research basin has an area of 0.87 km² (Figure 2.2) and is located about 30 km northeast of Norrköping (Figure 2.1). The bedrock is granitic and covered by sandy till, but the percentage of outcrop is high. Podzolic and brown forest soils, covered by coniferous forests, dominate the area, but some mires are found. Annual average precipitation and runoff are about 700 and 250 mm respectively.

Hydrological and hydrochemical investigations have been carried out since 1986. Measurements at site 2 and site 3 are presented in the simulation studies. Soil samples were taken at the two locations, and the soil moisture characteristic curves were established for each soil layer by laboratory analysis. At site 2 no soil samples representing the C-horizon were taken. The soil profile is shown in Figure 2.3, representing site 2, which is used for the long term simulations.

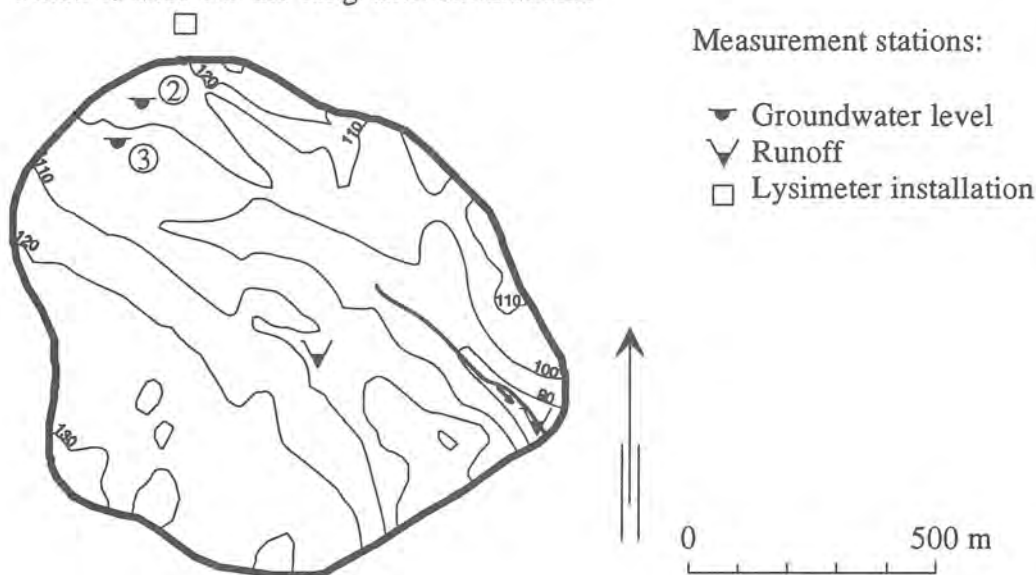


Figure 2.2. The Stubbetorp research basin.

Based on groundwater observations at site 2 during the period 1987 to 1990, the groundwater level in the long term simulations was set to be constant at 100 cm below ground level. A transect of groundwater tubes were installed between site 2 and the stream close to site 3. The simulations of groundwater levels (Section 3.6) were carried out for groundwater tube 21 (11 m above stream), 23 (9 m above stream), 26 (2.2 m above stream) and 30 (0.5 m above stream).

Soil lysimeters were installed. Soil cores of 20 cm diameter with varying depths were taken from three different sites. The soil cores were carefully transferred to polyethen tubes, and the drainage was collected and analysed for chemical composition from 1987 to 1990. The sampling was done approximately twice a month, depending on the flow situation. Six lysimeters with the depths 15, 40, and 80 cm, originating from sites 2 and 3 were selected for the lysimeter simulations. The ¹⁸O-concentration in the percolate from the six lysimeters and daily samples of precipitation was measured by mass spectrometry.

For the long term hydrological simulation, daily precipitation and temperature data were obtained from Simonstorp climatological station (about 15 km northwest of

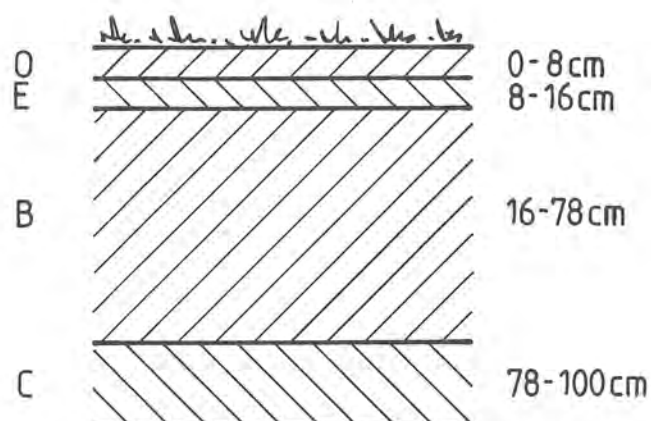


Figure 2.3. Soil profile at Stubbetorp. O = organic, E = eluvium, B = illuvium, C = parent.

Stubbetorp). For the lysimeter simulation, precipitation data were obtained from the Stubbetorp station and temperature data from the Norrköping-Sörby station. Monthly values of potential evapotranspiration (Norrköping-Sörby station) were taken from Eriksson (1981).

Table 2.1 presents the input parameters for the hydrochemical simulations at Stubbetorp.

Table 2.1. Input values to SAFE/PROFILE for the Stubbetorp site

Parameter	Unit	Soil layer			
		O	E	B	C
Soil layer height	m	0.08	0.08	0.62	0.22
Soil density	kg m ⁻³	110	1230	1415	1360
Cation exchange capacity	eq kg ⁻¹	250	21	6.3	5.5
Specific surface area	m ² m ⁻³	7 10 ⁵	1.5 10 ⁶	1.5 10 ⁶	1.5 10 ⁶
CO ₂ pressure	times ambient	3	5	10	20
Mg+Ca+K uptake	% of total max	20	20	60	0
N uptake	% of total max	20	20	60	0
log Al(OH) ₃ equ. const.	kmol ² m ⁻⁶	6.5	7.5	8.5	9.2
Mineral content:					
K-feldspar	%	32	32	30	30
Oligoclase	%	15	16	15	15
Hornblende	%	0	1.6	2.4	2.4
Biotite	%	0	0.1	0.2	0.2
Chlorite	%	0	0.6	1.1	1.1
Apatite	%	0	0	0.2	0.2
Quartz	%	53	49.7	48.5	48.5

2.2 MASBYN

The Masbyn basin (0.19 km², Figure 2.4) is situated in central Sweden (see Figure 2.1) within the Kloten research area, where different hydrological investigations have been carried out since the 1960'ies. Between 1968 and 1977 studies were carried out concerning the effects of forest fertilization and clear-cutting (Ramberg *et al.*, 1973). Extensive investigations of soil, soil water, and groundwater were made between 1973 and 1977 (Lundin, 1982). The system of notation, hereafter used for the different measurement sites at Masbyn, refers to Lundin (1982). Fifty percent of the basin area were clear-cut during the winter season 1975/76 and were thereafter reforested.

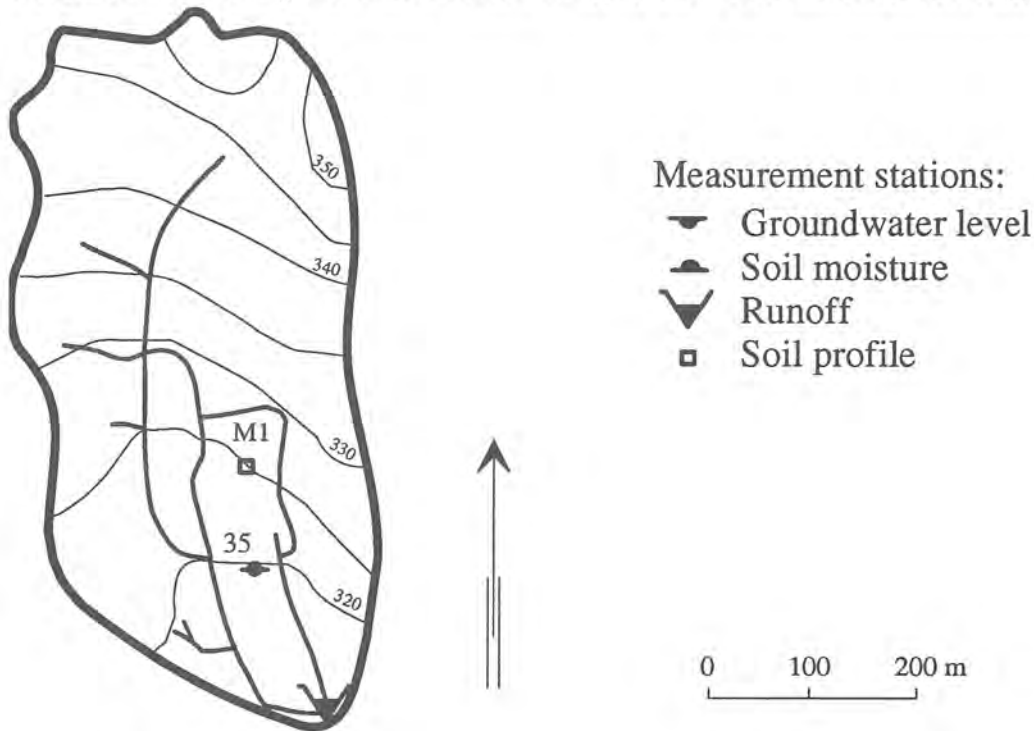


Figure 2.4. The Masbyn research basin.

Podzolic sandy silty till soils dominate the area. The soil profile used for the model simulations (Figure 2.5) was taken from station M1, where the water holding capacity relationships at different levels have been thoroughly determined (Lundin, 1982)

Model simulations for verification of the soil moisture calculations were made for the periods 1973-76 and 1986-89. The simulations were compared with neutron probe soil moisture measurements at 10 different depths in the upper meter of the soil at site 35.

Based on groundwater measurements at site 35 the groundwater level in the model was set to be constant at 100 cm below ground level for the simulation period 1973-76 (mature forest) and 50 cm below ground level for the period 1986-89 (young forest).

Daily values of precipitation were obtained from the Grängesberg climatological station and temperature data from the Ställdalen station. Monthly values of potential evapotranspiration (Ställdalen station) were taken from Eriksson (1981).

Table 2.2 presents the input parameters for the hydrochemical simulations at Masbyn.

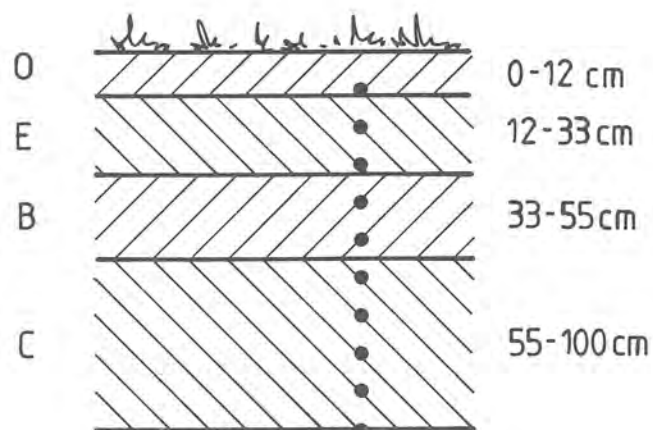


Figure 2.5. Soil profile (station M1) at Masbyn. Dots illustrate depths for soil moisture measurements (site 35). O = organic, E = eluvium, B = illuvium, C = parent.

Table 2.2. Input values to SAFE/PROFILE for the Masbyn site

Parameter	Unit	Soil layer			
		O	E	B	C
Soil layer height	m	0.12	0.21	0.22	0.45
Soil density	kgm ⁻³	234	471	1508	1586
Cation exchange capacity	eq kg ⁻¹	409	28	42	14
Specific surface area	m ² m ⁻³	1 10 ⁵	8 10 ⁵	8 10 ⁵	8 10 ⁵
CO ₂ pressure	times ambient	3	5	10	20
Mg+Ca+K uptake	% of total max	20	40	40	0
N uptake	% of total max	20	40	40	0
log Al(OH) ₃ equ. const.	kmol ² m ⁻⁶	6.5	7.5	8.5	9.2
Mineral content:					
K-feldspar	%	25	29	27	23
Oligoclase	%	15	22	23	23
Hornblende	%	0	0.7	1.1	1.1
Chlorite	%	0	0.6	1.1	1.1
Quartz	%	60	47.7	47.8	51.8

2.3 RISFALLET

The Risfallet research basin has an area of 0.45 km² (Figure 2.6) and is situated in central Sweden about 5 km north of Garpenberg (see Figure 2.1). Podzol on sandy loam and gravely till with a significant element of boulder and bare rock dominate in the area. Figure 2.7 shows the soil profile used for the model simulations. Neutron probe soil moisture measurements were carried out at 8 different depths in the soil profile and at 15 occasions during the period 1987-89.

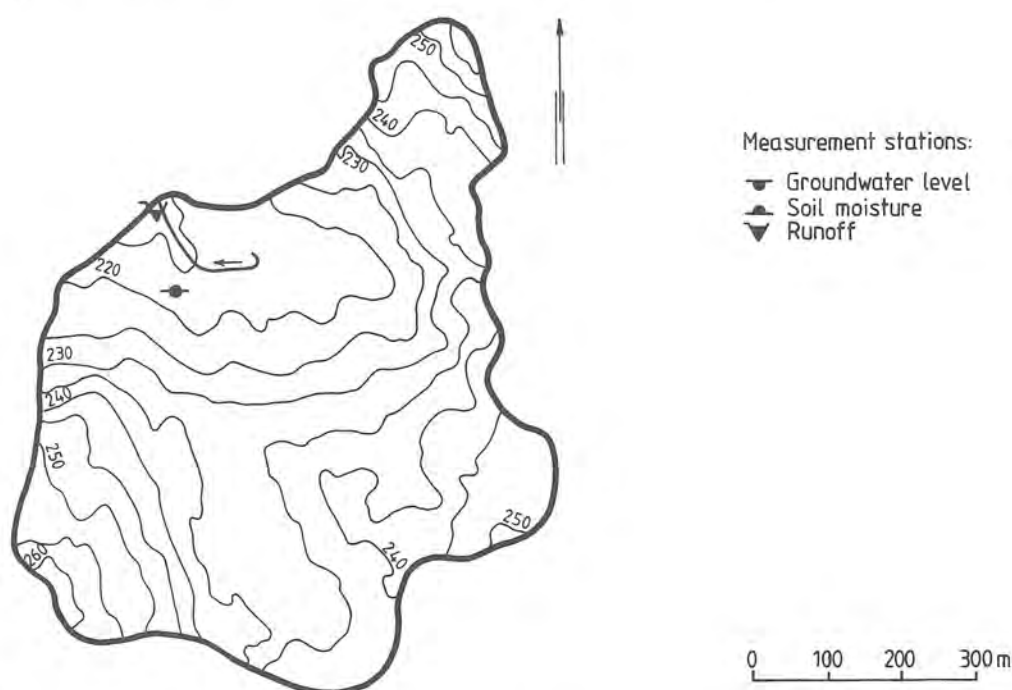


Figure 2.6. The Risfallet research basin.

The groundwater level in the model was set to be 250 cm below ground level during the simulation period.

Daily values of precipitation were obtained from the Folkärna and Hedemora climatological stations. Temperature data was obtained from the Folkärna station. Monthly standard values of potential evapotranspiration (Folkärna station) were taken from Eriksson (1981).

Table 2.3 presents the input parameters for the hydrochemical simulations at Risfallet.

Table 2.3. Input values to SAFE/PROFILE for the Risfallet site

Parameter	Unit	Soil layer			
		O	E	B	C
Soil layer height	m	0.08	0.08	0.60	0.24
Soil density	kgm ⁻³	200	1000	1600	2000
Cation exchange capacity	eq kg ⁻¹	122	4.8	18.6	8.27
Specific surface area	m ² m ⁻³	1 10 ⁵	2.4 10 ⁵	3.1 10 ⁵	4.9 10 ⁵
CO ₂ pressure	times ambient	3	5	10	20
Mg+Ca+K uptake	% of total max	20	40	40	0
N uptake	% of total max	20	40	40	0
log Al(OH) ₃ equ. const.	kmol ² m ⁻⁶	6.5	7.5	8.5	9.2
Mineral content:					
K-feldspar	%	22	22	25	25
Oligoclase	%	22	22	26	26
Hornblende	%	2	2	4.5	5
Chlorite	%	0	0	1	2
Apatite	%	0.1	0.1	0.1	0.3
Quartz	%	53.9	53.9	43.4	41.7

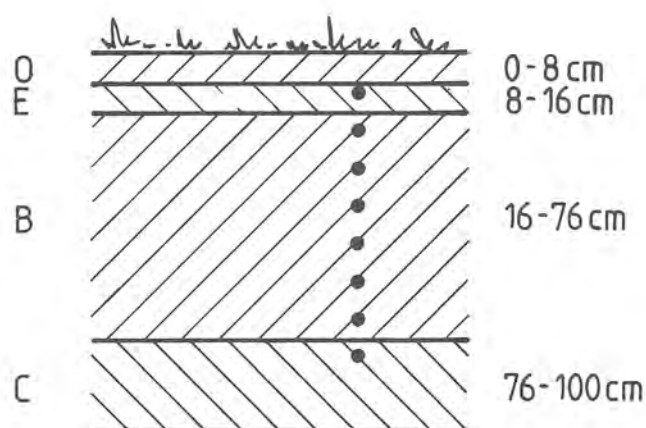


Figure 2.7. Soil profile at Risfallet. Dots illustrate depths for soil moisture measurements. O = organic, E = eluvium, B = illuvium, C = parent.

2.4 VELEN

During the International Hydrological Decade (IHD) the Velen research basin (45 km², Figure 2.8) was selected as representative for coniferous forest areas on till soils in the central part of southern Sweden. The soil is mainly sandy till, underlain by gneiss and granite. A detailed description of the basin and the IHD research programme is given by Hedin (1971). The location of the basin is shown in Figure 2.1.

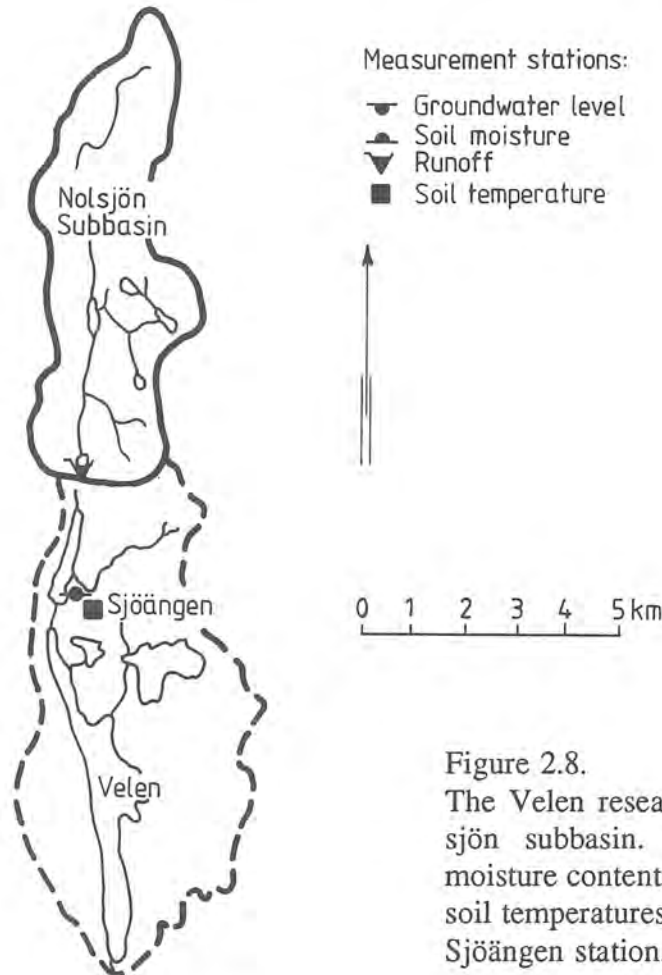


Figure 2.8.

The Velen research basin with the Nolsjön subbasin. Measurements of soil moisture content, groundwater levels and soil temperatures were obtained from the Sjöängen station.

Measurements of soil moisture content at two sites in the basin, Sjöängen 7 and Sjöängen 8, were used in this study. Neutron-probe field measurements were carried out weekly at Sjöängen 7 during the period 1967 to 1974. At Sjöängen 8 monthly measurements were made from 1967 to 1970, and weekly measurements from 1971 to 1974. The present study is based on measurements at 10 different depths in the upper meter of the soil. Altogether over 6 000 measurements were included in the study.

For the model simulation, daily precipitation and temperature data were taken from the climatological station at Sjöängen. Runoff measurements for the Nolsjön subbasin (18 km²) were used to calibrate the water balance in the PULSE model. Monthly values of potential evapotranspiration (Örebro station) were taken from Wallén (1966).

Groundwater level data is available for the period 1967-1972, with a frequency of 1 - 2 readings per month. Based on this data set the groundwater level in the PULSE model

was set to be constant at one meter below ground during the simulation period. The same data set was used in the simulation with the SOIL model. Figure 2.9 shows the soil profile used in the model simulation for Sjöängen 7 and 8. The thickness of the different horizons and the water holding capacity were mainly determined from limited soil analysis made by Andersson (personal communication). The water retention was determined at three pF values (0.7, 2.0, and 4.2) at three depths in the soil profile (0 - 10 cm, 30 - 40 cm, and 60 - 70 cm). No thorough soil analysis was carried out within the IHD program.

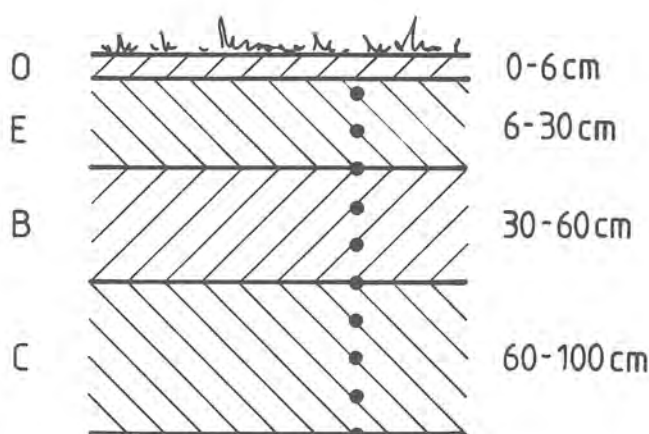


Figure 2.9. Soil profile at Sjöängen, Velen research basin. Dots illustrate depths for soil moisture measurements. O = organic, E = eluvium, B = illuvium, C = parent.

Measurements of soil temperatures at the Sjöängen station were carried out weekly at a grass covered site about 100 meters from the forested site of the soil moisture measurements. Temperature data for the period 1971 to 1974 from three depths in the soil profile (20, 50 and 100 cm) was used in the study.

2.5 TRYSILELVA

Model-calculated snow water equivalents were compared with extensive snow course data upstream of the Höljes reservoir in the Trysilvelva river basin, situated mainly in Norway (Figure 2.1). Snow course measurements were conducted regularly at six sites within the river basin during the period 1969 to 1985 (Figure 2.10). Snow water equivalent was measured on 8 to 9 occasions each winter season for hydropower operation purposes. The data was made available by Uddeholm Kraft AB.

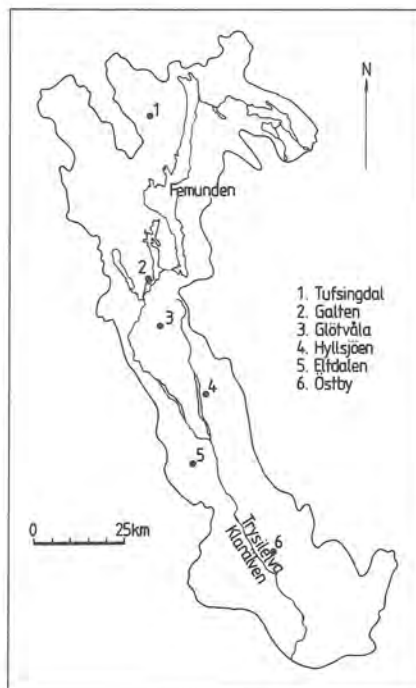


Figure 2.10.
Höljes part of Klarälven/Trysilvelva river basin. Sites where snow course measurements were performed during 1969-85.

The size of the basin is 5 975 km². It is largely forested, but in the northern part dominated by high mountains and several large lakes. Daily values of precipitation and temperature were obtained from 8 climatological stations.

2.6 DEPOSITION DATA

In all hydrochemical calculations, the deposition of substances affecting the ANC of the rain is crucial. The data source used is the state-of-the-science evaluation carried out by Lövblad *et al.* (1992). The deposition data is given as wet and dry deposition of the anions SO₄, NO₃ and Cl, as well as the cations Na, K, Ca, Mg and NH₄. The deposition to spruce stands, mixed/deciduous forest and open land is evaluated for each square in the 50 by 50 km sub-system to the European Monitoring and Evaluation Program (EMEP) 150 by 150 km grid system. The values used is a synthesis of wet deposition and throughfall data, as well as model output from the EMEP model.

The values used for the study sites are given in Table 2.4. At one of the sites, Masbyn, the forest was clear-cut in the mid 1970-ies. Since this affects the deposition of gaseous and particulate pollutants to the area, the effect of forest scavenging can be quantified in terms of a filter factor. As the forest stand gains in height, this filter factor changes. The filter factor *f* for the mature stand is given by:

$$f = \frac{\text{total deposition}}{\text{wet deposition}} - 1 \quad (2.1)$$

It was assumed that the filter factor is proportional to the square root of the standing biomass. The growth rate pattern of a stand was taken from the review by Sverdrup *et al.* (1990).

Table 2.4. Deposition values used for 1985 and onward.

Site		SO ₄	NO ₃	Cl	NH ₄	Na	Ca	Mg	K
		meq m ⁻² yr ⁻¹							
Stubbetorp	Total	65.00	27.3	25.2	30.32	20.06	11.35	2.87	6.93
	Wet	32.00	18.67	11.20	17.90	8.88	5.03	1.27	3.07
Masbyn	Total	78.15	31.68	23.90	36.23	19.22	8.99	3.87	7.46
	Wet	41.01	24.39	9.81	22.49	7.89	6.26	1.5	93.04
Risfallet	Total	67.75	26.10	19.61	30.83	15.90	7.07	2.80	5.87
	Wet	30.76	18.47	8.35	16.68	6.77	4.92	1.19	2.48

The deposition history was based on known emissions of sulfur, NO_x and historic data on livestock in Europe. The latter is the main source of ammonia, a very important acidifier on a local scale. The historical deposition patterns used were prepared for a spruce stand in southern Sweden. The patterns are shown in Figure 2.11.

The complexity in the final deposition patterns is illustrated by Figure 2.12, showing the pattern of S deposition of the Masbyn site. The clear-cutting results in a decreased total deposition in 1975, and the total level drops to the level of the wet deposition alone. After 1980, the wet deposition drops, while the filter factor is increased due to

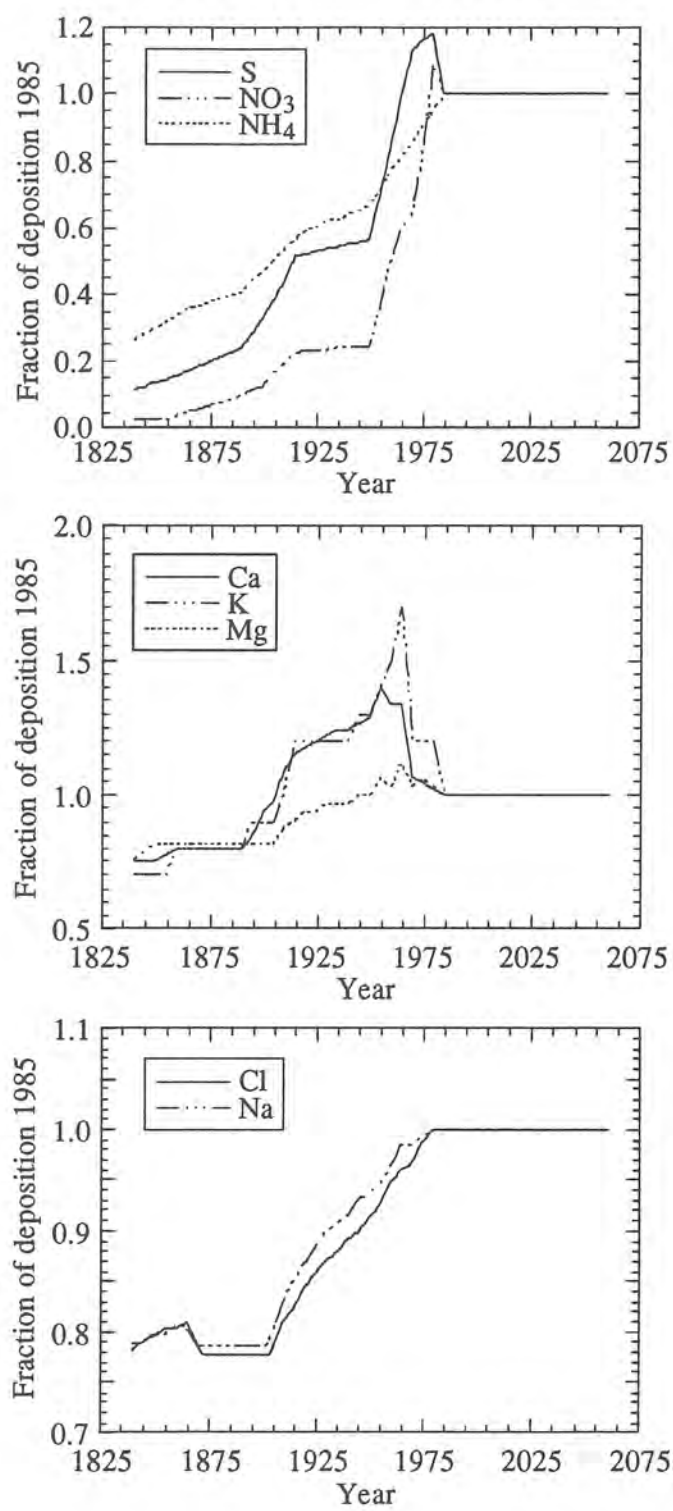


Figure 2.11. Historical deposition for a spruce forest in southern Sweden

the growth of the new tree generation. After 1985, the total deposition will increase, although the wet deposition is held constant.

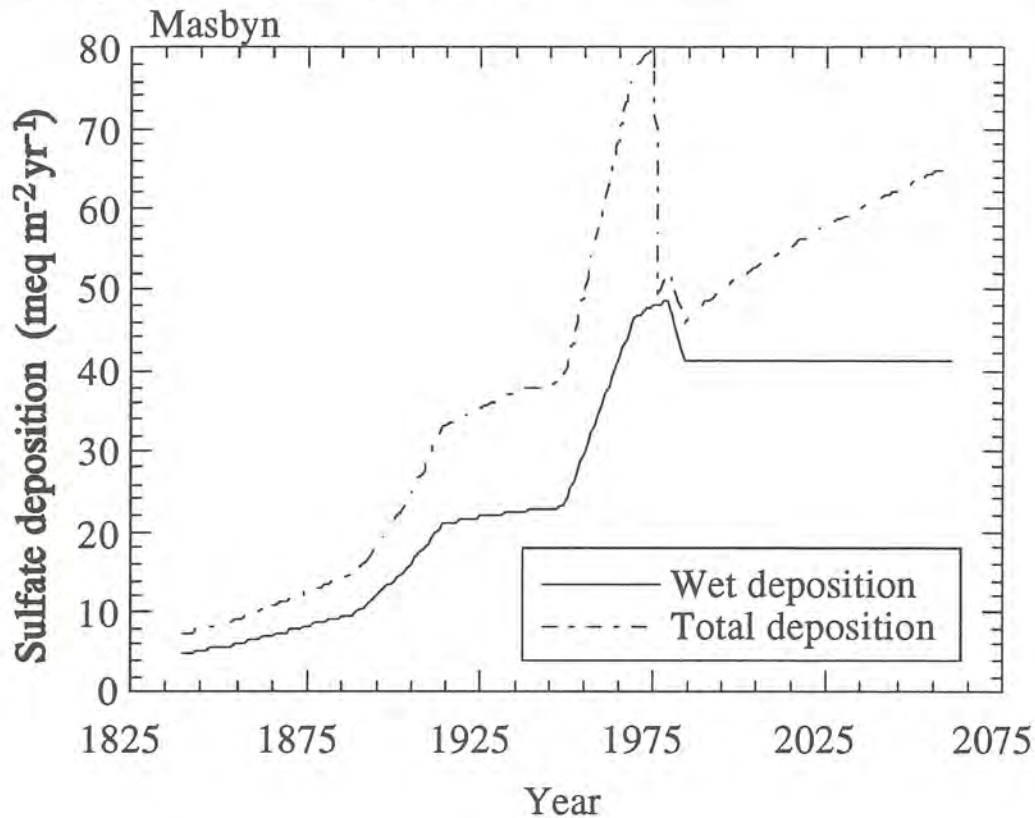


Figure 2.12. The complex S deposition pattern used for the long term scenario calculation at Masbyn.

In summary, the deposition scenarios are subject to a number of uncertainties:

- Emission records in Europe
- Present throughfall values
- Variations in filter factors due to stand growth
- Variations in filter factors due to non-linear co-deposition effects

While the former three items have been considered, the effect of co-deposition is extremely complex and has not been addressed at all. Thus, the filter factors have been held constant in time, based on present values.

2.7 UPTAKE DATA

The nitrogen and base cation uptake in the terrestrial ecosystem is the process that supplies building material to the biomass. Since these processes affect the internal production of acidity in the ecosystem, the uptake must be quantified accurately.

2.7.1 Nitrogen uptake

What we observe in terms of nitrogen uptake is the integrated result of a myriad of biogeochemical processes. For groundwater, it is only necessary to consider the net result of all of these, expressed as total uptake. Based on the data from the different sites, it is assumed that there is no N leaching from the soil column. Thus, the N uptake always equals the N deposition. In comparison with flux measurements from lysimeter and runoff studies This introduces an error in total load of acidity in the range of 5 meq $\text{m}^{-2} \text{yr}^{-1}$. In addition, it is assumed that all NH_4 is nitrified in the upper soil layer. Thereby, all N deposition can be treated as acidity, and all uptake as a source of alkalinity.

2.7.2 Base cation uptake

The fundamental assumption with respect to base cation uptake, is that the uptake rates should both be limited by the N supply, and conform with the observed growth rates at the different sites. In practice, this means that N is the limiting growth factor until the 1930-ies, from then on other factors are limiting.

For Stubbetorp, the land owner estimates that the average age of the trees in the stand at site 2 at Stubbetorp was 105 years in 1981. The yield class is 4.0 which corresponds to a annual stem growth of $5.3 \text{ m}^3 \text{ ha}^{-1}$. Based on the total standing volume and the incremental growth, the uptake of different nutrient cations could be calculated from data on base cation contents in biomass, provided by Rosén (pers. comm).

In Table 2.5, the percentage of different elements in Scots Pine and Norway Spruce is given. By weighing these figures according to the proportions of different parts of the tree (Table 2.6), equivalent weights and dry density of the tree, the mass of a specific element expressed in keq m^{-3} biomass, was calculated (Table 2.7). The values were calculated for a density of 700 kg m^{-3} . The cation content in Scots Pine then becomes 91 eq m^{-3} , and 155 eq m^{-3} for Norway Spruce. For Stubbetorp, the mix of forest is 20% Norway Spruce and 80% Scots Pine. With these values, the average cation content is therefore 104 eq m^{-3} . Finally, it was assumed that 1 m^3 of tree stem corresponds 1.5 m^3 of total tree biomass. As the total biomass volume does amount to $230 \text{ m}^3 \text{ ha}^{-1}$, the storage accumulated between 1876 and 1981 would be 23.9 keq ha^{-1} . Thus, the average annual uptake rate would be $0.228 \text{ keq ha}^{-1}$.

However, the base cation uptake must be distributed over time in a manner that is not in conflict with the deposition pattern, and the constraint that trees cannot live from nitrogen or base cations alone. The same set of data shows that ratio of BC to N in a stand with 80% Scots Pine and 20% Norway Spruce should be 0.97 at the latitude of Stubbetorp. This sets the upper limit of the base cation uptake to 97% of the N deposition. This ratio is maintained until a certain level from which it is constant. This level

Table 2.5. % mass in tree biomass for different elements and species at latitude 59°.

	Scots Pine			Norway Spruce		
	Stems	Branches	Needles	Stems	Branches	Needles
% Mg	0.018	0.05	0.08	0.02	0.07	0.1
% K	0.05	0.07	0.5	0.07	0.18	0.5
% Ca	0.07	0.2	0.35	0.15	0.4	0.6

Table 2.6. Distribution of biomass in trees.

Compartment	% of mass
Stem, bark and root	85
Needles	5
Branches	10

Table 2.7. Total element content in stand at Stubbetorp.

		Scots Pine	Norway Spruce
Mg	Eq m ⁻³ dry wood	14	17
K	Eq m ⁻³ dry wood	13	18
Ca	Eq m ⁻³ dry wood	34	69
Mg+Ca+K	Eq m ⁻³ biomass	91	155

is adjusted to meet the condition that the accumulated uptake from 1876 to 1981 should be 23.9 keq ha⁻¹. In addition a fixed uptake of 0.1 keq ha⁻¹ was added to account for additional storage in the understory vegetation and stand thinning.

The result from this elaborate exercise is shown in Figure 2.13. For the other sites, the same basic principles have been applied, but the annual average uptake during a rotation period is 0.51 and 0.44 keq ha⁻¹ yr⁻¹ for Risfallet and Masbyn respectively. The growth of the stand planted in 1975 at Masbyn and Risfallet is assumed to have an uptake pattern as given by Sverdrup *et al.* (1990).

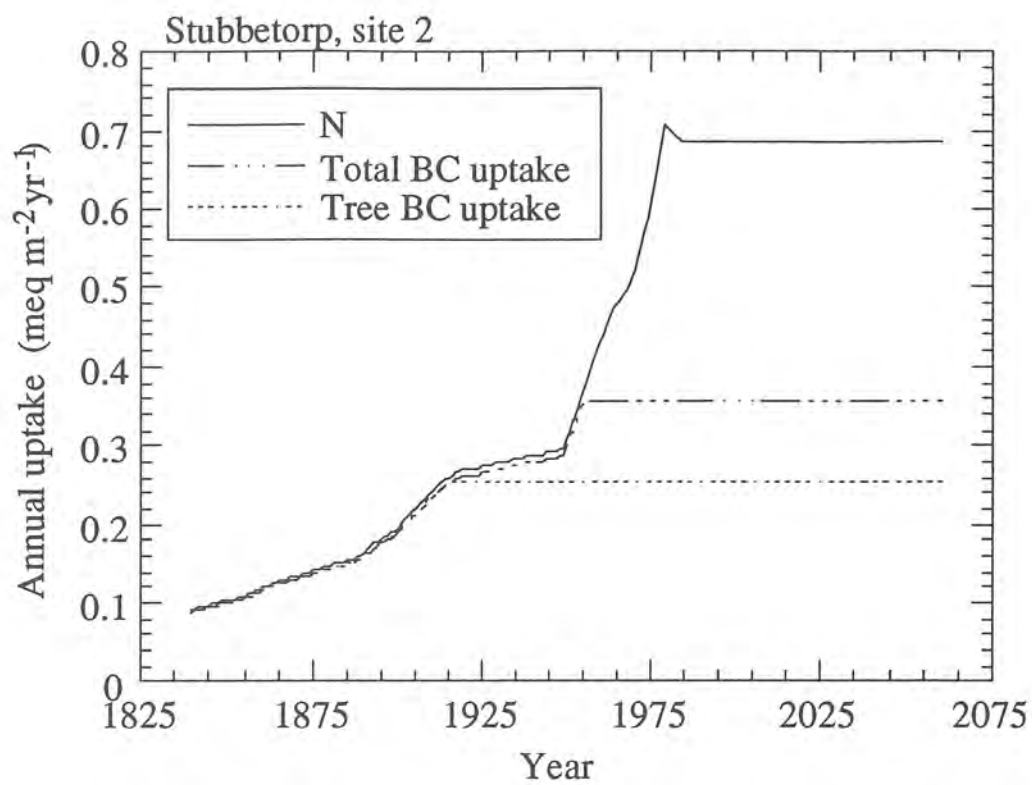


Figure 2.13. Uptake sequence for nitrogen and base cations used in the long term simulations with SAFE.

3 HYDROLOGICAL MODELLING

A large number of models have been developed in different countries for studies of the complex interaction between acidic deposition and the chemistry of soil water, ground water and surface water. A review of seven of these models has been carried out, from a hydrological point of view, within this project (Bergström and Lindström, 1989). The models often include a hydrologic submodel originating from a rainfall runoff model. An accurate description of the runoff hydrograph does not, however, imply a sound description of water pathways and water residence times within the model, which is a prerequisite for proper hydrochemical modelling.

The main hypothesis of this part of the project is that a vertically distributed modification of the PULSE model (Bergström *et al.*, 1985) can be used to provide input to hydrochemical models of the unsaturated zone.

Great effort was put into validation and sensitivity analysis of the hydrologic model. The different sites in Sweden, where different aspects of model performance were tested are described in Chapter 2. Results are presented both from this project and from previous modelling studies at the SMHI. A complete description of the model structure used in this study is given in Section 3.1.

As the change of the quality of groundwater recharge was considered the most important question to answer, the hydrological modelling concentrated on the vertical movement in the unsaturated zone. The modified PULSE model is hence vertically distributed according to the different soil horizons. Daily estimates of soil moisture content, evapotranspiration, water flux, residence time, and temperature at the different horizons were calculated to provide input for the dynamic hydrochemical modelling.

The performance of the snow accumulation routine was studied in a comparison between model-calculated water equivalent and extensive snow course data from the Klarälven/ Trysilälva river basin during 1969-85 (Section 3.2).

The model calculations of soil moisture content in the unsaturated zone were controlled by soil moisture measurements at mainly three basins (Section 3.3). The most extensive data sets were obtained from two stations in the Velen representative basin. Measurements of soil moisture content at two of the project's research basins, Masbyn and Risfallet, also offered valuable opportunities for model control.

Conservative tracers provide a valuable possibility for more detailed understanding of water pathways, storage volumes and transit times in the unsaturated zone. Lindström and Rodhe (1986) had to modify the structure of the original PULSE model for simulation of water flux through a catchment, traced by the stable isotope ^{18}O . Similar findings were reported for applications of the Birkenes model (Hooper *et al.*, 1988, and Stone and Seip, 1989). Measurements of ^{18}O in precipitation and drainage from soil lysimeters at the Stubbetorp research basin were used to control these aspects of the model structure and model performance (Section 3.4). Drainage was collected over a two year period from two sites, each with three different lysimeter depths.

The time-dependent reactions incorporated in the hydrochemical model require dynamic soil temperature estimates at the different soil horizons. A simple submodel for daily soil temperature calculations was therefore included in the hydrologic model and controlled by field measurements from the Velen representative IHD basin (Section 3.5).

The ability of the PULSE model to calculate groundwater levels is discussed in Section 3.6, and an example of a simulation and comparison with field measurements at the Stubbetorp basin is presented.

Further analysis of the behavior of the modified PULSE model has been obtained by a comparison with the SOIL model (Jansson and Halldin, 1979). The SOIL model is a physically based model for simulation of water and heat transport in a layered soil profile. The same sets of input data were applied to simulations with both the PULSE and the SOIL model at the Velen research basin (Section 3.7).

Finally long term simulations were carried out of soil moisture, evapotranspiration, water flux, transit time and soil temperature for the project's research sites as input to the hydrochemical modelling (Section 3.8).

3.1 MODEL STRUCTURE (G. Lindström and M. Gardelin)

The PULSE model (Bergström *et al.*, 1985, Carlsson *et al.*, 1987) forms the hydrological modelling framework for the modified model. The model is a conceptual rainfall-runoff model based on the HBV model (Bergström and Forsman, 1973, Bergström, 1975, Bergström, 1976).

In contrast to the original PULSE model the soil moisture accounting routine of the modified PULSE model is distributed vertically according to the different soil horizons. Daily estimates of soil moisture content, evapotranspiration, water flux, residence time, and temperature in the different horizons are calculated as input for the hydrochemical modelling. The modified PULSE model structure chosen for the present study, with an explanation of the parameters, is shown in Figure 3.1. A daily time step was used in the model calculations, except in the soil moisture routine where the calculations within one day were made mm by mm.

The observed precipitation (PREC) can be adjusted by a factor (CPREC) to eliminate systematic errors in the observations. The snow routine is identical to the one developed for the HBV model. Precipitation is accumulated as snow, if the air temperature is lower than a threshold value (TTPREC). A snowfall correction factor (CSF) accounts for winter evaporation, aerodynamic losses at the precipitation gauge and its representativeness. The melt routine is essentially a degree-day approach where the melt volume is determined by a degree-day melt factor (CMELT) and a threshold temperature for snowmelt (TTMELT). A liquid water holding capacity (CWH) of the snow has to be exceeded before any meltwater can leave the snowpack. The degree-day approach has proved to be very efficient in an intercomparison of basinwide modelling (WMO, 1986).

In the soil moisture accounting routine the water balance is calculated individually for each layer according to:

$$\frac{\Delta SM_i}{\Delta t} = IN_i - PERC_i - EVP_i \quad (3.1)$$

where SM_i is soil moisture in layer i ,
 IN_i is inflow to layer i ,
 $PERC_i$ is percolation from layer i ,
 EVP_i is evapotranspiration from layer i .

The downward flux is assumed to be dependent only on the inflow to and water content in each soil layer:

$$PERC_i = K_i IN_i \quad (3.2)$$

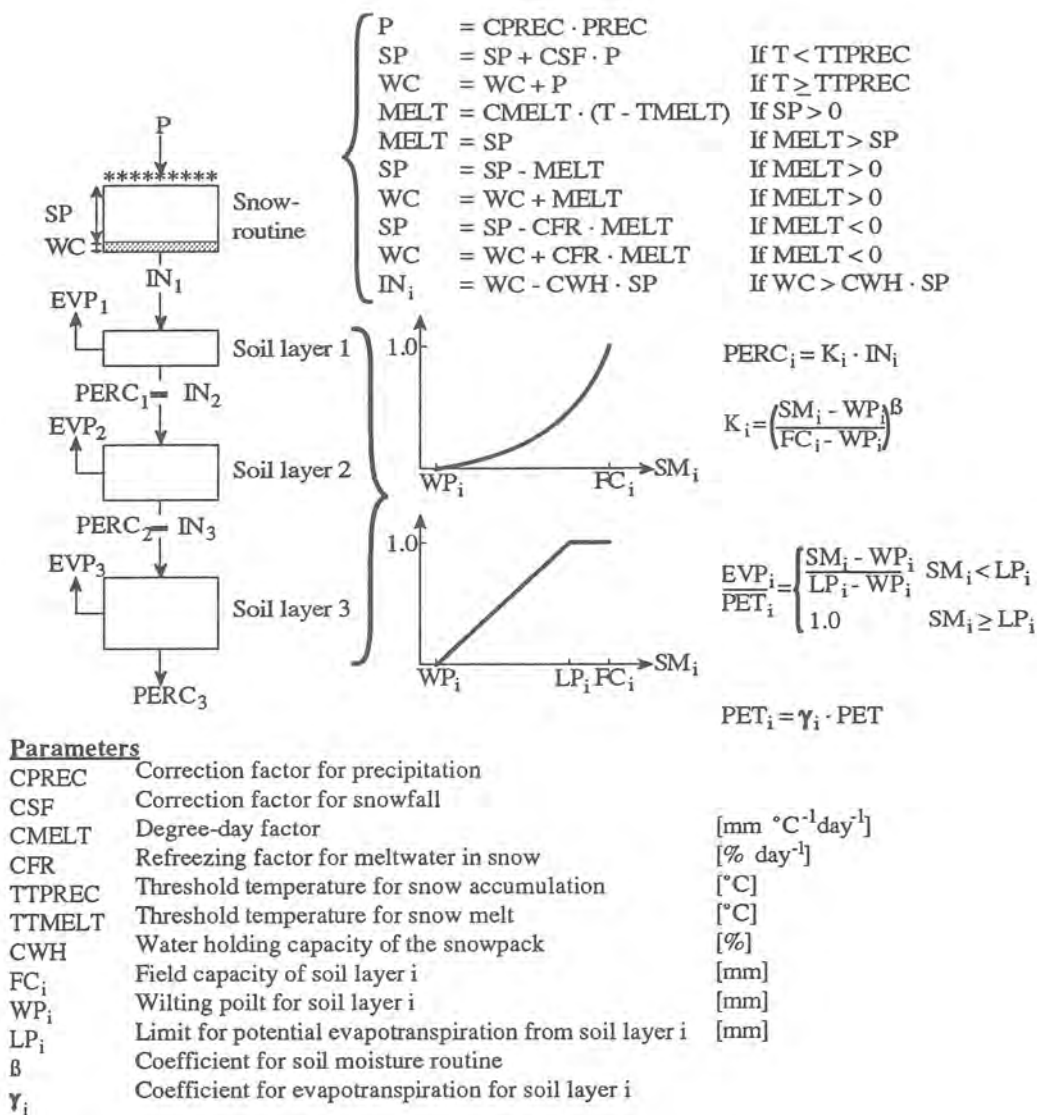


Figure 3.1 Model structure for simulation of unsaturated flow in a soil profile. Example with three soil layers.

$$K_i = \left(\frac{SM_i - WP_i}{FC_i - WP_i} \right)^\beta \quad (3.3)$$

where FC_i represents the total water volume held in layer i at field capacity,
 WP_i represents the water volume held below wilting point in layer i ,
 β is an model coefficient.

The flow in the model is thus not driven by a gradient in the soil moisture potential based on Darcy's law and Richards equation (Richard, 1931), as is most common in the modelling of flow in the unsaturated zone (e.g. Jansson and Halldin, 1979). In earlier descriptions of the PULSE model the FC parameter represented only water available for evapotranspiration. Thus the FC parameter in this description is larger by the amount of WP and represents the total water volume in the soil.

Evapotranspiration is calculated as a fraction of the potential evapotranspiration depending on the current soil moisture status according to:

$$\frac{EVP_i}{PET_i} = \begin{cases} \frac{SM_i - WP_i}{LP_i - WP_i} & SM_i < LP_i \\ 1.0 & SM_i \geq LP_i \end{cases} \quad (3.4)$$

where EVP_i is evapotranspiration from soil layer i ,
 PET_i is potential evapotranspiration from soil layer i ,
 LP_i is the limit for potential evapotranspiration from soil layer i .

The potential evapotranspiration from the unsaturated zone is distributed between the different soil layers according to an exponential expression, in which the evapotranspiration decreases with soil depth:

$$PET_i = PET \cdot \frac{e^{-\alpha l_i} \cdot s_i}{\sum_{j=1}^n e^{-\alpha l_j} \cdot s_j} \quad (3.5)$$

where PET are monthly values of potential evapotranspiration,
 n is the number of soil layers,
 l is depth to the middle of the soil layer,
 s is thickness of the soil layer,
 α is an empirical coefficient.

Andersson and Harding (1991) achieved a significant improvement in model performance by introducing a simple temperature regulation of the potential evapotranspiration. The routine uses daily mean air temperatures to determine the reduction in transpiration rates. Below 5 °C the potential evapotranspiration is put to zero, between 5 °C and 10 °C there is a linear increase in the evapotranspiration factor, and above 10 °C there

is no temperature regulation of the evapotranspiration. This modification was also included in the present model.

Two alternative flow assumptions within each soil layer were tested in the O^{18} -study, namely either ideal mixing or piston flow. In the piston flow model, the water from each inflow event was stored in separate pulses, and the outflow was taken from the oldest water pulse in the layer. When the water flow and storage had been calculated, the ^{18}O flow and storage followed from mass balance considerations. In the ideal mixing model the outflow is composed of an equal portion of each pulse in the layer. For each water pulse, the model keeps track of the age, i.e. the time that has elapsed since the moment of inflow. The transit time was calculated as the volume-weighted mean age of the outflowing water pulses.

In the lysimeter study particle flow velocities were calculated as the lysimeter depth divided by the transit time. To obtain the transit time distribution for average flow conditions, stationary flow was assumed. The evaporation was set equal to zero, and the precipitation was set equal to the average drainage for the two years in the simulation. The soil moisture was set equal to the field capacity (FC). By simulation of a unit tracer impulse, the transit time distribution was obtained as the outflow concentration.

The hydrochemical model requires daily soil temperature estimates at various depths in the soil profile. A separate submodel for soil temperature calculation has been developed and is described in detail in Section 3.5.

3.2 SNOW MODELLING (S. Bergström and M. Gardelin)

The degree-day routine for snow accumulation and melt in the modified PULSE model is identical with the one developed for the HBV model (Bergström, 1975). The model routine and the parameters included are described in detail in Section 3.1.

The snow accumulation and melt routines of the PULSE model are of great importance for its overall performance. There are, however, only limited data available for its verification. Most snow surveys in field research basins are restricted to one or a few observations per season, a number which is inadequate for any dynamic study. The best data available in Sweden have been collected by the Uddeholm Kraft AB for hydro power operation purposes. Gardelin and Bergström (1987) analysed the potential use of these data for forecasting of inflow to the Höljes reservoir in River Klarälven (Trysilelva is the name of the river upstream of the reservoir).

As the snow routines of the PULSE model (Section 3.1) are identical to those of the HBV model the results from the Gardelin and Bergström analysis is highly relevant as a control of the snow simulation part of the modified model used in this project. In order to take advantage of the valuable data from Trysilelva and to make the presentation of controls of internal variables of the model as complete as possible we have chosen to include some of the results from this work in this report. A description of the basin and the data base is given in Chapter 2.

3.2.1 Results

In Figure 3.2 are shown examples of the model simulations of snow water equivalent and runoff for three of the studied years. In Figure 3.3, is presented a comparison of model-calculated and measured snow water equivalents for all the available snow course occasions. The modelled snowpack shows a dynamic pattern which is in agreement with observations although the error can be considerable for single observations. The largest errors are in the order of 50 mm water equivalents.

3.2.2 Discussion and conclusion

The snow accumulation and melt routines of the HBV and PULSE models are well tested under different conditions in a number of countries. The HBV model participated in the WMO intercomparison of snowmelt runoff models (WMO, 1986) in which models, varying in complexity from the simple degree-day approach to more complex energy balance computations were examined under well controlled conditions. It was found that the HBV model with the simple degree-day approach was very efficient in basinwide modelling. One of the conclusions from the intercomparison was that the complexity of the model structure could not be related to the quality of the simulations and that it was not possible to rank the tested models in order of performance.

Although there are numerous indications that the HBV and PULSE models describe the snow accumulation and melt in a reasonable way the tests have mostly been restricted to comparisons with runoff generated by snowmelt. There are few examples of direct comparison with field snow survey data, mainly due to lack of time series of such data.

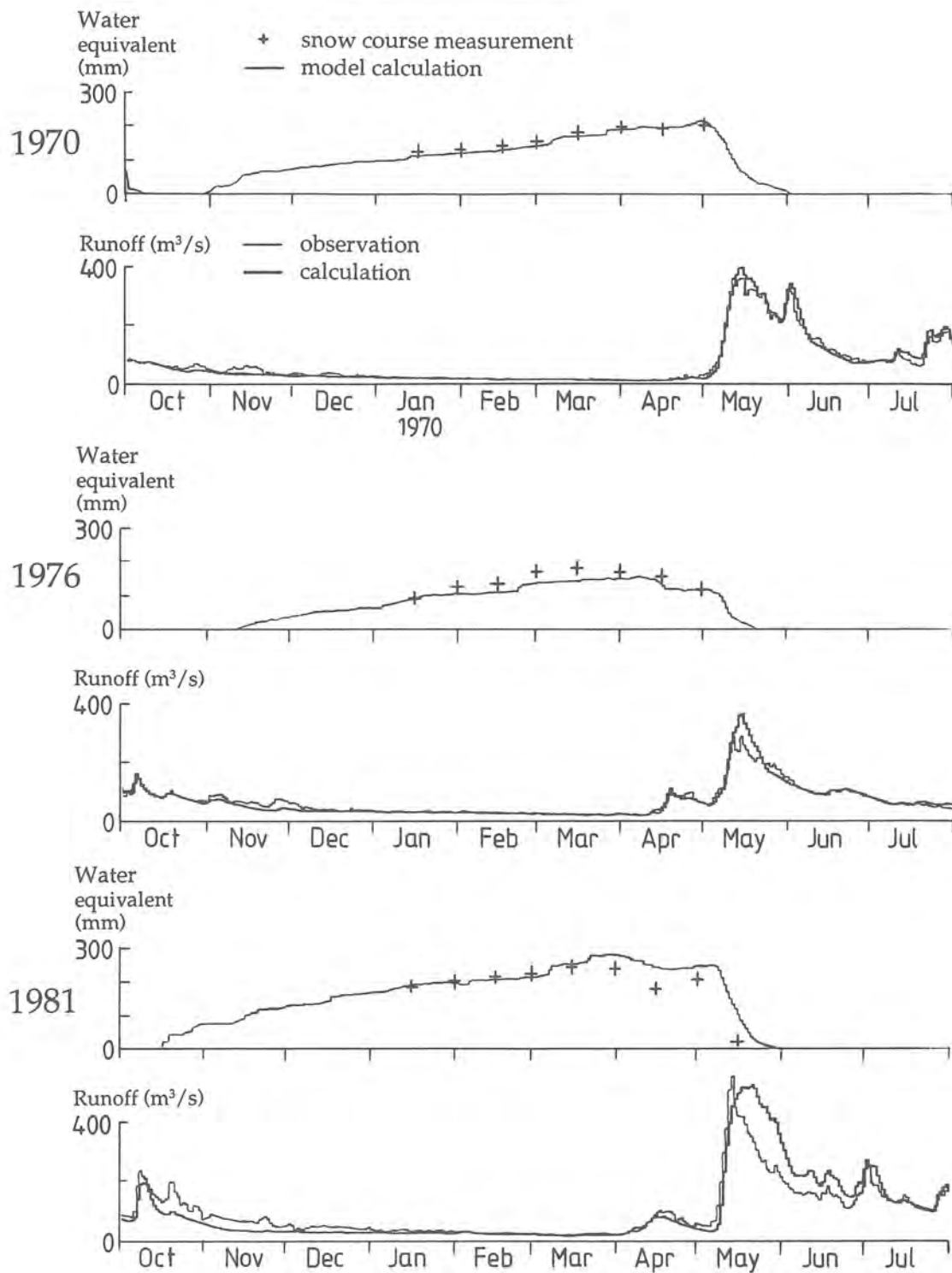


Figure 3.2. Model simulations and measurements of snow water equivalent and runoff for the years 1970, 1976, and 1981 in the Trysil-elva basin.

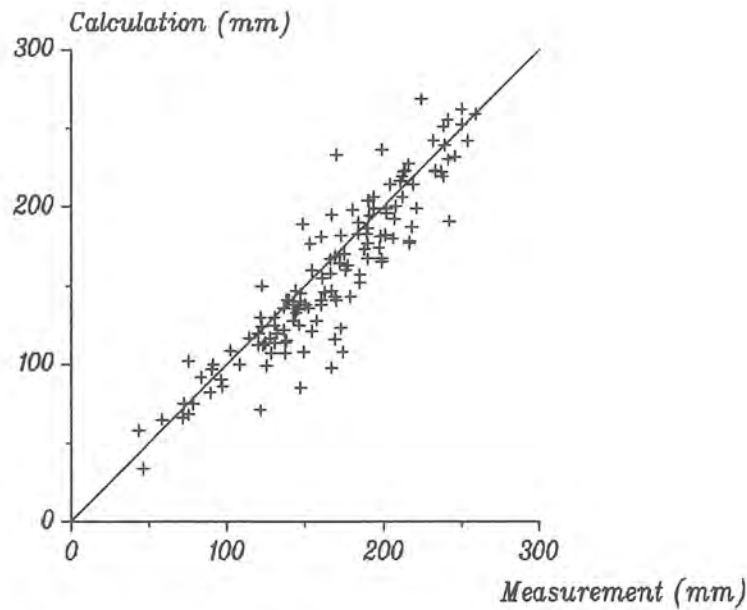


Figure 3.3. Comparison between model-calculated snow water equivalent and water equivalent from snow course measurements at the Trysiløva river basin during 1969-85.

Another problem is the areal representativity of snow surveys when compared to basin-wide coverage.

The situation in Trysiløva is very favorable for snow model verification. The basin is relatively homogeneous and mostly forested and the snow sampling is extensive, carried out relatively frequently and in a consistent manner. Therefore the results from the modelling study have supported our confidence in the snow routine of the HBV and PULSE models.

3.3 SOIL MOISTURE (M.Gardelin)

Simulations of soil moisture dynamics with the PULSE model have previously been reported by Andersson (1988). The simulations were made for average conditions in the upper meter of the soil, at several sites in the Velen research basin.

The simulations presented in this study were performed for the different soil horizons in the upper metre of the soil and controlled by soil moisture measurements, mainly in three basins in Sweden. The most extensive data sets were obtained from two stations in the Velen basin. Measurements of soil moisture content at two of the project's research basins, Masbyn and Risfallet, also offered valuable opportunities for control of the model (see Chapter 2, Figure 2.1). Descriptions of the sites and data base are given in Chapter 2.

3.3.1 Parameter estimation

The parameters CPREC, CSF, CMELT, TTPREC, and TTMELT (the parameters are explained in Section 3.1) were calibrated against runoff measurements for the entire catchments. The parameters CWH and CFR are in the model fixed at 10 % and 5 % respectively.

In the soil moisture accounting routine the parameter FC was determined from measured soil moisture retention curves for each soil layer. A constant groundwater level was then assumed in the model, corresponding to the measured average groundwater level for the simulation period.

The parameter WP, representing water held below wilting point, was determined for each soil layer from water retention curves at a suction of 150 m (pF-value 4.2).

The application of the model to vertical point simulations and not mainly to basin simulations resulted in a simplification of the soil moisture routine. The number of empirical parameter combinations was reduced by setting β and LP equal to 1. None of the parameters in the soil moisture routine was thus calibrated against measurements of runoff or soil moisture.

Monthly standard values of potential evapotranspiration was taken from Eriksson (1981) and Wallén (1966).

The empirical coefficient α , affecting the distribution of the evapotranspiration between the soil layers, was in the soil moisture simulations determined by fitting the exponential equation to literature data on depth profile of root density (Marshall and Holmes, 1979; Jansson and Halldin, 1980; and Lundmark, 1988).

3.3.2 Velen

Figure 3.4 and Figure 3.5 show the soil moisture simulations for the period 1967-70 at Sjöängen.

A drift in the soil moisture measurements during winter 1970/71, which caused too high readings, had previously been observed by Andersson (1988). This divergence could clearly be observed at the two Sjöängen stations during the period 1971-72. The absolute values were consistently too high, but the dynamics of the moisture variations

could still be studied during this period. No measurements representing the upper soil layer were performed.

The soil moisture dynamics as well as the level of soil moisture content at saturation in the three soil layers at both stations were well described by the model simulation.

The weak point of the Sjöängen simulation is certainly the determination of the FC parameter which is based on the available brief soil analysis of water holding capacity. This uncertainty results in uncertain levels of soil moisture at saturation but has little effect on soil moisture dynamics.

3.3.3 Masbyn

Figure 3.6 shows the soil moisture simulation at Masbyn for the period 1973-76. In this simulation no change in the parameter set was made at the time of the clear-cutting during winter 1975/76. The depth to the groundwater level in the model was assumed to be constant during the entire simulation. The effect of the clear-cutting on the water balance can clearly be observed during 1976. The actual soil moisture content increased significantly due to diminishing water uptake, while the model simulation is similar to that of the previous growth season of 1975.

Figure 3.7 shows the model simulation for the period 1986-89. During both simulation periods, the measured soil moisture content in the upper soil layer is significantly higher than the simulation.

In the three deeper soil layers the level of the soil moisture content as well as the dynamic of the soil moisture variations are well described by the model during both simulation periods.

3.3.4 Risfallet

Figure 3.8 shows the soil moisture simulation for Risfallet. In this simulation there are no measurements representing the upper soil layer.

Good agreement with the measurements was obtained in the E-horizon. In soil layer B the level of soil moisture at saturation was correct, but the observed variations of soil moisture content were much smaller than the simulated variations. In soil layer C the simulated values were consistently too high compared with the measurements.

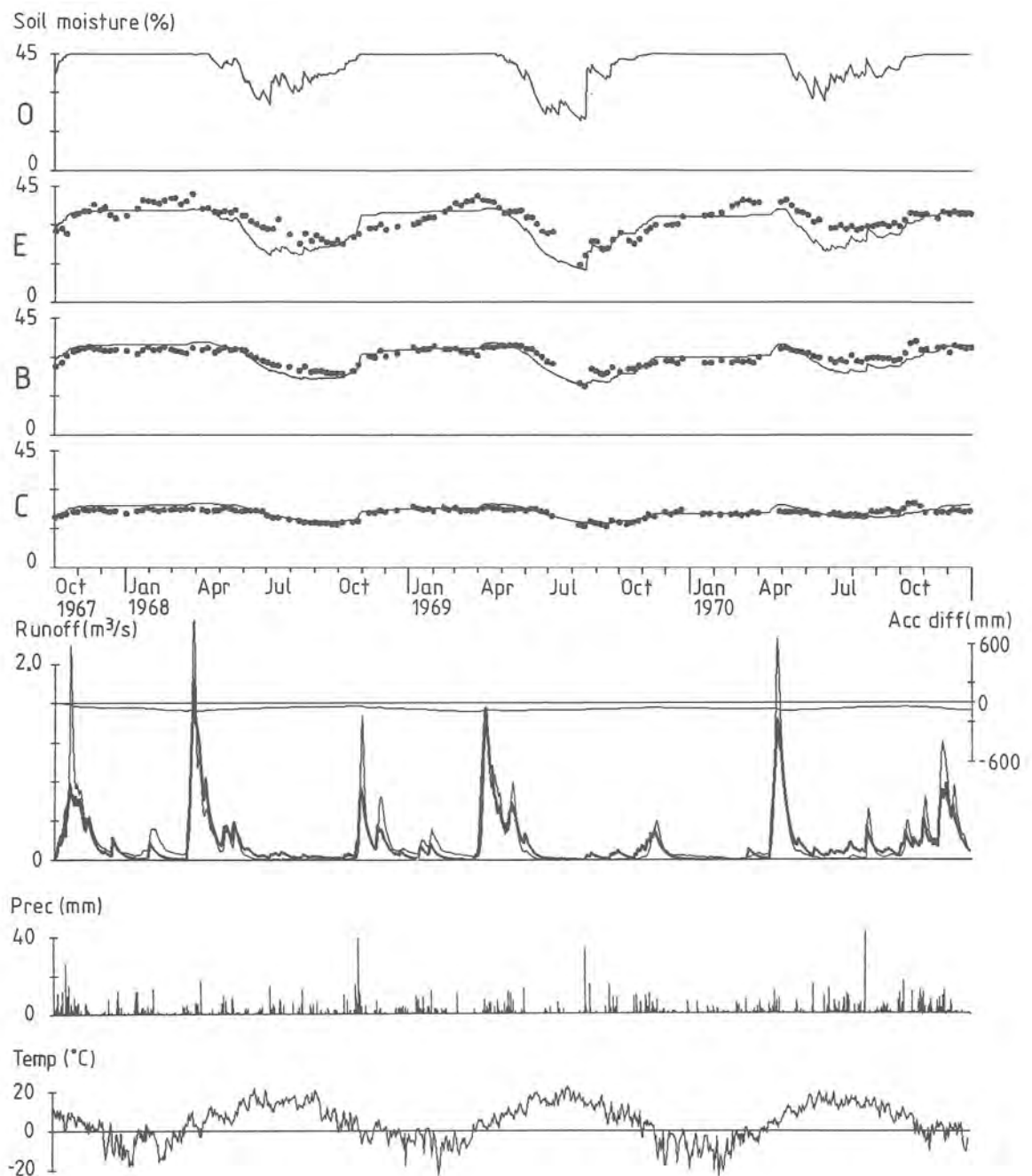


Figure 3.4. Model simulation of soil moisture content in 4 soil layers at Sjöäng-en 7. Dots represent mean values of the soil moisture measurements within each soil layer. Below: Simulation (thick line) and measurement (thin line) of runoff from the Nolsjön basin, together with accumulated difference between runoff simulation and measurement. The model's daily input data of precipitation and mean air temperature are shown at the bottom.

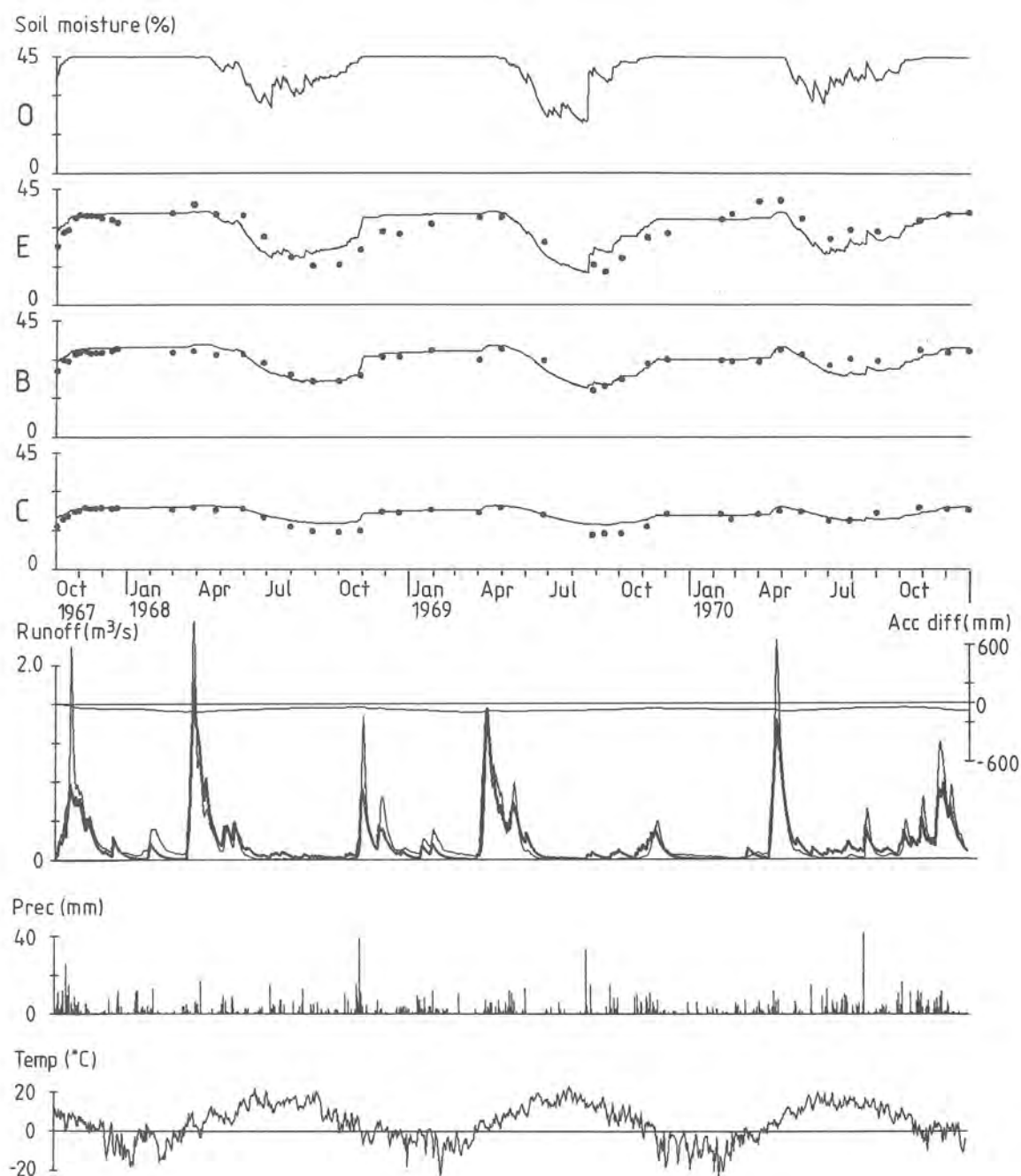


Figure 3.5. Model simulation of soil moisture content in 4 soil layers at Sjöäng-en 8. Dots represent mean values of the soil moisture measurements within each soil layer. Below: Simulation (thick line) and measurement (thin line) of runoff from the Nolsjön basin, together with accumulated difference between runoff simulation and measurement. The model's daily input data of precipitation and mean air temperature are shown at the bottom.

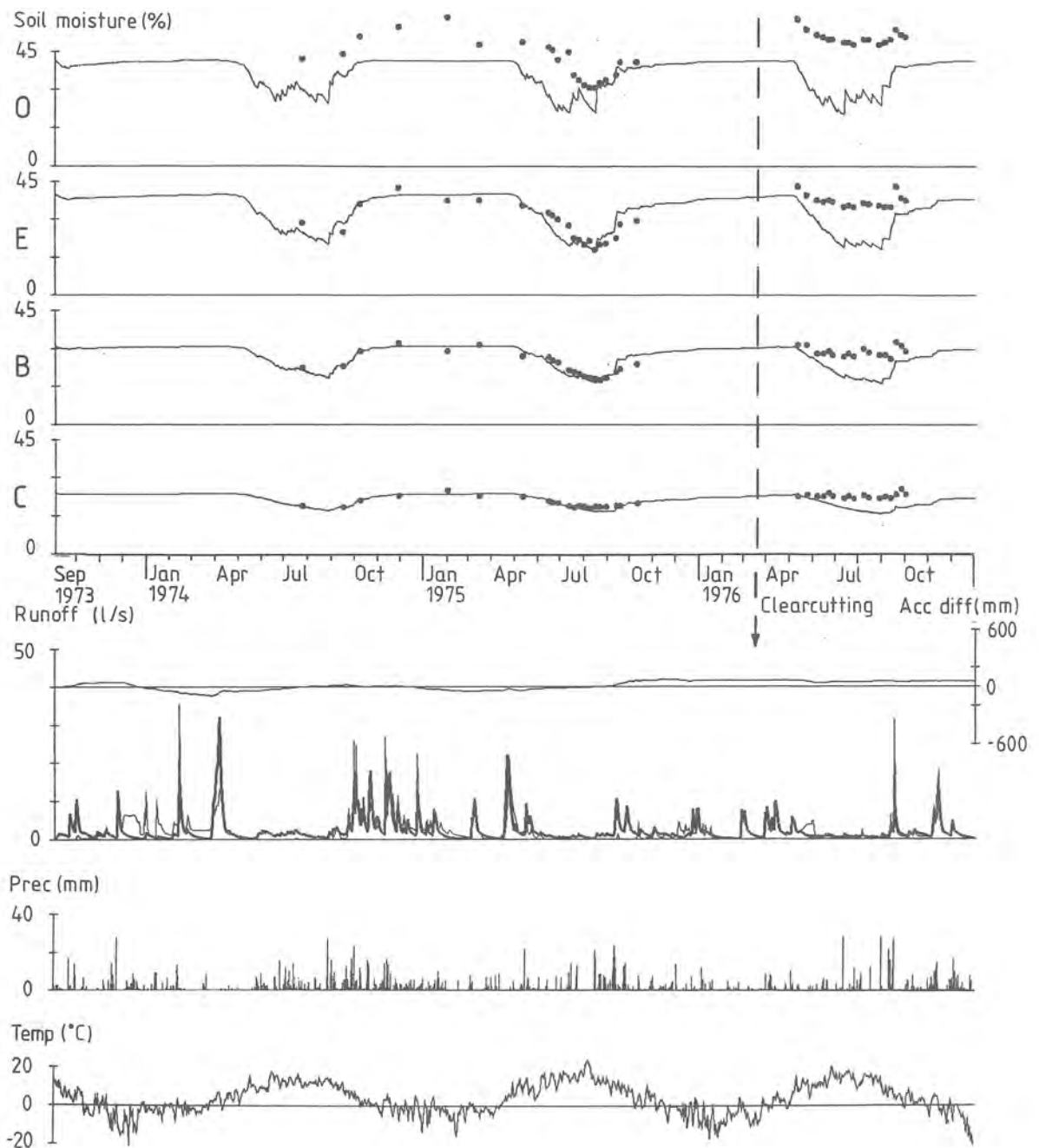


Figure 3.6. Model simulation of soil moisture content in 4 soil layers at Masbyn for the periods before and after clear-cutting 1973-76. Dots represent mean values of the soil moisture measurements within each soil layer. Below: Simulation (thick line) and measurement (thin line) of runoff, together with accumulated difference between runoff simulation and measurement. The model's daily input data of precipitation and mean air temperature are shown at the bottom.

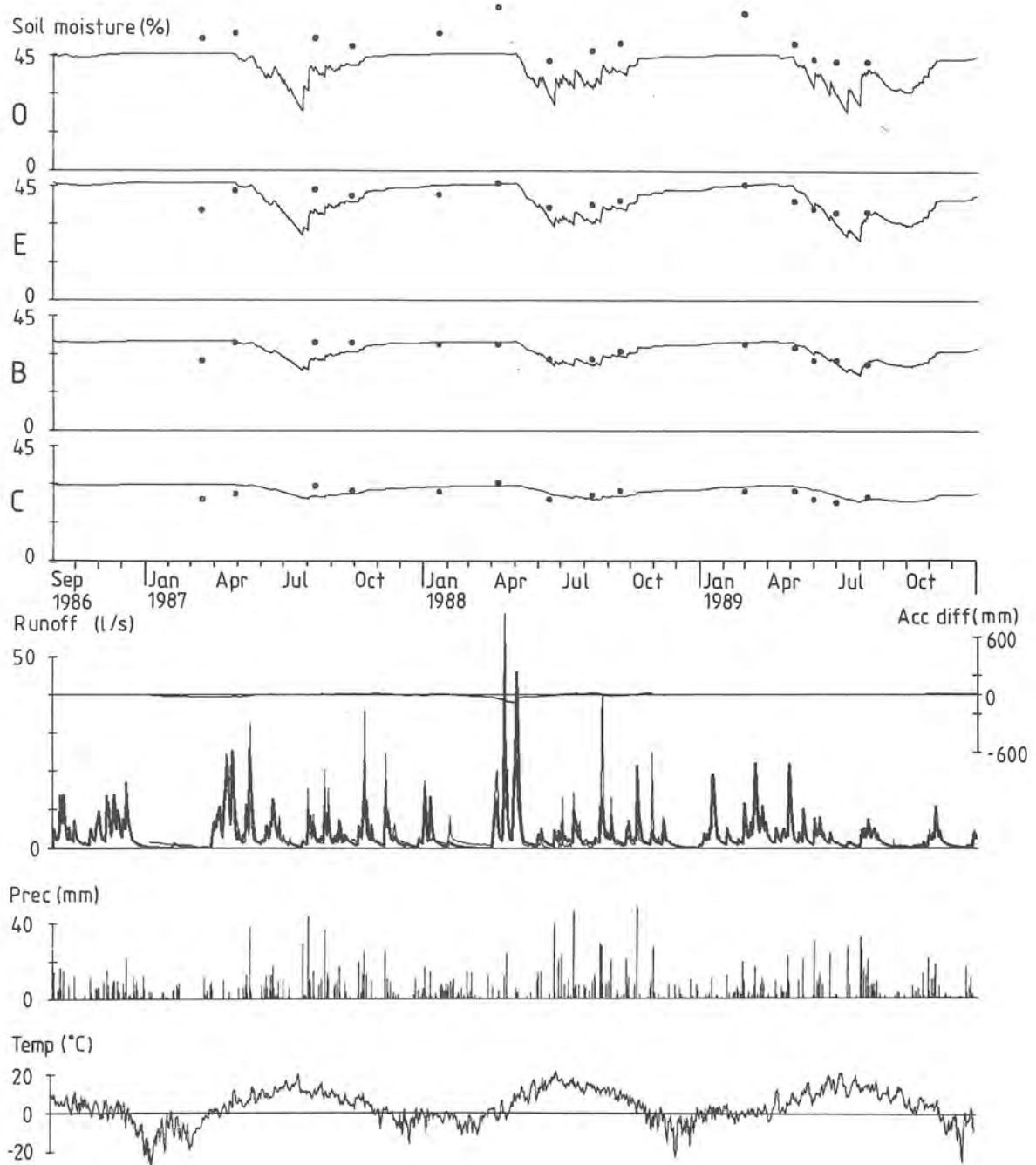


Figure 3.7. Model simulation of soil moisture content in 4 soil layers at Masbyn for the period 1986-89. Dots represent mean values of the soil moisture measurements within each soil layer. Below: Simulation (thick line) and measurement (thin line) of runoff, together with accumulated difference between runoff simulation and measurement. The model's daily input data of precipitation and mean air temperature are shown at the bottom.

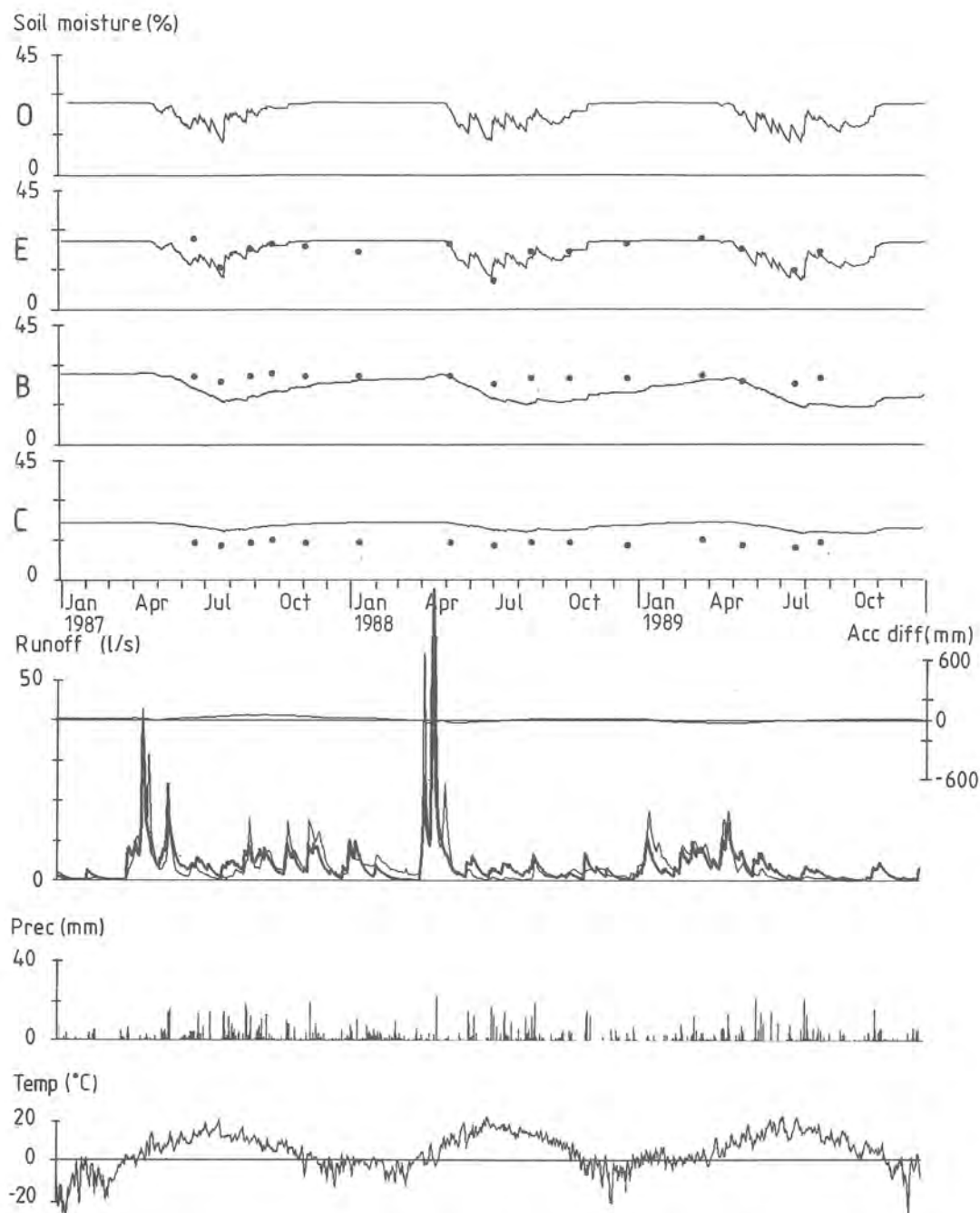


Figure 3.8. Model simulation of soil moisture content in 4 soil layers at Risfallet. Dots represent mean values of the soil moisture measurements within each soil layer. Below: Simulation (thick line) and measurement (thin line) of runoff, together with accumulated difference between runoff simulation and measurement. The model's daily input data of precipitation and mean air temperature are shown at the bottom.

3.3.5 Discussion and conclusions

The vast data material on soil moisture dynamics collected during the IHD-period offered a unique opportunity to control the performance of the modified PULSE model. The data from the Velen basin has previously been used by Andersson (1988) for a similar study where different model approaches were tested. That study was, however, restricted to the total soil moisture content of the upper meter of the soil, while the present study separates the dynamics of soil moisture in four horizons.

The difference between observed and simulated soil moisture of the O-horizon at Masbyn could be due to the model formulation. The observations are considered correct despite the problems of neutron probe measurements close to the surface. The high values have been controlled by soil analysis (Lundin, pers comm.). The model formulation does not allow the soil moisture to increase above the specified pF-value, which is determined by the fixed groundwater level.

The weak modelling result representing horizons B and C at Risfallet could be explained by large elements of rock and boulder in the upper meter of the soil and by the fact that the water retention curves were determined only from analysis of material smaller than 20 millimeters. In the upper meter of this soil only 22 percent of the total soil volume is material smaller than 20 millimeters. The neutron probe measurements are also sensitive to rocks and stones in the vicinity of the probe. Although the model formulation might be too simplistic, the problem with estimating the field capacity and measuring soil moisture has to be considered in this soil type.

The conclusion that a relatively simple model structure with limited data demand can be useful for the simulation of soil moisture dynamics is further supported by the work by Calder *et al* (1983). In Section 3.7 is shown one more study of model complexity versus performance, as we compare the simulations from the conceptual PULSE model to results from the physically based SOIL model.

When judging the results of the present study it is important to bear in mind the objective of the research project. For regional applications we have to accept that no data normally is available for model calibration and that little is known about soil characteristics. It is, therefore encouraging that the model performs relatively well without calibration and that this seems to be a general conclusion for a number of sites. The model is not site specific, nor overparameterized. Some results may look questionable and this reveals the uncertainty that we have to face in uncontrolled applications. The effect of this uncertainty on the hydrochemical modelling is subject to a sensitivity analysis in Chapter 5.

In this section emphasis is put on simulations of the soil moisture dynamics at different depths. Runoff data has also been used as a control of the model. This has, however, to be regarded only as qualitative information since there is a great difference between the groundwater recharge to an aquifer, which is being modelled, and discharge from the basin, which is being measured.

3.4 TRANSIT TIMES (G. Lindström and A. Rodhe)

The dynamic weathering reactions in the hydrochemical model (Chapter 4) call for a realistic description of water flow patterns and transit times in the unsaturated zone. The measurements of ^{18}O in precipitation and drainage from the lysimeters at Stubbetorp were used for control of the flow patterns and transit times as described by the hydrological model. The necessary field information was collected from the Stubbetorp research basin. A description of the basin and the data base is given in Chapter 2. The modified PULSE model which was used is described in Section 3.1.

The hydrological conditions in soil lysimeters differ from natural conditions. The soil water has no capillary contact with the ground water level outside the soil lysimeters. A temporary saturation in the bottom of the lysimeter, must be built up before water can be drained. The existence of this temporary groundwater level, relatively close to the soil surface, means that the water content at a given depth in general is higher in the lysimeters than in the surrounding soil. Furthermore, the absence of water uptake by trees results in a low transpiration.

3.4.1 ^{18}O as a tracer

Due to different origins of the air masses and fractionation processes during condensations in the atmosphere, the ^{18}O content of precipitation in temperate regions shows a seasonal variation in the monthly mean values, with comparatively low values in winter and high values in summer. Overlain this seasonal variation there is a large scatter in the daily values. ^{18}O -concentrations are usually expressed in δ -notation, i.e. as the relative deviation of the isotopic ratio $^{18}\text{O}/^{16}\text{O}$ of the sample to that of Standard Mean Ocean Water (SMOW). At northern latitudes the ^{18}O -concentration is usually lower than that of SMOW, resulting in negative $\delta^{18}\text{O}$ values. The deviations are in general small, and expressed in per mille. Analytical accuracy in measuring $\delta^{18}\text{O}$ is about ± 0.1 per mille.

Since it is chemically inert and forms a part of the water molecule itself, ^{18}O is a near ideal tracer in many hydrological studies. In studies of groundwater, ^{18}O can safely be treated as a conservative tracer, but in water in contact with the atmosphere there is a possibility for isotopic change by fractionation during evaporation and molecular exchange with the atmospheric water vapour. Evaporation from open water bodies enriches the remaining water, but transpiration is non fractionating. Enrichment in ^{18}O may also occur by evaporation from soil water, but in vegetated soils such enrichment is probably very small. Some fractionation during interception was observed by Saxena (1986). A snowpack may be enriched in ^{18}O by fractionation taking place during melting, tending to deplete the meltwater in ^{18}O as compared to the snowpack (see for example Herrmann *et al.*, 1981), but this latter fractionation mainly changes the time variation of the ^{18}O input to the ground and not the total input. Discussions on the possibility to use ^{18}O for tracing water flow through a basin have been given by for example Dincer and Davis (1984) and Rodhe (1987).

In the present study, the output ^{18}O signal from soil lysimeters, i.e. the ^{18}O concentration of the drainage water, was modelled from observations of the input signal, i.e., the ^{18}O concentration of precipitation. ^{18}O was regarded as a purely conservative tracer, from

precipitation to lysimeter drainage. Any fractionation, commented upon above, was thus disregarded.

3.4.2 Parameter estimation

The parameters CMELT, TTPREC and TTMELT were calibrated against runoff measurements, in the same way as for the soil moisture simulation. CSF and CPREC were set equal to 1. The parameters CWH and CFR are fixed at 10 % and 5 % respectively in the model.

Two different methods were used to determine FC. The first alternative was to use the measured soil moisture characteristic curve and integrate the water content in each soil layer, assuming that the groundwater level was situated at the bottom of the lysimeter. The second alternative, which was chosen as the reference method, was to decrease the above established FC values slightly, in order to match the measured total water contents of the lysimeters better. The FC values used are summarized in Table 3.1.

Table 3.1. Chosen model values for the FC parameter. The numbers within brackets show the values established from the soil moisture characteristic curves.

Lysimeter	Depth (cm)	FC (mm)	Total FC (mm)	Water content (θ) at FC (%)
15 cm	0 - 15	60 (75)	60 (75)	40 (50)
40 cm	0 - 15	45 (60)	120 (160)	30 (40)
	15 - 40	75 (100)		
80 cm	0 - 15	40 (45)	200 (240)	25 (30)
	15 - 40	60 (75)		
	40 - 80	100 (120)		

The wilting point does not have any great influence on the simulations in this application, since evapotranspiration and soil moisture deficit always are low. The parameters WP was therefore set equal to 0 in these simulations. The β should in theory be set to a very large value to avoid drainage from the lysimeter until the soil moisture has reached field capacity. Field observations and dissection of the lysimeters suggests that they did not follow this ideal behavior (see Lundin *et al.* 1992). To reduce the number of empirical parameters β and LP was therefore set to 1.

The absence of higher vegetation on the lysimeters reduces the evapotranspiration. The potential evapotranspiration, taken from Eriksson (1981) and Wallén (1966) was therefore reduced considerably (in all cases to less than 15 % of the standard value). Since the total evapotranspiration from the lysimeters is small compared to natural conditions the reduction of evapotranspiration at low temperatures suggested by Ander-

sson and Harding (1991) was neglected. The exponential distribution of evapotranspiration between the soil layers was also neglected, for the same reason.

In addition to visual inspection of computed and measured ^{18}O in the drainage, the criterion R^2_{O18} was used as a measure of the model performance and was calculated as:

$$R^2_{O18} = 1 - \frac{\sum_{i=1}^n ({}^{18}\text{O}_{com(i)} - {}^{18}\text{O}_{obs(i)})^2}{\sum_{i=1}^n ({}^{18}\text{O}_{obs(i)} - \overline{{}^{18}\text{O}_{obs}})^2} \quad \overline{{}^{18}\text{O}_{obs}} = \frac{1}{n} \sum_{i=1}^n {}^{18}\text{O}_{obs(i)} \quad (3.6)$$

3.4.3 Results

Water and ^{18}O simulations

Figure 3.9 shows a water balance simulation for lysimeter 15 cm, with the chosen parameter values. All results presented in this section refers to lysimeters from site 2.

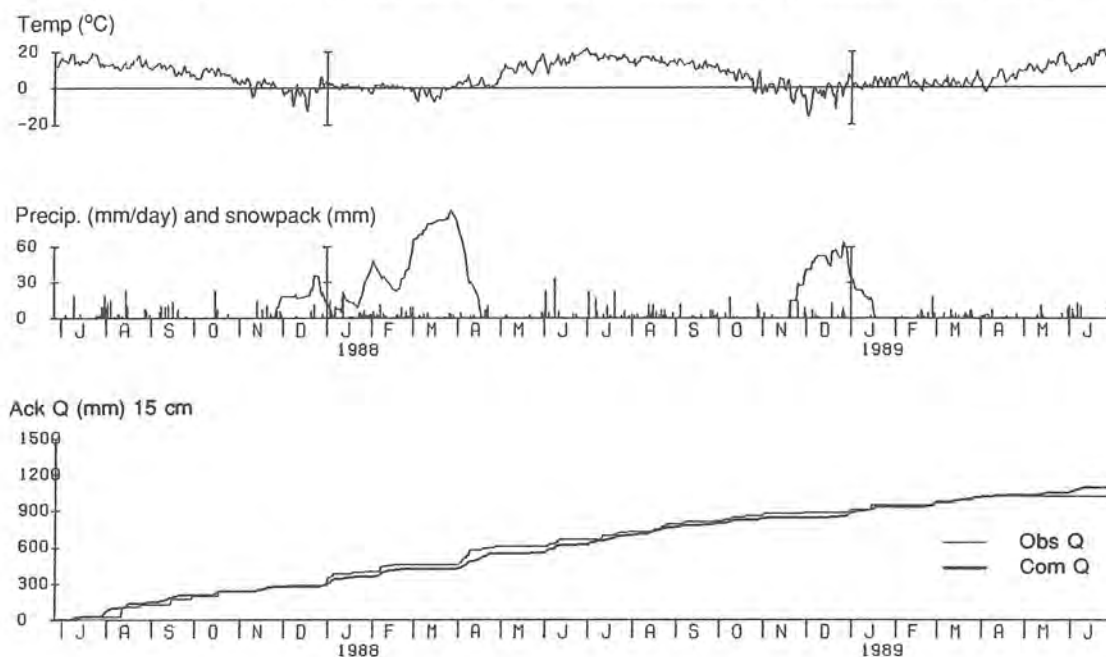


Figure 3.9. Water balance check for lysimeter 15 cm.

The simulated and recorded drainage volumes for lysimeter 80 cm showed similar agreement. However, for lysimeter 40 cm, the recorded drainage significantly exceeded the precipitation. This was probably due to additional meltwater entering the lysimeter during the snowmelt in the spring of 1988.

Figure 3.10 shows a simulation of ^{18}O for the lysimeters taken from site 2 (see Chapter 2). For the lysimeters from site 3, results of similar agreement and characteristics were obtained.

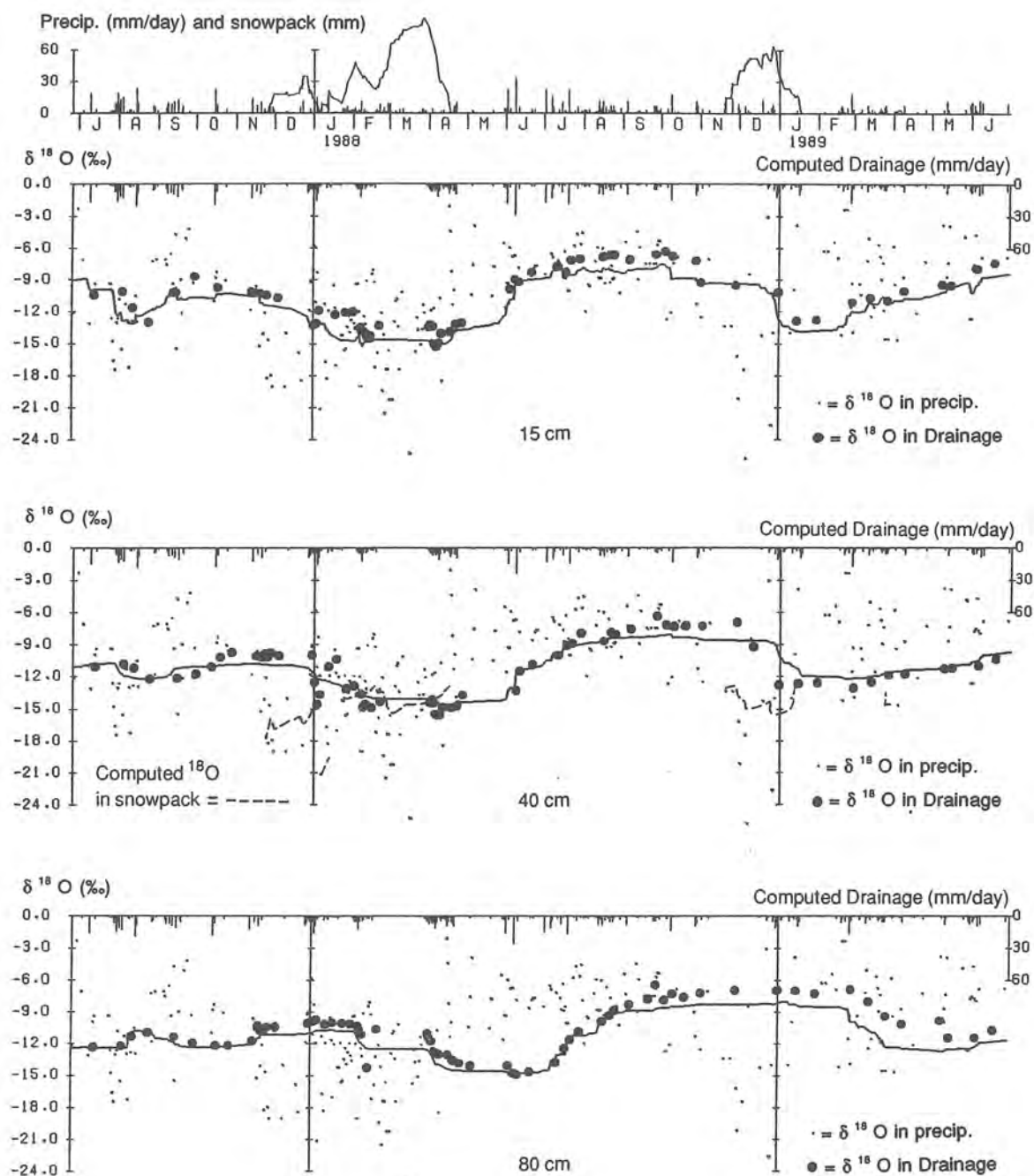


Figure 3.10. ^{18}O simulations for lysimeters 15 cm, 40 cm and 80 cm with the chosen parameter values, and model structures. Continuous curves = model calculated ^{18}O in drainage.

Table 3.2 shows the R^2_{O18} values for different combinations of flow patterns within each soil layer. According to the R^2_{O18} values the best choice concerning flow patterns was a combination of ideal mixing within the layers 0 - 15 cm and 15 - 40 cm, and piston flow thereafter. From the analysis, it is clear that ideal mixing was a better choice than piston flow for the upper 15 cm. However, as is shown by Figure 3.11, the R^2_{O18} values may in other cases be somewhat misleading. The figure shows that a model with ideal mixing in the upper 15 cm followed by piston flow was better than a model with ideal mixing in all three layers, although the R^2_{O18} values are very similar. Furthermore, according to the figure, a model with ideal mixing in the top 15 cm, followed by piston flow, gives almost as good results as those obtained using the chosen model structure.

Table 3.2. Model fit as measured by the criterion R^2_{O18} for different model structures.

Lysimeter	Depth	Flow pattern	R^2_{O18}
15 cm	0 - 15	Ideal mixing	0.80 (chosen)
	0 - 15	Piston flow	-0.16
40 cm	0 - 15	Ideal mixing	0.84 (chosen)
	15 - 40	Ideal mixing	
	0 - 15	Ideal mixing	0.71
	15 - 40	Piston flow	
80 cm	0 - 15	Ideal mixing	0.53
	15 - 40	Piston flow	
	40 - 80	Piston flow	
	0 - 15	Ideal mixing	0.70 (chosen)
	15 - 40	Ideal mixing	
	40 - 80	Piston flow	
	0 - 15	Ideal mixing	0.50
	15 - 40	Ideal mixing	
	40 - 80	Ideal mixing	

Transit time simulations

Simulations of average transit times for lysimeter 80 cm are presented in Figure 3.12. To give an idea of the uncertainty range in the simulation, two FC values were used according to the two alternative methods described above.

The transit time distributions for average flow conditions in lysimeter 80 cm are shown in Figure 3.13 for two different combinations of ideal mixing and piston flow. The two combinations gave almost the same goodness of fit for ^{18}O according to Figure 3.11. In this simulation the net inflow was set constant and equal to the average drainage for the period 25 June, 1987 - 30 June, 1989. Water transit times and particle flow velocities in the three lysimeters are summarized in Table 3.3.

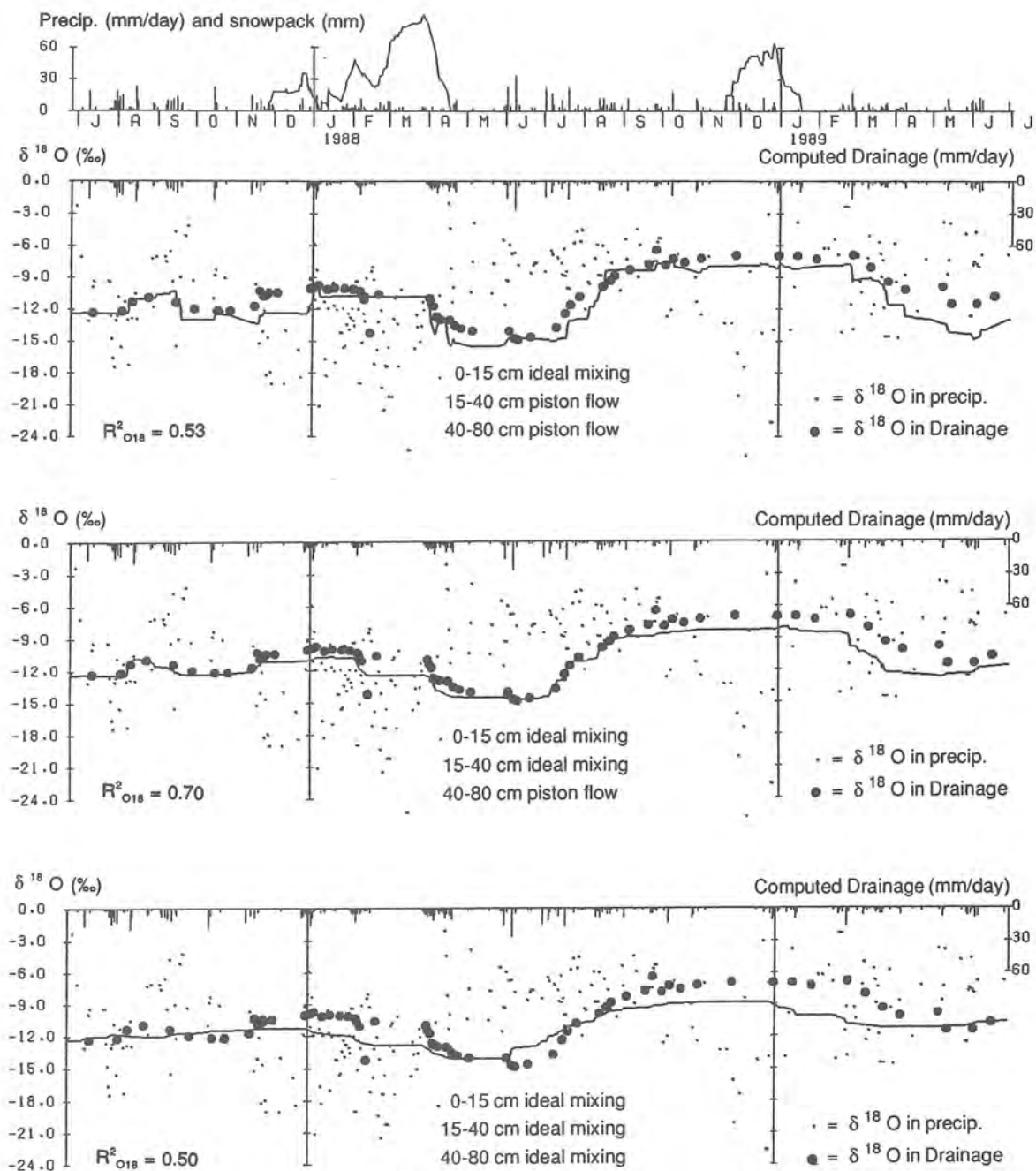


Figure 3.11. Sensitivity in the ^{18}O simulation for lysimeter 80 cm, to the choice of model structure. Continuous curves = model calculated ^{18}O in drainage.

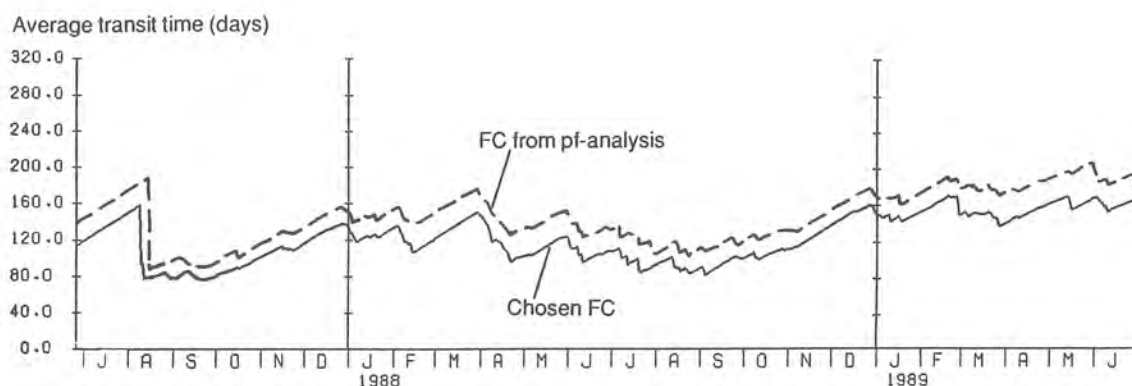


Figure 3.12. Simulations of average transit times for the drainage from lysimeter 80 cm. Chosen FC values and FC values established by pF-analysis are shown to give an idea of the uncertainty range in the simulation.

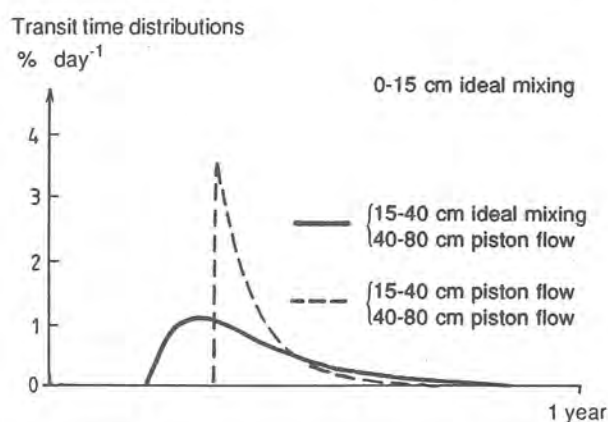


Figure 3.13. Transit time distributions simulated for lysimeter 80 cm. The results using two alternative combinations of flow models for the layers 15 - 40 cm and 40 - 80 cm are shown.

Table 3.3. Model results for three soil lysimeters at Stubbetorp, 87-06-25 - 89-06-30.

Lysimeters	Mean transit time (months)	Mean particle velocity (cm/day)
15 cm	1.0	0.5
40 cm	2.2	0.6
80 cm	4.0	0.7

Parameter sensitivity analysis

To identify uncertainties and the sensitivity to assumptions, a sensitivity analysis was performed. Table 3.4 shows the sensitivity of the ^{18}O simulation for lysimeter 15 cm to changes in the soil moisture routine. During each sensitivity run, all other assumptions and parameters were the same as in the reference run.

Table 3.4 shows that the ^{18}O -simulations were rather insensitive to the assumptions about β , LP, and the potential evapotranspiration. The reason is that the evapotranspiration was always low and the soil moisture was consequently relatively high.

The sensitivity of the ^{18}O fit to changes in FC is summarized in Figure 3.14. The figure shows that there is a wide range of FC values that give approximately the same agreement between computed and measured ^{18}O concentrations in the lysimeter drainage, at least for lysimeters 15 cm and 40 cm. Figure 3.15 shows the response in an ^{18}O simulation to a small change in the FC values. In the figure, the FC values are the ones that were established according to the two different methods described above.

Table 3.4. Sensitivity analysis for Lysimeter 15 cm for some assumptions in the soil moisture routine.

Sensitivity run	β	LP	Factor applied to pot. evaporation	$R^2_{^{18}\text{O}}$
Reference	1	1	0.15	0.80
Change in β	100	1	0.15	0.79
Change in LP	1	0	0.15	0.80
No evaporation	1	1	0.00	0.78

3.4.4 Discussion and conclusions

The model was despite its simplicity able to reproduce much of the variations of ^{18}O concentration in the lysimeter drainage, as well as to give reasonable drainage volume simulations.

The best simulation results were obtained when ideal mixing was chosen for the upper 15 cm soil layer, indicating a fairly exponential transit time distribution and large differences in particle velocities in this layer. In the next soil layer, 15 - 40 cm, the flow pattern was slightly more similar to that obtained in an ideally mixed reservoir than to that obtained by piston flow through the layer. In the deepest layer, 40 - 80 cm, piston flow was found to be a good approximation of the flow pattern. In Swedish till soils Saxena (1984) was able to trace soil moisture layers, depleted in ^{18}O , for two consecutive melt periods. This indicates that water at larger depths in the unsaturated zone percolates in a manner close to piston flow, pushing down older water to the ground-water zone. Similar results for till have been reported by Bengtsson *et al.* (1987) from studies with both natural ^{18}O and artificially injected tritium.

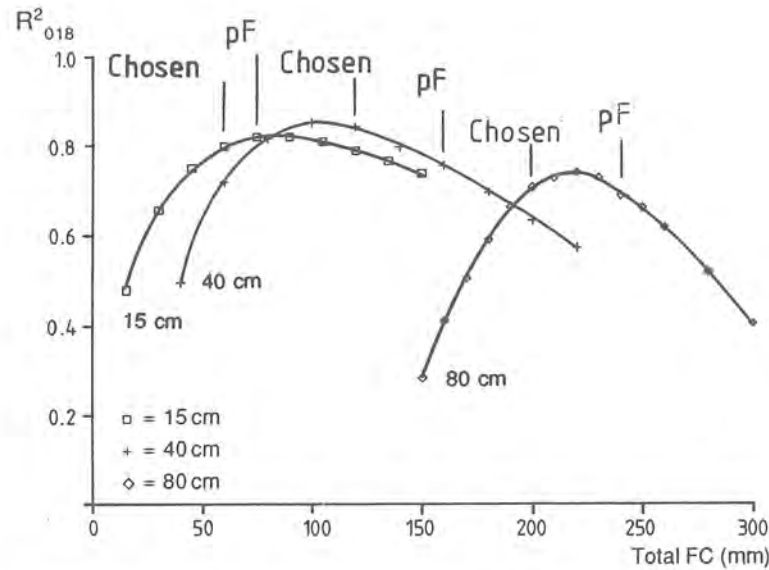


Figure 3.14. Sensitivity in R^2_{O18} to changes in the Field Capacity (FC) for lysimeters 15 cm, 40 cm, and 80 cm. Chosen FC values and FC values established by pF-analysis are shown.

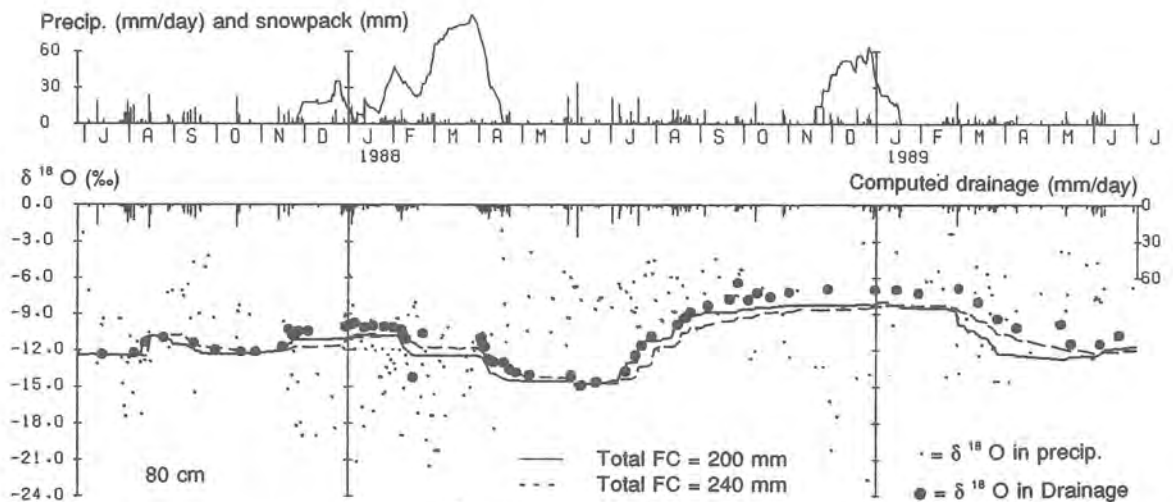


Figure 3.15. Sensitivity in the ^{18}O simulation for lysimeter 80 cm to a change in FC. Chosen FC values and FC values established by pF-analysis are shown.

In this application to soil lysimeters, the calculated water flow was rather insensitive to changes in parameter values. One reason was the low evapotranspiration, giving a water content close to field capacity. Under such conditions, the water outflow from the lysimeters reacts almost directly to the input, and the model performance for ^{18}O flow is largely dependent on the field capacity. This most crucial parameter was determined from field observations of total water content in the lysimeters determined by weighing. The only model calibration was therefore the reduction of the evapotranspiration to match the measured drainage volumes, and the choice between ideal mixing and piston flow for each layer.

The model tested in this study, assumed that all water in the soil participates in the flow. The field capacity values from weighing were relatively close to the best fit value according to the R^2_{O18} analysis, indicating that the possible existence of immobile water is less important. However, the sensitivity of the ^{18}O fit to changes in field capacity was rather small around the optimal value, at least for lysimeters 15 cm and 40 cm. Based on the ^{18}O signal and this model, the existence of immobile water can therefore not be completely rejected, although it appears to be less important.

The ^{18}O signal in the drainage was considerably damped compared to that of the precipitation, a feature that the model captured well. In general, the day to day scatter in the ^{18}O of precipitation could not be seen in the ^{18}O of the drainage. Preferential flow through macropores has been discussed by many authors, for example Beven and Germann (1982) and Andersson (1988). On a few occasions there were indications of rapid flow through the lysimeters, with apparently large portions of new water in the drainage from the lysimeters. A few simple routines were tried to simulate preferential flow. These tests did not improve the simulations. One possible source of errors is that the drainage was collected in large integrated samples, and that the macropore flow thereby became invisible. Preferential flow does, however, not appear to be a key process, in the modelling of water flux through the lysimeters at Stubbetorp.

The model disregards ^{18}O enrichment due to evaporation from the soil lysimeters. This may be the reason for the underestimation of ^{18}O in the drainage water on some occasions, particularly in the summer and autumn months.

Knowledge was gained about the lysimeter water content, drainage, and flow pattern. As a consequence, both the average transit times, the particle flow velocities, and the shape of the transit time distribution could be roughly estimated. The average transit times for the three lysimeters were estimated to be 1, 2, and 4 months for lysimeters 15 cm, 40 cm and 80 cm respectively. This corresponds to average particle velocities of 0.5-0.7 cm/day for the three lysimeters. These particle velocities, around 2 m/year, are similar to those found in sand profiles by Saxena (1984) and by Andersen and Sevel (1974). The accuracy of the calculated transit times and particle velocities depends greatly on the accuracy of the estimated field capacity. This parameter was determined by weighing the lysimeters, and was further checked by the R^2_{O18} analysis. The estimated transit times and particle velocities should therefore be rather close to the correct values.

The criterion R^2_{O18} was used as a measure of fit for the ^{18}O flux. The criterion was sometimes found to be misleading, and a visual inspection of the results seemed to be more reliable for judging the model performance. The difficulty to formulate a numerical criterion to describe the goodness of fit is a common experience also in runoff modelling.

Many authors have calculated long term average water transit times and reservoir volumes in catchments from the isotope signals in precipitation and runoff (e.g. Dincer *et al.*, 1970). By using a hydrological model for simulation of ^{18}O in the runoff, not only long term values, but also time series of the average transit times for the discharging water, could be simulated for catchments (Lindström *et al.*, 1990), and in the present study for lysimeters. Time series of average transit times for water in catchments were also simulated by Turner *et al.* (1987), using Kalman filtering technique for analysing the stable isotope shift between precipitation and streamflow.

The simulation for soil lysimeters from two different locations with different hydrological conditions within the Stubbetorp basin did not reveal any considerable spatial variation in the validity of the model assumptions. However, the field capacity was

slightly higher in the soil lysimeter taken from site 3, which resulted in longer transit times.

The piston flow concept is computationally much more complex than ideal mixing, particularly if the flow description of the hydrological model is to be linked with the full hydrochemical model. The two flow patterns give different shapes of the transit time distribution but with the same mean value. For long range predictions of groundwater acidification ideal mixing was assumed within each soil layer. It should be pointed out, however, that piston flow can be approximated by dividing the soil profile into thin layers with ideal mixing within each layer (see for example Himmelblau and Bischoff, 1968).

3.5 SOIL TEMPERATURES (P. Sandén)

Hydrochemical models that take the reaction rate (kinetics) into account rely on temperature as an important driving variable. The SAFE-model (described in Chapter 4) is of this type. It is a dynamic model, which needs dynamic input of soil temperatures for the different soil layers.

The simplest way to address the problem of soil temperature, is to use the long-term average air temperature. This does not take the seasonal variability into account. As the main variation in soil temperatures, at high latitudes, is between summer and winter conditions, a sinuous function could describe a significant portion of this variation. The most complete way to assess soil temperature, is to use a physically based dynamic model. In this type of model the heat flow is explicitly modelled, as well as freezing-thawing. This type of model needs many driving variables and physical parameters, which can either be measured or calibrated. In Section 3.7 there is a description of the SOIL model (Jansson and Halldin, 1979), which is a model of this type.

For the present study, it was important to use a dynamic model with a limited number of driving variables and parameters. The reason for this is, that the hydrochemical model should be used to assess long-term acidification of soil and groundwater on a regional scale. The heterogeneity of variables and parameters is considered a major problem in this respect. The chosen model structure is therefore in essence based on moving averages. It has one calibrated parameter, and rely upon air temperature as the driving variable. It also uses the snow pack, if available, to reduce the influence of air temperature during winter. The model is run with a daily time step. More than 95% of the temperature variation in the different soil layers is explained by the model. The results also show a reasonable damping and time-lag of the temperature wave.

3.5.1 Model structure

The model had to fulfill a number of requirements. As the hydrological and hydrochemical models are fairly complex and time consuming in the long-term simulations. The temperature model should increase the computation time as little as possible.

To be able to run the model on a regional scale measured parameters had to be avoided. Input data also had to be limited and easily attainable. The number of calibrated parameters should be kept at a minimum.

The physical properties of the soil will smooth and time-shift the air temperature variations. This can in the simplest way be modelled by moving averages. This will produce a smoothing and lag of the soil temperatures. The model can be written as:

$$T_{zi} = \frac{1}{n_z} T_i^{atm} + \frac{1}{n_z} T_{i-1}^{atm} + \dots + \frac{1}{n_z} T_{i-n_z}^{atm} \quad (3.7)$$

where T_i^{atm} = air temperature day i ,
 z = depth below soil surface.

The parameter n_z must be estimated for each soil depth of interest. This parameter is a function of depth and is calculated as:

$$n_z = \frac{D z}{\alpha - z} \quad (3.8)$$

where D = number of days in a year (365),
 α = empirical coefficient.

When z is equal to α the moving average is calculated with temperature data from a whole year. The value of n_z is rounded to the nearest integer. With this formulation we are left with one parameter that needs to be calibrated. This model structure was shown to be insufficient when tested against field measurements. The model could not produce reasonable time lag and damping with the same value of α . To handle this, the air temperature was damped by a function which does not give any lag. The air temperature T_i^{atm} in the moving average equations (3.7) is thus substituted by:

$$T_{zi}^{atm} = T_i^{atm} + (\bar{T} - T_i^{atm}) \frac{n_z}{D} \quad (3.9)$$

where $\bar{T}$ = long-term average annual air temperature.

By this formulation no extra parameters are needed.

To handle the isolating effect of snow cover the air temperature were corrected according to:

$$\begin{aligned} T^{cor} &= 0 & SP > 5mm \\ T^{cor} &= T^{atm} \cdot 0.1 & SP < 5mm, T^{atm} < 0 \\ T^{cor} &= T^{atm} & SP < 5mm, T^{atm} > 0 \end{aligned} \quad (3.10)$$

where SP = snow pack in mm water as calculated by the PULS-model (see Section 3.1).

3.5.2 Results

Soil temperature measurements from an unforested area in the Velen research basin were used to test the model. A short site description is given in Chapter 2. Figure 3.16 presents the result using observed air temperature. It is clearly shown that when the damping of the variation is correct, the time lag is too large.

In Figure 3.17 are shown the results from the chosen model, using equation (3.9). The simulation is significantly better and the resemblance between observed and simulated soil temperature is satisfactory. The model explains more than 95% of the observed variation at all three soil depths.

Figure 3.18 presents a sensitivity analysis regarding the parameter α . The model is rather insensitive to reasonable changes of this parameter.

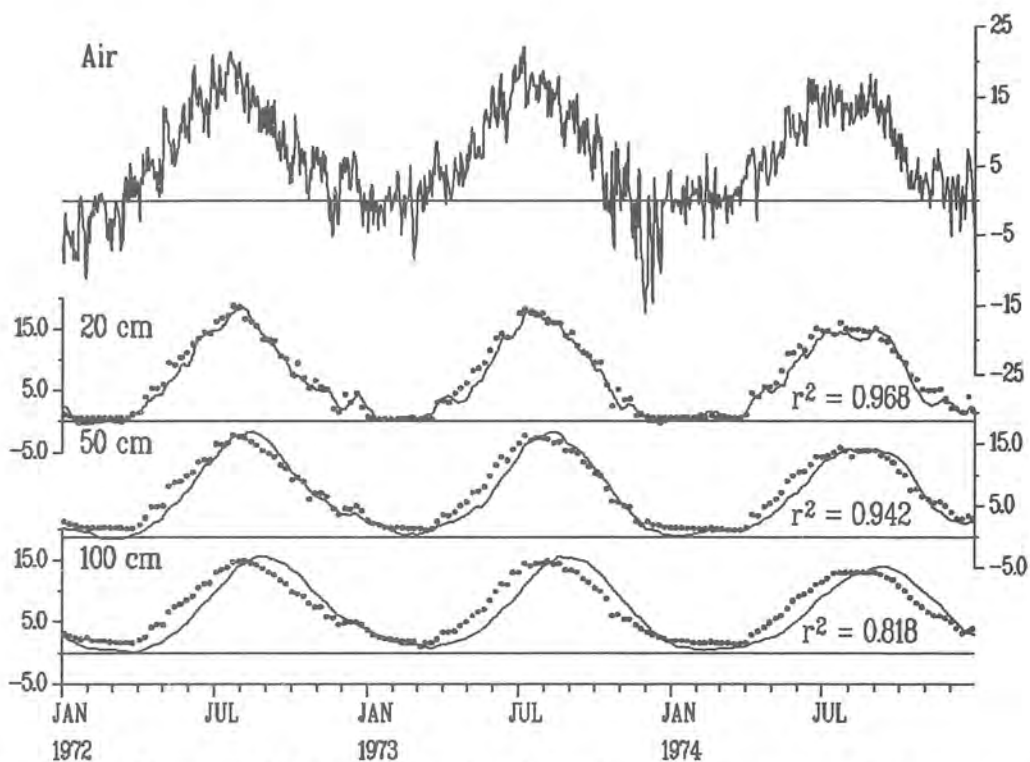


Figure 3.16. Observed (dots) and simulated (line) soil temperatures at three depth at Sjöängen 7. Moving averages without additional damping were used. The value for α is 6 meters.

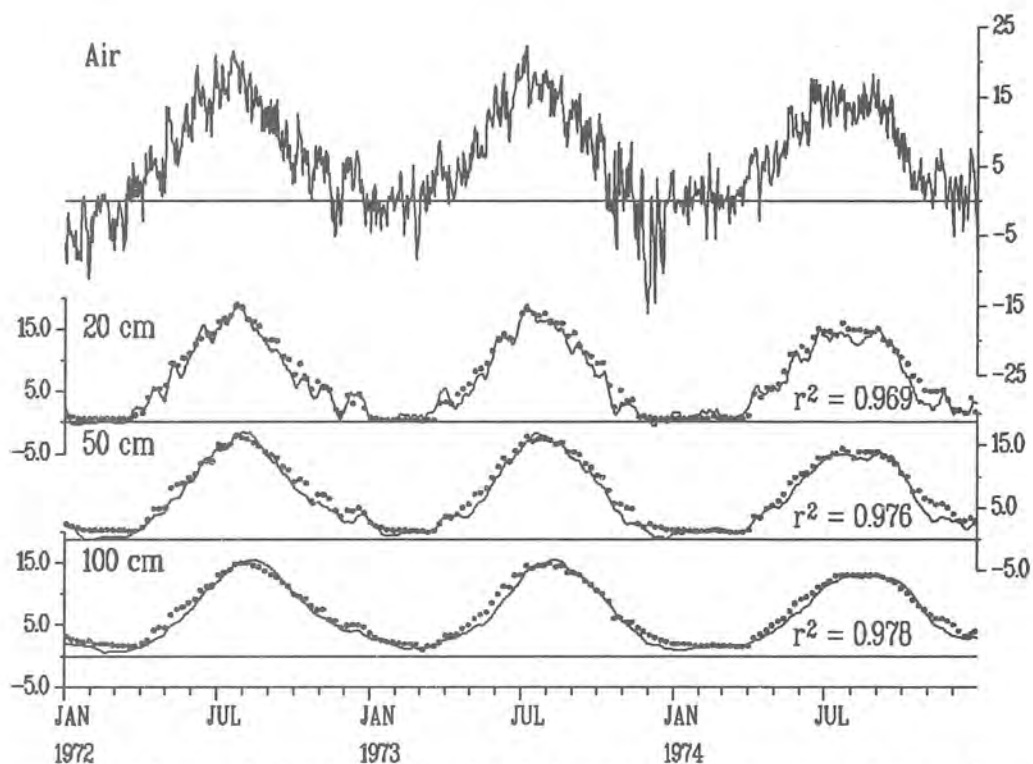


Figure 3.17. Observed (dots) and simulated (line) soil temperatures at three depths at Sjöängen 7. Moving average with extra damping were used. The value for α is 6 meters.

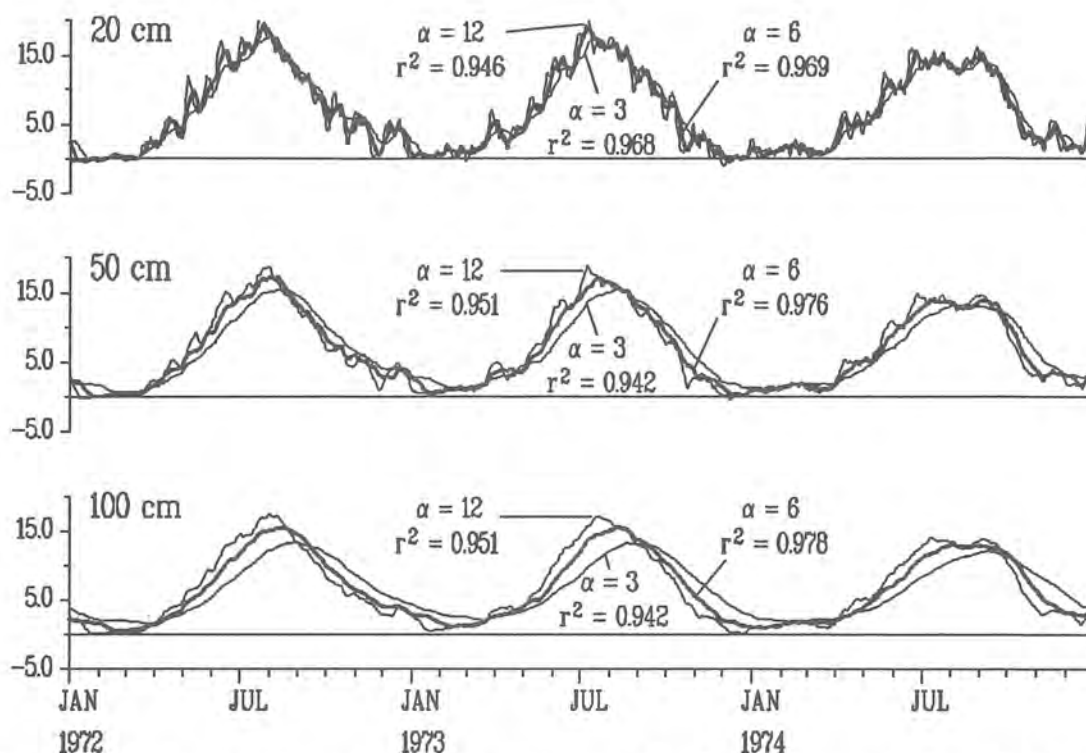


Figure 3.18. Sensitivity analysis of the parameter α . Three different values for α are used. The simulation is valid for the Velen station.

3.5.3 Discussion and conclusions

The large improvement in model performance by the introduction of air temperature damping justifies the increased complexity. This is especially true as no additional parameters are needed.

The relatively simple problem of soil temperature simulation is the main reason for the surprisingly good results obtained with this crude model. To further improve the model performance, the complexity would have to be increased largely. That could not be justified by the purpose of this modelling exercise. The model results should, however, only be trusted in the calibration range (20 - 100 cm). There is no information, so far, on how the model behaves compared with observations outside this range.

The sensitivity analysis performed on the hydrological model (see Chapter 5) suggests that the model does describe the soil temperature dynamics in a satisfactory way. Those results also show that the hydrochemical model is insensitive to fairly large errors in the α parameter. The problem of temperature damping by the forest is not considered in this section. The low sensitivity of the model to both damping and time lag errors, suggest that this could be overlooked.

For hydrochemical models, that need soil temperature data, the present model is sufficient in most cases. It is simple, with low demands on input data and parameters. The model also takes little amount of computational resources.

3.6 GROUNDWATER LEVELS (S. Bergström and P. Sandén)

Although the simulation of groundwater levels is not a primary objective of this project groundwater readings offer an opportunity to check that the modelled recharge is reasonable. Such studies have previously been carried out by use of the PULSE model both in Sweden and Finland (Bergström and Sandberg, 1983, Bergström *et al.*, 1990, Lemmelä and Tattari, 1988).

One main problem when modelling groundwater levels with these types of conceptual models is the transformation of groundwater storage to levels. This is made by the introduction of a coefficient representing the specific yield (effective porosity) of the aquifer. As the porosity of the aquifer is normally decreasing with depth the specific yield of the model is consequently varying as well. The details of this procedure is described by Bergström and Sandberg (1983).

The groundwater readings in Stubbetorp offered a good opportunity to study the models capability to reconstruct records of groundwater observations along a hill slope in the forest. This means that the readings represent both recharge and discharge areas. The tubes are numbered 21, 23, 26 and 30 from the upper parts to the lower parts of the slope.

During the modelling process it was found that the record length was not long enough for a split sample application with an independent test of the calibrated model. The entire record had to be used for model calibration.

3.6.1 Results

An important component of the calibration procedure is the assessment of different values of specific yield at different depths. These values are given in Table 3.5.

Table 3.5. Values of specific yield (effective porosity) used in the simulations of groundwater levels in the Stubbetorp basin.

Groundwater tube	Depth below surface (cm)	Specific yield (%)
21 and 23	0 - 20	23
	20 - 30	5
	30 - 110	4
	110 -	2
26 and 30	0 - 18	23
	18 - 50	5
	50 -	2

As there is a strong link between these and the parameters of the response routine in the model, the specific yields were checked against pF measurements of the different soil horizons. The values are within the range of the measured volume between pF=0 and

$pF=1$, which corresponds to the decrease in water storage when the groundwater level is lowered by 10 cm.

A full presentation of the simulations of groundwater levels in Stubbetorp is given in Figure 3.19.

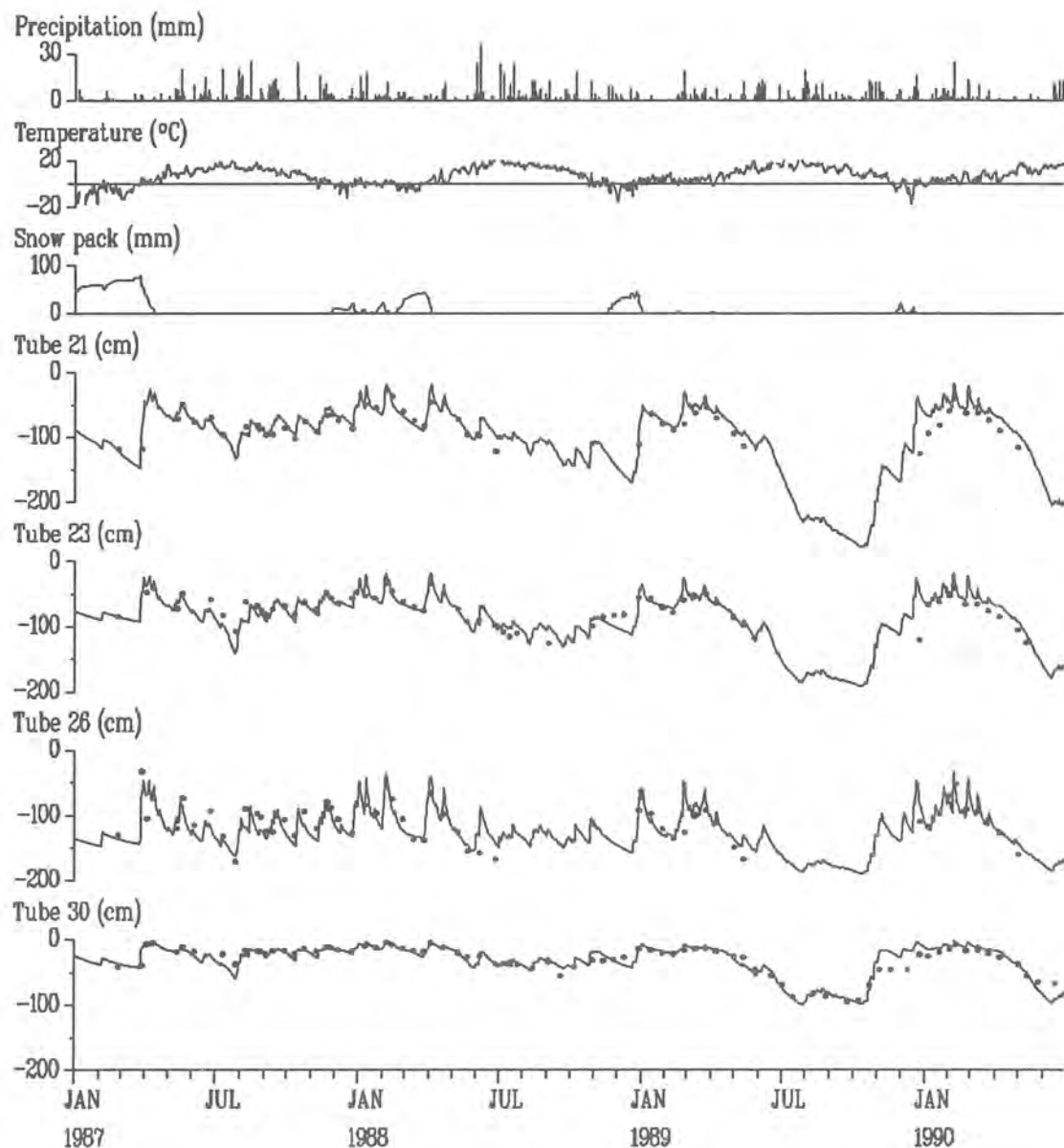


Figure 3.19. Pulse model simulations of groundwater levels (cm below surface) in the Stubbetorp basin (calibration period). Dots represents measurements.

3.6.2 Discussion and conclusions

The results in Figure 3.19 show that the model captures the general dynamics of the groundwater readings, although periods with errors in the order of 10 cm can be found. There were large differences in the hydrological situation during the simulation period.

The summers of 1989 and 1990 were dry and the winters were warm with short periods of snow cover. The three upper tubes dried out completely during these summers. The winter 1987 was characterized by a continuous snow cover, while 1988 were closer to the average hydrological regime. This wide range of variation is a fortunate situation which helps in the estimation of stable parameter values.

The introduction of specific yield into the model is a complication but it is necessary if we want to compare the simulation to observations. Its main drawback is that it increases the number of free parameters of the model and thus the risk for overparameterization.

This study and previous applications of the PULSE model to groundwater observations indicates that a model of this type has a reasonable description of the recharge process.

The fact that the record length, this time, did not allow for an independent test of the model is a source of uncertainty. Experience from similar applications to other data (e.g. Bergström and Sandberg, 1983) has, however, shown that the risk for overfit is not dramatic.

3.7 COMPARISON WITH THE SOIL MODEL (B. Espeby and P. Sandén)

In the previous sections various data sets have been used to test different parts of the PULSE model. In this section soil moisture simulations are compared between a physically based water and heat model SOIL (Jansson and Halldin, 1979) and the conceptual PULSE model using the same input data (precipitation, temperature, etc). The Velen research basin was selected because of the length of soil moisture records.

3.7.1 Model structure

The SOIL model was originally developed by Jansson and Halldin (1979) for the Swedish Coniferous Forest Project to be utilized for simulating water and heat flow in forest soils. For a detailed technical description of the model see Jansson and Halldin (1980). Recent development of the model is found in Jansson (1987).

The model describes water and heat transfer in a vertical soil profile using two partial differential equations solved by an explicit forward finite difference scheme (the Euler method). The two flow equations, for water and energy, describe the change in water content and temperature over time and depth. The unsaturated water flow is given by Darcy's law in combination with the continuity equation (Richards, 1931):

$$\frac{\partial \theta}{\partial t} = -\frac{\partial}{\partial z} \left(k_w(\theta) \left(\frac{\partial \psi_w}{\partial z} + 1 \right) \right) - s_w \quad (3.11)$$

where k_w is the hydraulic conductivity,
 θ is the water content,
 ψ_w is the soilwater tension,
 s_w is a sink-source term accounting for root water uptake.

The water retention characteristic is treated with the analytical form derived by Brooks and Corey (1964) not accounting for any hysteresis effects.

Heat flow is given by Fourier's law (Carslaw and Jaeger, 1959) in combination with the continuity equation:

$$\frac{\partial (CT)}{\partial t} - L_f \rho_i \frac{\partial \theta_i}{\partial t} = \frac{\partial}{\partial z} \left(k_h \frac{\partial T}{\partial z} \right) - C_w \frac{\partial (T_w q)}{\partial z} - s_h \quad (3.12)$$

where C is the heat capacity of the soil,
 C_w is the heat capacity of the water,
 q is the flow of water,
 T_w is the temperature of the water,
 k_h is the heat conductivity.

The left hand term describes the change in sensible heat, CT , and the latent heat of freezing, L_f , to ice, θ_i . The first term on the right hand side describes the divergence of

the heat flow, the second term the convective heat flow and the third term, s_h , describes a sink-source term to accounting for heat extraction.

A maximum of 22 compartments of soil layers can be used in the model (Figure 3.20). The appropriate thicknesses of the compartments are chosen to account for the morphological structure of the soil and the numerical requirements of the Euler method and is thus chosen to increase with depth, i. e., the smallest compartments are needed near the soil surface to account for the more pronounced variations in soil properties and state variables. Soil properties and state variables are calculated linearly between midpoints of consecutive model compartments.

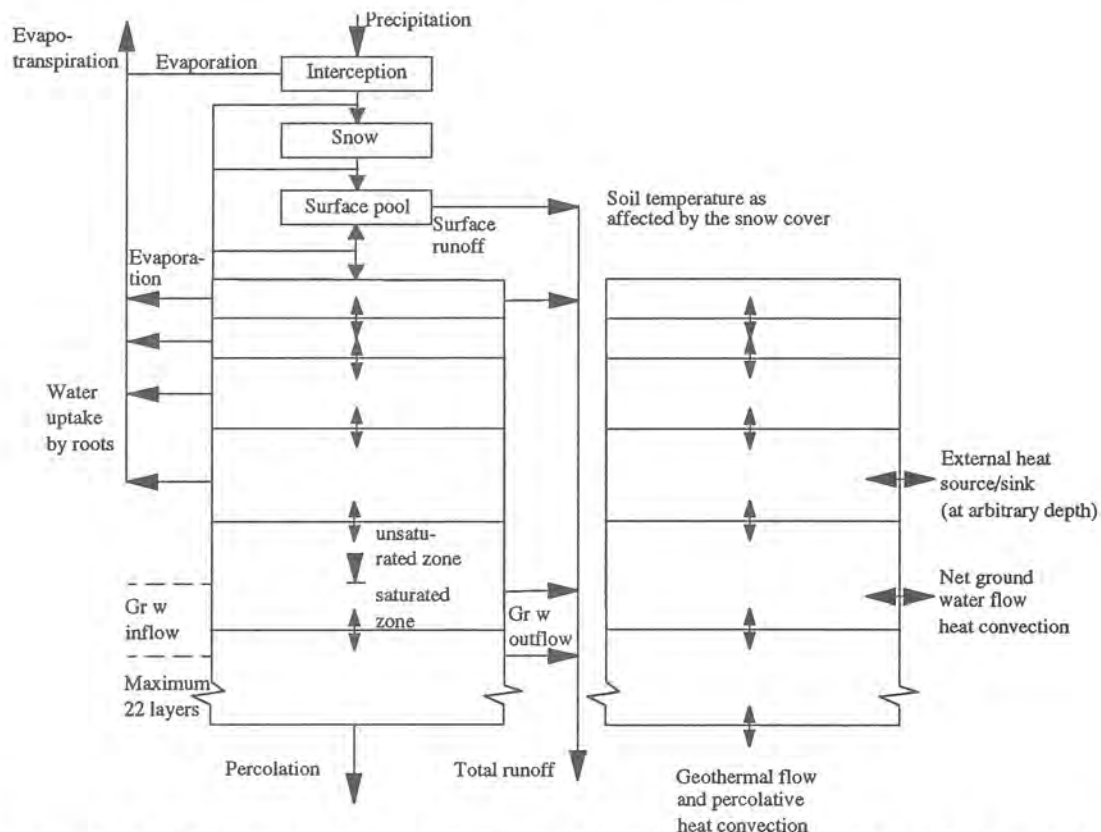


Figure 3.20. The structure of the SOIL-model (from Jansson and Gustafsson, 1987).

Appropriate upper boundary conditions of the model are given by submodels for precipitation, snow and frost dynamics, interception storage and the evapotranspiration. Daily amounts of snow melt are calculated from a heat sum, a factor accounting for the influence of solar radiation and the surface heat flow (Jansson and Halldin, 1980). The lower boundary condition in the water flow equation can be considered as horizontal groundwater outflow, which may be affected by a drainage level. Conceptually this can be a drainage pipe in a field or a sloping groundwater table. The lower boundary can also be represented by a free drainage to an infinite groundwater body. The position of the groundwater table is calculated as the level where soil moisture tension is nil (cf. Johansson, 1986). Initial values of tensions, and the location of the groundwater table are used to calculate initial storage of water. An initial equilibrium tension profile above the groundwater table is assumed (i.e. no vertical flow). From each one of the model

compartments, free water exceeding a given retention threshold is lost to infiltration either vertically to an infinite groundwater table or horizontally if the groundwater table is located in the compartment immediately below the compartment with excess water. A geothermal heat flow or a variable temperature is used as the lower energy boundary.

3.7.2 Parameter estimation

The database used for this comparison is taken from the Velen research basin, which is described in Chapter 2. Transpiration parameters, leaf area index etc have been taken according to the measurements performed in the Velen catchment during the IHD-period (Bringfeldt, 1982, Bringfeldt and Lindroth, 1987). The draining gradient was given a value close to the slope gradient at the Sjöängen station, i.e. approximately 1.6° slope (Andersson, 1988).

The water retention characteristics (see Chapter 2) were fitted to an analytical expression of the water content/tension relation proposed by Brooks and Corey (1964) in the suction range between 0.10 - 159 m of water. The three soil layers, for which data were available, were complemented with two horizons to account for surface and deeper soil characteristics, one organic surface horizon (0-6 cm) and one denser till horizon (100-200 cm). The shapes of these two curves are based on comparisons with other soil profiles of similar conditions found in a data base at the Dept. of Soil Sciences at the Swedish University of Agricultural (Jansson, 1989). The saturated hydraulic conductivity had not been determined for the samples and consequently had to be estimated from the literature (Cozzarelli *et al.*, 1987; Espeby, 1990) taking into account the relationship between drainable porosity and saturated hydraulic conductivity (Ahuja *et al.*, 1984; Espeby, 1990).

Unsaturated hydraulic conductivities were determined by the analytical expression of Mualem (1976), modified by Jansson and Thoms-Järpe (1986) to account for the contribution by macropores, and based on the expression of effective saturation defined by Brooks and Corey (1964).

The model soil profile was divided into ten compartments to account for the morphological structure and the numerical requirements of the finite difference technique according to Table 3.6 and Figure 3.21 (cf. Chapter 2 Figure 2.9). The estimated root distribution in the soil profile is also noted.

In-situ measured air temperatures and precipitation were used as driving variables together with estimated values of relative air humidity, wind speed, and cloudiness.

Seven years (1967-1974) of water content data and four years of groundwater level data (1967-1972) from Sjöängen station 7 were used to calibrate and test the model. Water content measurements from 10, 20, and 30 cm depths were averaged and compared with simulation results into one layer in accordance with the model profile layer 6-30 cm. Measurements from 40, 50, and 60 cm, 70 and 80 cm, and 90 and 100 cm depths were averaged into layers 30-60 cm, 60-80 cm, and 80-100 cm respectively.

First the model was tested and calibrated for the period 1967-1968. After this calibration, the model was run for the whole seven year period. The groundwater level was used to balance the model at the lower boundary and several root distributions were tested to find the best fit (see Table 3.6).

Table 3.6. Model soil profile (numbers in parentheses are estimated values)

Soil depth (cm)	Soil designation	Model compartment (cm)	Roots (%)	pF=0.00 (porosity)	pF=0.07	pF=2.00 (FC)	pF=4.50 (WP)	$K_s(\text{tot})$ ($\times 10^{-6} \text{ m s}^{-1}$)
0-6	Organic (O)	0-6	20	(90)	(-)	(-)	(7)	416.7
6-30	Eluvium (E)	6-18	20	48.0	43.9	33.7	7.0	120.0
		18-30	20	48.0	43.9	33.7	7.0	120.0
30-60	Illuvium (B)	30-45	15	49.6	39.4	31.8	6.9	41.7
		45-60	10	49.6	39.4	31.8	6.9	41.7
60-200	Parent (C)	60-80	10	34.6	27.6	22.5	3.4	0.85
		80-100	5	34.6	27.6	22.5	3.4	0.85
		100-125		(20)	(-)	(-)	(5)	0.16
		125-150		(20)	(-)	(-)	(5)	0.16
		150-200		(20)	(-)	(-)	(5)	0.16

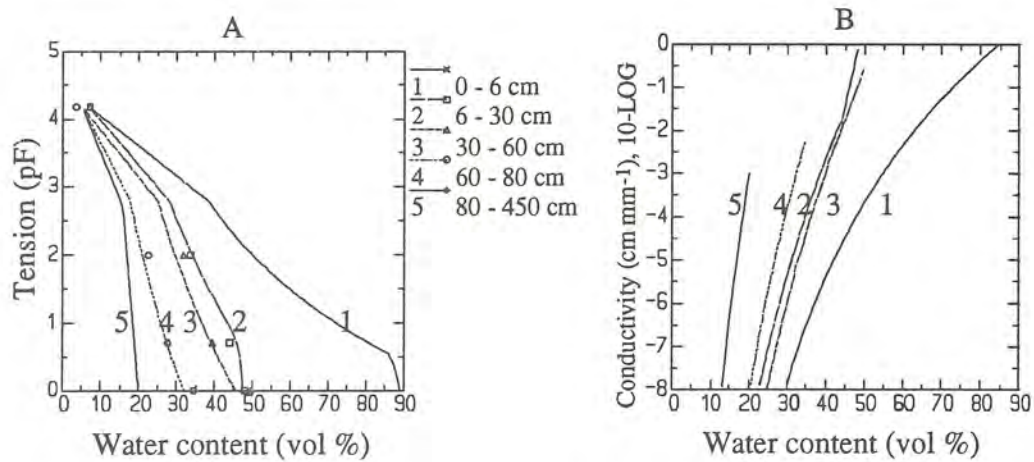


Figure 3.21. A. Water retention properties. B. Estimated unsaturated hydraulic conductivity (K_s) versus water content. Horizons 1 and 5 from the literature. Dots = measured values.

3.7.3 Results

Figure 3.22 shows a simulation of groundwater levels. There is fairly good agreement between simulated and observed groundwater levels, if the winter 1969/1970 and the

summer 1970 are disregarded. Observations close to the bottom of the tube (about 1.3 m) might be questionable.

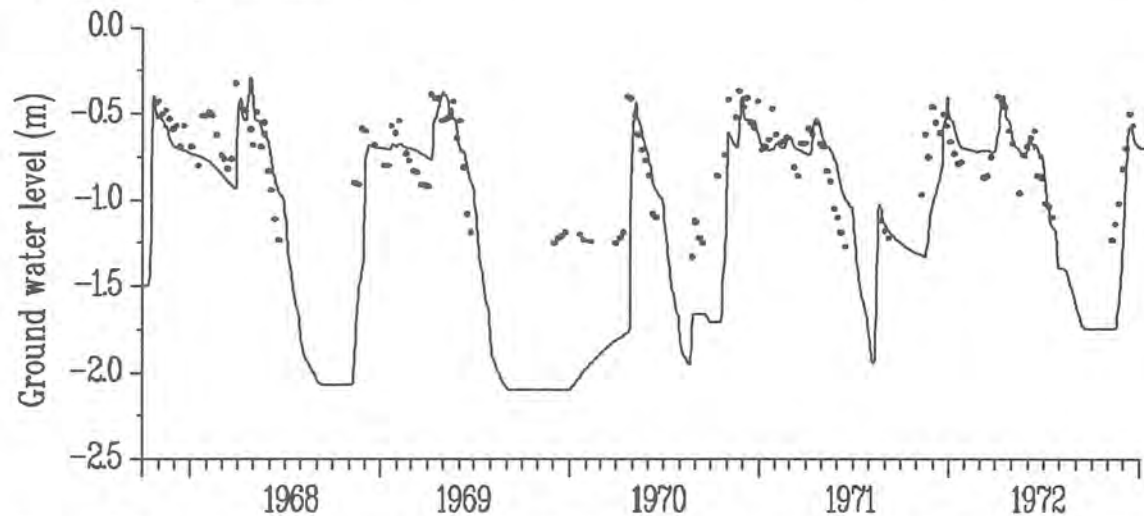


Figure 3.22. Measured groundwater levels in forest (m below ground surface) (1967-1972) in relation to the groundwater levels simulated with the SOIL model (1967-1972).

The soil moisture as simulated by SOIL and PULSE are presented in Figure 3.23. During the winter 1970/1971 a drift occurred in the observed water content, which caused too high readings (T. Milanov, pers comm.). This is seen in the presentation of the 80 cm level. The drift seems to be corrected in the summer of 1972, but a new drift occurs in the beginning of 1974. Overall, both models capture the soil moisture dynamics, although some errors are substantial. The SOIL model gives a higher variation and show high peaks during snow melt, especially at the 45 cm level, which are not found in the observations.

3.7.4 Discussion and conclusions

The two models do portray the main dynamics of the soil moisture variation, although some errors are considerable. The SOIL model have larger short term variations and gives sharp peaks in soil moisture during periods with high soil moisture, especially during snow melt. This is due to the groundwater table which reaches up to the 45 cm level at these events.

In this comparison the same model compartments have been used in both SOIL and PULSE. The same driving variables (precipitation and air temperature) have been used in both models. In addition SOIL uses average values for relative humidity, cloudiness, and wind speed when calculating the evaporation.

The soil moisture routine in the PULSE model is not calibrated. Calibration of the SOIL model is mainly done by varying the root distribution and other evapotranspiration effective parameters, i.e. surface resistance.

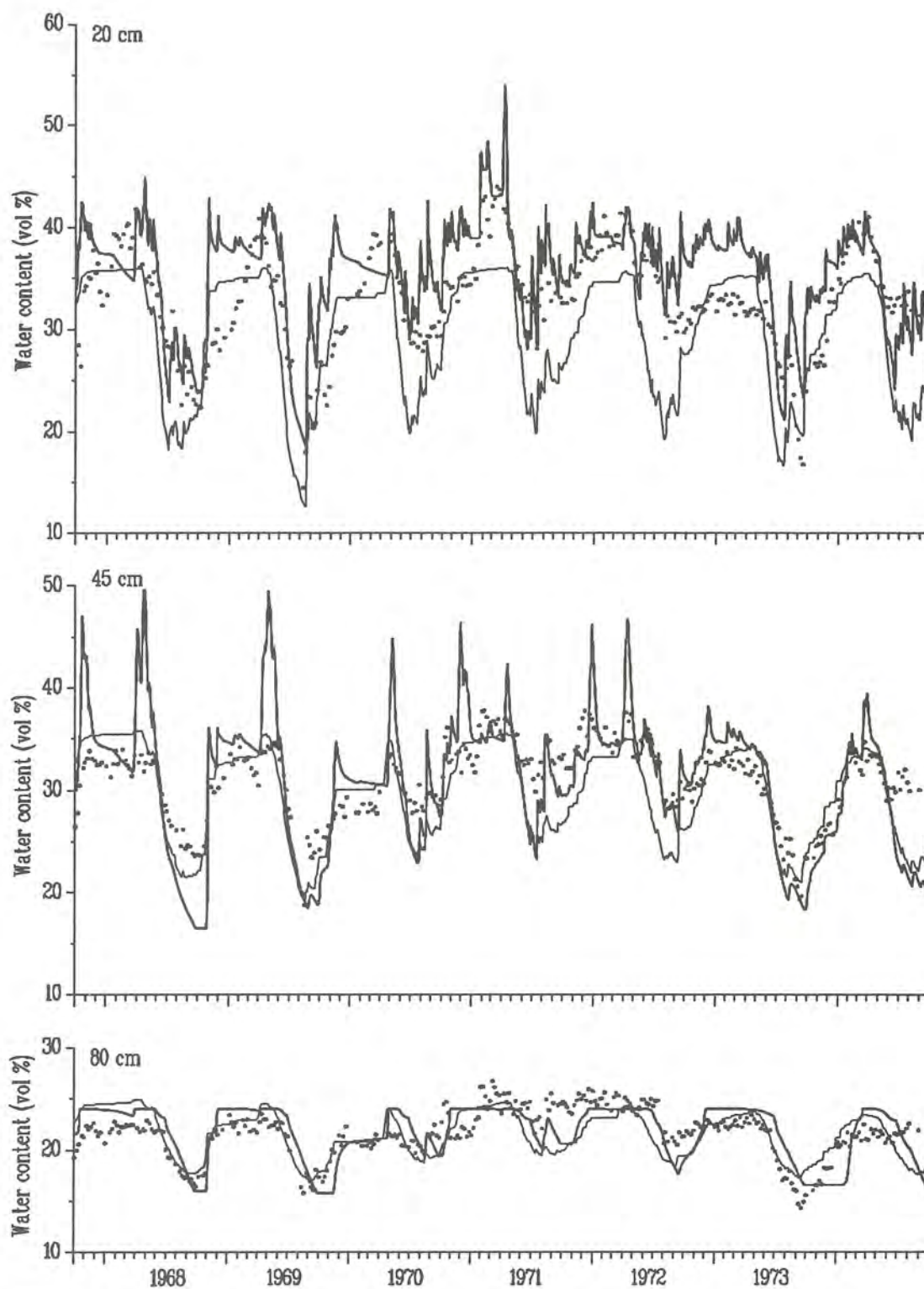


Figure 3.23. Measured (dots), SOIL simulated (thick line) and PULSE simulated (thin line) water content at three depths for the period 1967-10-01 - 1974-09-30.

The SOIL model calculates the water content in relation to the simulated tensions. If freezing conditions occur the model will separate the total amount of water in one liquid and one solid (frozen) part. To compare simulation results from SOIL with observations the two phases of water are added to produce total water content (Figure 3.23).

It is important to note that the SOIL model simulations are based on several uncertainties. Firstly, there is an uncertainty concerning the root distribution and the actual time when the roots in different parts of the profile are active. These uncertainties strongly effects the computed soil moisture conditions in the upper part of the profile. Secondly, the saturated hydraulic conductivities are based on other soil profiles from similar geological conditions, since no analyses of saturated hydraulic conductivity have been made at Sjöängen. Thirdly, water retention properties for the surface layer and the bottom layer of the soil profile were also transferred from other similar geological conditions. In till it has been shown that the soil physical properties of the bottom layer influence much of storage and flow of water in the upper part of the profile (Espeby, 1989). These facts may explain some of the deviations from observed levels.

During 1971/1972 the wrong scaler was used with the neutron probe at the Sjöängen station (T. Milanov, pers. comm.). This resulted in a shift upwards in the soil moisture readings. The dynamics should, however, be correct.

The SOIL model is a good tool for basic research on soil water processes. Having the objective of this work in mind, however, the conclusion must be that the PULSE model, with its limited data demand and ease of handling, is better suited for the basinwide and regionalized long term simulations for acidification forecasts.

3.8 LONG TERM HYDROLOGICAL SIMULATIONS (M. Gardelin)

The main objective of the hydrological modelling was to provide long term simulations of soil temperature, moisture and water flux of the different soil horizons for the hydrochemical submodel. Such simulations were carried out for three of the project's research sites (Stubbetorp, Masbyn and Risfallet). A summary of the input data, simulation periods and significant parameter values is given in Table 3.7.

Table 3.7. Input data and parameter values for the long term hydrological simulations.

	Stubbe- torp	Masbyn young forest	Masbyn mature forest	Risfallet
Simulation period	1961-01-01 - 1990-07-31	1966-01-01 - 1990-06-30	1966-01-01 - 1990-06-30	1965-01-01 - 1990-06-30
Precipitation station	Simonstorp	Grängesberg	Grängesberg	Folkärna/ Hedemora
Temperature station	Simonstorp	Ställdalen	Ställdalen	Folkärna
Soil horizons (cm)				
O	8	12	12	8
E	8	21	21	8
B	62	22	22	60
C	22	45	45	24
Average depth to groundwater table (cm)	100	50	100	250
Parameter CPREC	0.80	1.04	0.95	0.80
Parameter FC (mm)				
O	22	55	50	22
E	19	97	84	21
B	143	77	68	165
C	88	134	107	52
Σ FC	272	363	309	260
Parameter WP (mm)				
O	2	7	7	2
E	2	4	4	1
B	15	8	8	33
C	5	22	22	18
Σ WP	24	41	41	54

Two different simulations were made for Masbyn. One simulation represents mature forest conditions and the other represents the young forest approximately 10 years after clear-cutting.

The simulation periods were determined by the availability of good climatological data. As long simulation periods as possible were desirable. The homogeneity of the

climatological data series were tested with the double-mass method, where climatological data from the selected stations were compared with several adjacent stations.

Figure 3.24 to Figure 3.28 show parts of the long term simulations for the Stubbetorp basin. Simulated soil moisture content in the four soil layers are shown in Figure 3.24. Figure 3.25, Figure 3.26, and Figure 3.27 show evapotranspiration, water flux, and residence time for the different soil layers. In Figure 3.28 are shown simulated soil temperatures at the different soil layers.

Examples from the soil moisture simulations at Masbyn and Risfallet are shown in Section 3.3.

The results in Section 3.4 indicates that ideal mixing is a fair description of water flow in the soil as long as the horizons are less than 25 cm thick. One horizon in each basin does not fulfill this requirement (Table 3.7). However, the chemical model does not explicitly consider the transit time and ideal mixing gives the same mean transit time as piston flow. It was, therefore, concluded that the improvement from using piston flow did not justify the increase in computational effort.

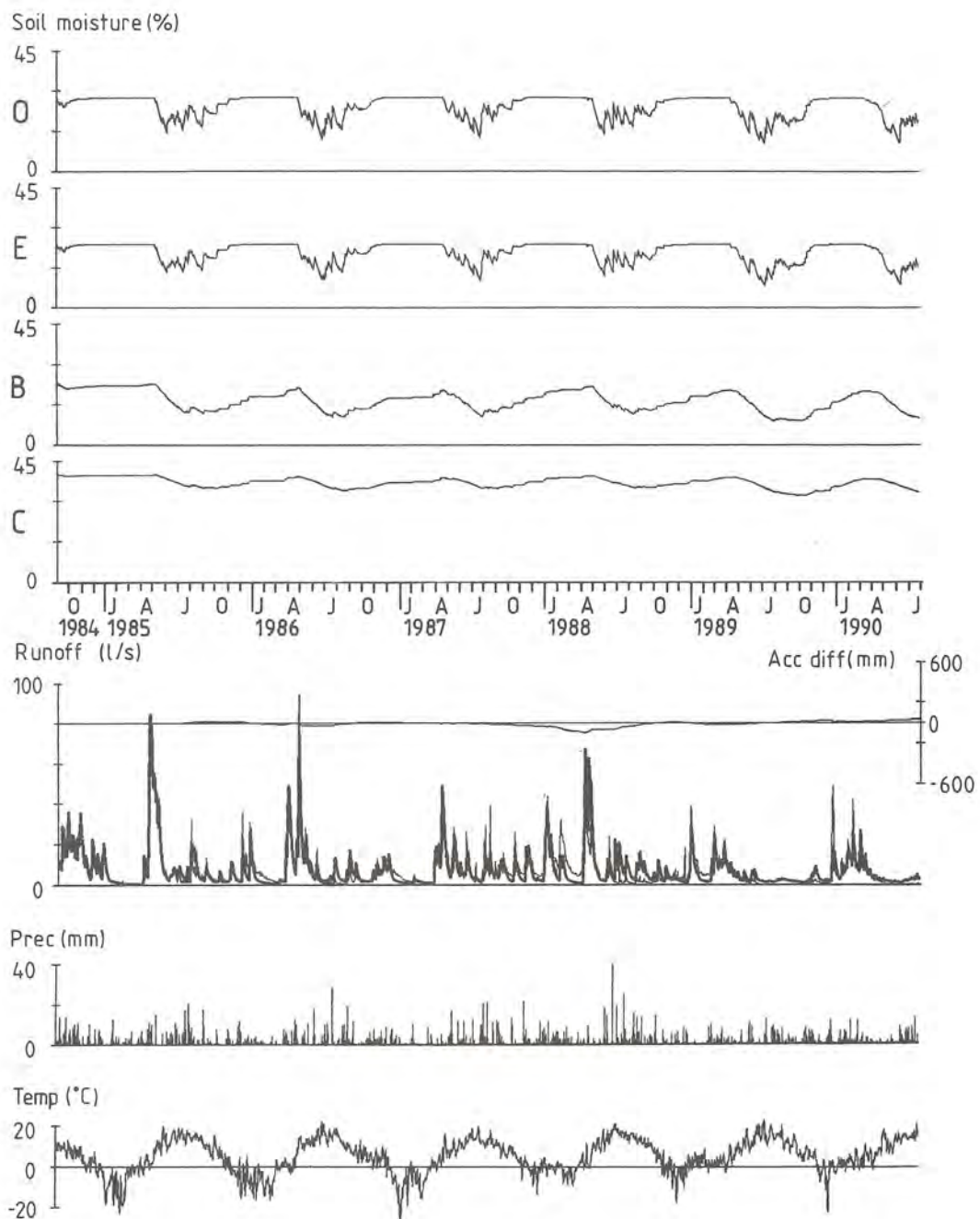


Figure 3.24. Model simulation of soil moisture content in 4 soil layers at Stubbetorp. Below: Simulation (thick line) and measurement (thin line) of runoff, together with accumulated difference between runoff simulation and measurement. The model's daily input data of precipitation and mean air temperature are shown at the bottom.

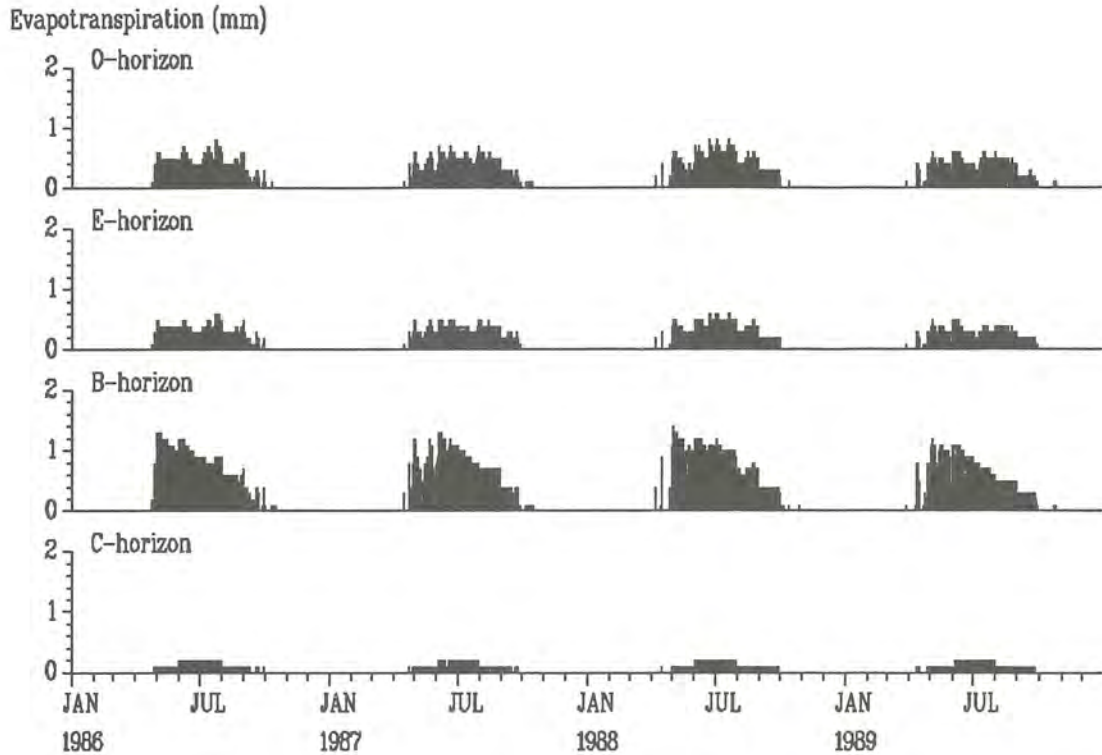


Figure 3.25. Simulated evapotranspiration from the different soil horizons at Stubbetorp 1986-1989.

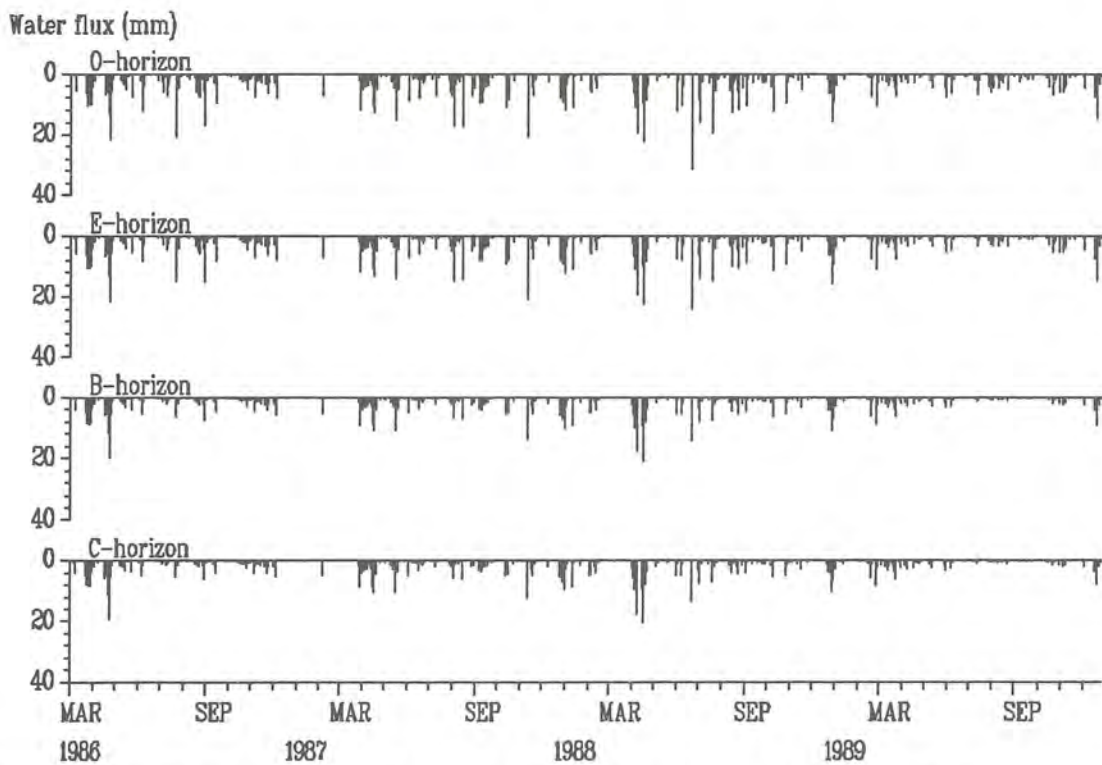


Figure 3.26. Simulated water flux out of the different soil horizons at Stubbetorp 1986-1989.

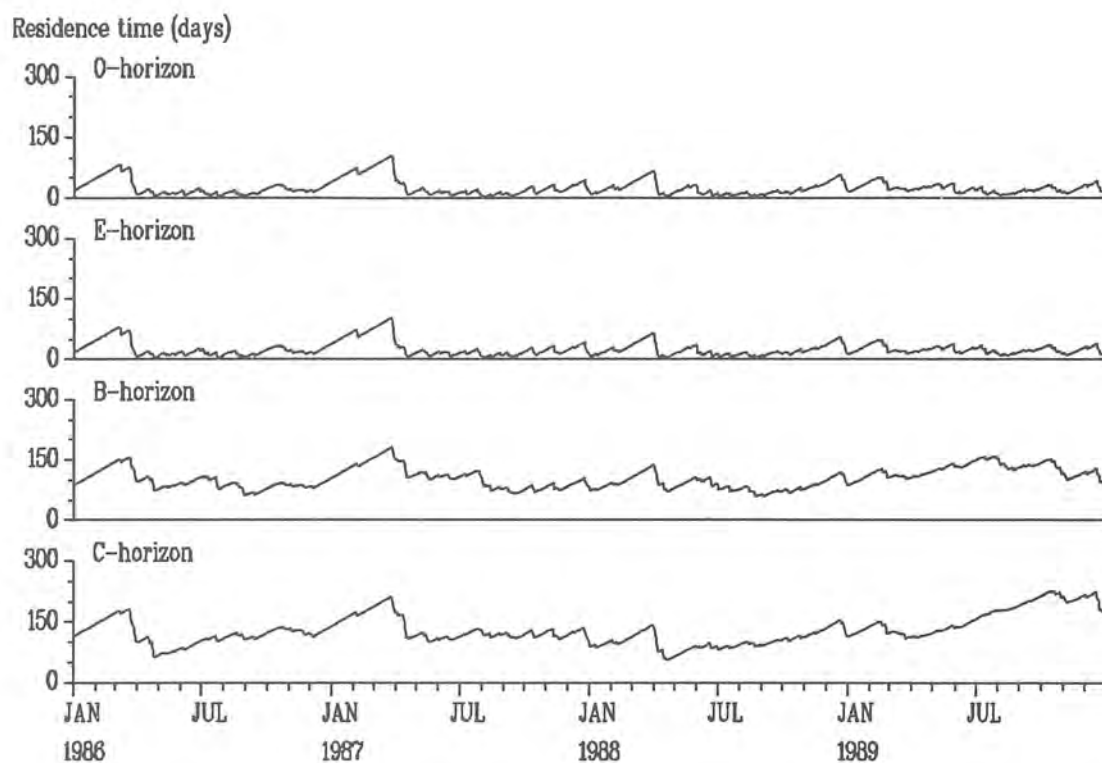


Figure 3.27. Simulated residence time for the outflow water from the different soil horizons at Stubbetorp 1986-1989.

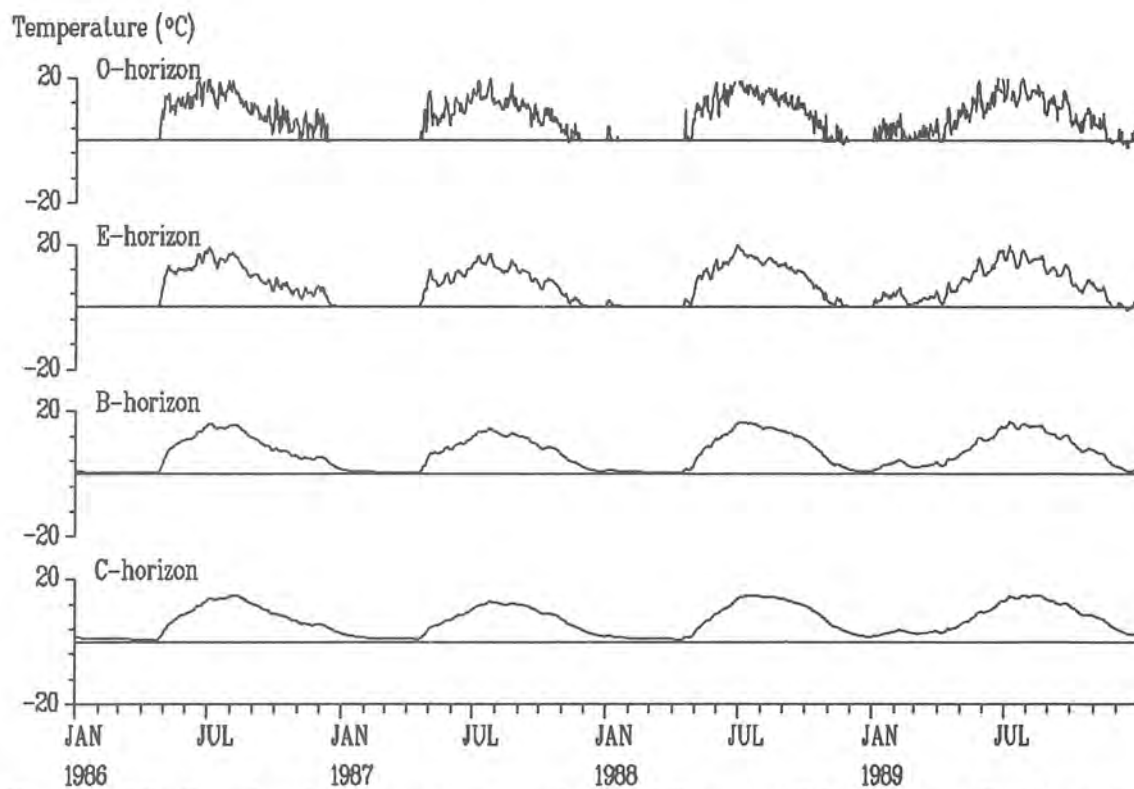


Figure 3.28. Simulated soil temperatures in the different soil horizons at Stubbetorp 1986-1989.

4 HYDROCHEMICAL MODELLING

(P. Warfvinge and H. Sverdrup)

Several studies have dealt with models to describe the chemical impact of acid deposition on soils. Although there appears to be a general consensus among model developers which processes are important to explain experimental observations, the models differ in the way they are expressed mathematically [de Vries *et al.*, 1989]. This does, in turn, reflect different opinions on how these processes act and interact, but also that the models are designed to operate with different time scales and address different questions.

For the purpose of modelling groundwater quality as affected by acidification, modelling efforts have been carried out on different levels, at the process level, and at the conceptual and implementation level integrating different processes into a larger structure. Modeling is also used as a term for applying models to individual sites. Here, the term modeling is used in all three meanings.

In Section 4.2, we describe how the different models developed within the project are linked together.

Section 4.3 gives the details on the mathematical formulations in the two hydrochemical models SAFE and PROFILE. SAFE (Soil Acidification in Forest Ecosystems) is the model that calculates the soil and solution chemistry as a function of time. PROFILE calculates the steady-state conditions in a soil PROFILE, subject to a certain acid load and uptake rate. In particular, the section includes the concepts for the kinetics of the weathering reactions, and the mass transfer approach taken to describe cation exchange reactions. The values of different built-in chemical coefficients are given, such as solution equilibrium coefficients and rate coefficients for the weathering reactions. While the PROFILE and SAFE are based on the same principles and equations, the steady-state constraint that applies to PROFILE makes the solution methods different. Section 4.3 shows how the equations are solved for the two cases.

Section 4.4 includes some experience from the model development process regarding numerical methods used to solve the equations in the models.

Section 4.5 includes examples of applications of the chemical models to data. The PROFILE model was tested against soil water data from Gårdsjön in Sweden. The performance of the weathering submodel is demonstrated since mineral weathering is a key mechanism for the long term neutralization of acid inputs. Calculated rates are compared with data from several catchments, among them are Risfallet and Svartberget. The SAFE model is tested versus measured decrease in exchangeable base cations observed at three sites in southern Sweden.

4.1 MODEL STRUCTURE

In order to calculate the time series for groundwater chemistry, a number of different models have been used. The final step in the process is to run SAFE which calculates key quantities such as soil solution composition and base saturation as a function of time. This is illustrated in Figure 4.1.

The SAFE model is based on certain principles and chemical and physical processes, as described in this section. These are expressed in mathematical terms,

and finally forms a computer code and an application. Before the calculations are initiated, a lot of data must be made available to SAFE. Some of these varies with time, some are constant throughout the simulation period. Others still are initial conditions, used only during the first time step of the calculation.

The time series data needed fall into three categories:

- Hydrological data, such as water fluxes, soil moisture content and soil temperature. This data are supplied by the hydrological model, PULSE. This model is described in Chapter 3.
- Biomass uptake data, specifies the annual removal or supply of base cations and nitrogen to the soil profile. These data are based on the stand characteristics of each site.
- Atmospheric deposition data, hindcast and forecast.

Basically, the soil data include all parameters that go into the equations of the model, and that do not change in time. They include:

- Soil morphology, expressed in terms of number of soil horizons and thickness of each layer.
- Capacity and intensity factors, including cation exchange capacity, soil texture, mineralogy and CO₂ pressure.
- Constants such as equilibrium coefficient, kinetic and mass transfer rate constants.

Finally, the initial conditions for all soil state variables, such as ANC (Acid Neutralizing Capacity) and base cation concentration, must be specified. These are calculated with a separate routine PROFILE. PROFILE is based on the same principles and includes the same processes as SAFE, but calculates steady-state conditions, rather than a time series. PROFILE does therefore need only one single value for all time dependent input. For initial conditions, this should be the value for the first year of the simulation. The starting year should therefore be taken at a time when the soil system is in equilibrium with external influential factors, such as deposition and uptake. With the exception of cation exchange parameters, the need for different soil chemistry parameters are the same for PROFILE and SAFE.

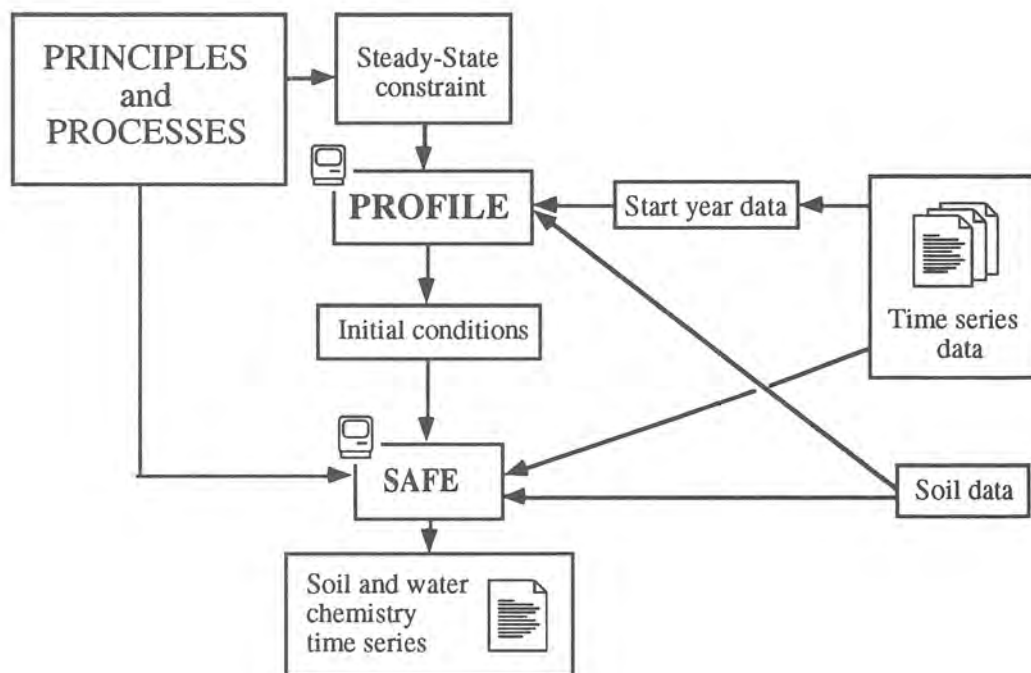


Figure 4.1: Flow sheet illustrating major model components and information flow. The hydrochemical modeling is based on a series of principles and processes. To define these are the most important part of the modeling work, the remaining part is a technological exercise to solve the equations that are the mathematical representation of the chemical principles.

4.2 BASIC PRINCIPLES OF THE MODEL

Since SAFE and PROFILE is designed to calculate the chemistry of soils, ground-water recharge as well as surface waters, the model operates with different system boundaries. The smallest subsystem is a soil horizon as shown in the upper part of Figure 4.2. The soil profile itself is divided into compartments corresponding to the natural soil stratification. Within each of these the mixing of the liquid phase is assumed to correspond to a mixed bucket model. It is a formal requirement that each compartment in the model is chemically isotropic, and the division of the soil profile according to the horizons is the largest unit that at least to some extent can fulfill this requirement.

In each of the soil compartments, a number of chemical reactions take place, represented either by equilibrium relationships or kinetic equations. The reaction systems considered are soil solution equilibrium reactions, silicate weathering, uptake of nutrient cations, NO_3^- and NH_4^+ , nitrification and cation exchange reactions (Figure 4.2). All processes interact via the soil solution. For instance, there is no mechanism for roots to strip nutrients directly from weathering materials.

These reactions only represent a selection of chemical processes in the soil environment. Consequently a number of general assumptions have been made. The most important of these are:

- Each soil compartment is chemically isotropic and the soil solution perfectly mixed.
- Sulfur reactions do not serve as a net sink or source of acid neutralizing capacity.
- Only the net effect of all N reactions such as NO_3^- and NH_4^+ uptake, nitrification and denitrification is included.
- Internal element cycling of elements such as K, Ca and Mg in the upper soil layers is not modelled regularly.
- Dissolved organic matter is specified as input data, not generated by mineralization.
- Organic complexing of metals, such as Al is not modelled.

The first condition is justified by the mere existence of soil horizons, while assuming complete mixing in a soil layer is less obvious.

Sulfuric acid adsorption and certain sulfate adsorption processes may buffer soils from being acidified by acid deposition [Reuss and Johnsson, 1985]. This phenomenon is particularly important in highly weathered soils, that were not covered during the last glaciation. Quantitatively, the sulfate adsorption capacity of young soils are at least one order of magnitude less than the buffering by cation exchange capacity. With these proportions, sulfate adsorption was not included in SAFE. For PROFILE, sulfate adsorption would automatically be redundant, since the contribution of exchange reactions is zero under steady-state conditions. There are also indications that sulfate may have an important effect on the mobilization of organic

matter by exchange mechanisms [Gobran and Nilsson, 1988]. If these processes prove to be quantitatively important, the decision to exclude sulfate reactions from the model should be reconsidered.

The net production or consumption of acid neutralizing capacity, ANC, in a forest soil is the integrated result of vast number of chemical reactions [Reuss and Johnsson, 1986]. The ANC is defined as the difference between acid-consuming and acid-producing components in the soil solution. If the ANC is positive, it is referred to as alkalinity.

Due to the allocation of these reactions, N transformations can also serve to reallocate acidity between horizons. Comprehensive models of N fluxes in soils need, not only mass balances for nitrate and ammonia, but also pools of stored organic nitrogen and carbon. Then the effects of uptake, immobilization and mineralization of N can be separated and quantified. To meet the objectives of this modelling work, it is important to understand the nature of the processes involved, but only the integrated effect of the N transformations are necessary to include in the model. The same reasoning is behind the decision to lump all base cations together into one entity. As long as no relations to calculate biological response to concentrations in solution are included, it is not necessary to distinguish between elements that have a similar integrated behaviour in the ecosystem.

Organic carbon and nitrogen are intermediate products formed when organic material is decomposed. In most forest soils, the soil solution in the upper soil layers is rich in dissolved organic, but the flux decrease rapidly from the B-horizon and below as a natural part in the podsolization process. To address questions regarding groundwater acidification, it has been concluded that the actual production and consumption of DOC does not have to be modeled as a process, and only the buffering aspects of the end product has been incorporated.

Al bonding to organic ligands appears to be an important feature of surficial soil water chemistry, and different models have recently been formulated to deal with this process [Tipping *et al.*, 1988]. In the models presented here, however, these reactions are not included. Instead, an empirical approach to Al bufferening of soil waters has been taken, the gibbsite equilibrium method. It emulates the the aqueous equilibrium system without actually comprising the correct reactions. Thereby, an acceptable titration curve is obtained. This is an intermediate modeling sacrifice, and an alternative has been developed within this project [Olausson *et al.*, 1990], but not yet integrated in the models.

The soil layers of the soil column can also be viewed as one unit, with the system boundary in Figure 4.2 shows. Thereby, both the groundwater recharge and the run-off chemistry can be assessed as the integrated result of chemical reactions in the entire soil column. The water leaving a layer may either percolate vertically or flow horizontally. Changing the proportions between these flow paths will alter the relative importance of different soil layers for the chemistry of the drainage water.

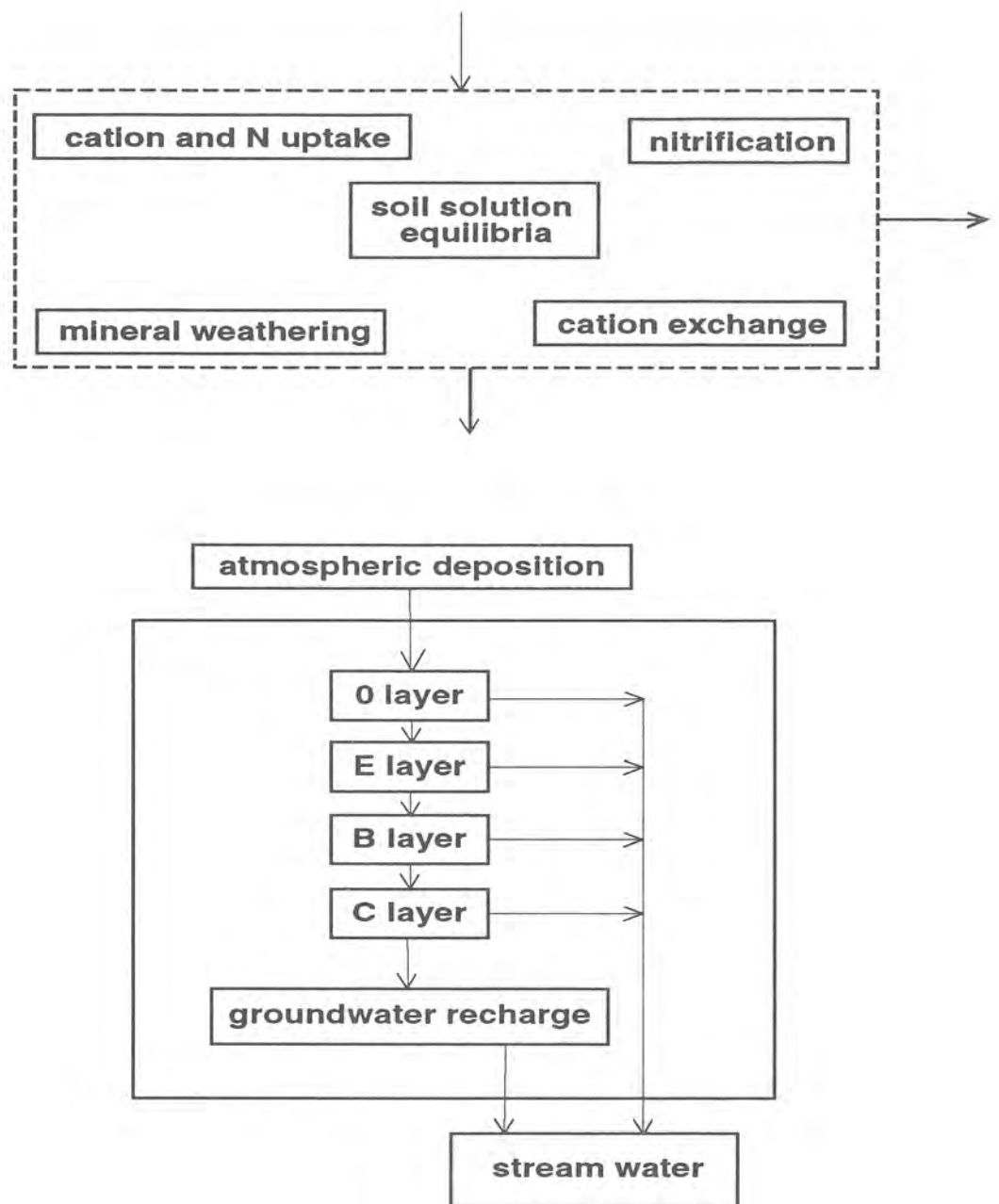


Figure 4.2: Upper part visualizes the soil processes interacting within one layer in PROFILE and SAFE. The lower part shows how the different compartments, each one corresponding to a soil horizon, are connected. Water can flow either vertically or horizontally. In all applications in this study, however, only vertical movement has been considered.

4.2.1 Mass balances

The change in soil solution chemistry and the subsequent change in the distribution of elements on the cation exchange matrix is calculated by means of conservation equations. In the present version of the model, the 'base' cations Mg, Ca, and K are simply lumped together into a divalent component, BC . Na is ignored, in the solution as well as an exchangeable species. The hydrogen ion is treated as dependent on the variable Acid Neutralizing Capacity, ANC . In the model, each soil horizon is assumed to be homogeneous, i. e. there are no macroscopic concentration gradients in the uppermost soil layer. The mass conservation equations, derived as differential mass balances, constituting the framework for the mathematical model are:

$$\frac{d[ANC]}{dt} = \frac{1}{z \cdot \Theta} \cdot (Q_0[ANC]_0 - (Q + z \cdot \frac{d\Theta}{dt}) \cdot [ANC]) + R_W + R_{exc} - R_{BC} + R_N \quad (4.1)$$

where z = soil layer height (m)
 Θ = soil water content ($m^3 m_s^{-3}$)
 Q = Flow rate ($m^3 m_s^{-2} yr^{-1}$)
 R_W = ANC production from weathering ($keq m^{-3} yr^{-1}$)
 R_{exc} = ANC production from cation exchange ($keq m^{-3} yr^{-1}$)
 R_{BC} = Base cation uptake ($keq m^{-3} yr^{-1}$)
 R_N = ANC production from N reactions/uptake ($keq m^{-3} yr^{-1}$)

No subscript refers to condition in the soil layer, and consequently also the leachate from a soil layer. Subscript 0 denotes concentrations in the inflow to the layer. The communications between phases and the reactants in the system do always take the path via the soil solution.

If the hydrological data fed to the model suggest variations in soil moisture content Θ , changes in solution chemistry will occur due to dilution/concentration. This is quantified in the equations through the $z \cdot \frac{d\Theta}{dt}$ term. For the other components in the system, base cations, nitrate and ammonia, the mass balances become:

$$\frac{d[BC^{2+}]}{dt} = \frac{1}{z \cdot \Theta} (Q_0[BC^{2+}]_0 - (Q + z \cdot \frac{d\Theta}{dt})[BC^{2+}]) + \frac{R_w + R_{exc} - R_{BC}}{2} \quad (4.2)$$

$$\frac{d[NO_3^-]}{dt} = \frac{1}{z \cdot \Theta} \cdot (Q_0[NO_3^-]_0 - Q \cdot [NO_3^-]) - R_{NO_3^-} + R_{nit} \quad (4.3)$$

$$\frac{d[NH_4^+]}{dt} = \frac{1}{z \cdot \Theta} \cdot (Q_0[NH_4^+]_0 - Q[NH_4^+]) - R_{NH_4^+} - R_{nit} \quad (4.4)$$

where $R_{NO_3^-}$ = Rate of NO_3^- uptake ($keq m^{-3} yr^{-1}$)
 R_{nit} = Rate of nitrification, $NH_4^+ \rightarrow NO_3^-$ ($keq m^{-3} yr^{-1}$)
 $R_{NH_4^+}$ = Rate of NH_4^+ uptake ($keq m^{-3} yr^{-1}$)

Steady-state solution

When the initial conditions or sensitivity to acidification, expressed in terms of a critical load, of a soil system is assessed it may not be necessary to reproduce the

entire acidification process, but sufficient to regard only the steady-state solution to equation 4.1, accordingly solving equation 4.1 for:

$$\frac{d[ANC]}{dt} = 0 \quad (4.5)$$

In all systems, the upper limit of removal of any component in solution is the supply. In order to calculate the ANC production from uptake of base cations and N uptake and other reactions, additional mass balances are required. The general form of all these equations are identical to equation 4.1. This leads to the following set of equations to be solved simultaneously:

$$0 = \frac{1}{z \cdot \Theta} \cdot (Q_0[ANC]_0 - Q \cdot [ANC]) + R_w - R_{BC} + R_N \quad (4.6)$$

$$0 = \frac{1}{z \cdot \Theta} \cdot (Q_0[BC^{2+}]_0 - Q \cdot [BC^{2+}]) + \frac{R_w - R_{BC}}{2} \quad (4.7)$$

$$0 = \frac{1}{z \cdot \Theta} \cdot (Q_0[NO_3^-]_0 - Q \cdot [NO_3^-]) - R_{NO_3^-} + R_{nit} \quad (4.8)$$

$$0 = \frac{1}{z \cdot \Theta} \cdot (Q_0[NH_4^+]_0 - Q \cdot [NH_4^+]) - R_{NH_4^+} - R_{nit} \quad (4.9)$$

These first two of these equations must be solved iteratively since the rate of ANC production from weathering, R_w , is a function of pH, which in turn is a non-linear function of the ANC. The solution of equation 4.1–4.4 will therefore also include the evaluation of all species that appear in the definition of ANC. With this set of equations, and the functional relationships discussed below, only reacting components in the soil system have to be considered to characterize the soil solution completely. Therefore, the solution of the charge balance becomes redundant, and the fluxes of SO_4^{2-} and Cl^- do not have to be included in soil chemistry calculations. For the uppermost soil layer, the input is the atmospheric deposition.

4.2.2 Soil solution equilibrium sub—model

In the model, the buffering in the liquid phase is controlled by the CO_2 -carbonate system, the acid-base reactions of an organic acid RH and an aluminium sub-model. The latter is based on the assumption that the concentration of Al-species is governed by the dissolution and precipitation of a solid gibbsite phase, $Al(OH)_3$.

ANC may be interpreted in terms of dissolved species participating in acid/base transformations in the aqueous phase. In the model it is assumed that the chemical reaction systems of the soil solutions include the auto-protolysis of water, the carbonate equilibrium reactions, acid-base reactions of a monovalent organic acid, as well as the precipitation and subsequent dissolution reactions of a solid gibbsite phase, producing different charged aluminium-hydroxyl species. Neglecting the presence of NH_4^+ , which is always protonized in the soil systems considered, the solution ANC is defined as:

$$[ANC] = \quad (4.10)$$

$$[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [R^-] - [H^+] - 3[Al^{3+}] - 2[Al(OH)^{2+}] - [Al(OH)_2^+]$$

With this definition, it is clear that ANC is a quantity derived from a reduced charge balance from which all solution components that are not believed to participate in acid-base reactions in the liquid phase have been omitted. Such components include SO_4^{2-} , NH_4^+ and BC^{2+} . In an equilibrium situation, each species on the right hand side of equation 4.10 can be explicitly calculated from the solution H^+ -concentration, and ANC will therefore be a unique function of the solution pH and, most important, vice versa. Numerically, ANC may be calculated explicitly from a given pH, while the H^+ -concentration corresponding to a given ANC must be calculated iteratively. In order to calculate the concentrations of the species of the CO_2 -system, equation (4.10) is combined with the equilibrium equations for the protolysis reactions of CO_2 , Henry's law for P_{CO_2} - H_2CO_3 equilibrium, as well as the autoprotolysis of water. Also needed are equations for calculating the concentrations of Al^{3+} , $Al(OH)^{2+}$ and $Al(OH)_2^+$. The H^+ concentration is solved for by finding the root to the equation:

$$0 = \quad (4.11)$$

$$[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [R^-] - [H^+] - 3[Al^{3+}] - 2[Al(OH)^{2+}] - [Al(OH)_2^+] - [ANC]$$

In the organic soil layers, the buffering reaction of organic components may be important. In PROFILE and SAFE, dissolved organic carbon (DOC) is modelled as a monovalent organic acid. The dissociation of the acid functional groups of the DOC is quantified using an expression as proposed by Oliver [Oliver *et al.*, 1983].

In general, the pH corresponding to a certain ANC is governed by the carbonate and the organic matter buffer systems at positive values for ANC, i.e. at pH-levels above 5. The aluminum buffering system has its effect below this level [Driscoll and Bisogni, 1984]. The one most important parameter for quantifying the importance of the aluminum buffering is the gibbsite solubility constant, K_G . As discussed by Schecher and Driscoll (1987), K_G values ranging over more than one order of magnitude have been reported, and the experimental uncertainties and variability regarding this quantity may be significant. The values selected for the different horizons will be given later in the text.

The applied equilibrium expression controlling the concentration of the aluminum species, have such a form that it may be interpreted as an apparent equilibrium with gibbsite. It must be remembered that this model is a simplification, and that the equilibrium expression probably lumps together several different mechanisms for aluminium concentration control. Both equilibrium and disequilibrium mechanisms are involved, and gibbsite may not necessarily be a part of any of these processes which are most likely to proceed a long non-ideal reaction paths [Paçes, 1978]. Most forest soils in Europe do not contain gibbsite in detectable amounts [Melkerud, 1983]. The justification for selecting the gibbsite dissolution/precipitation reaction as the foundation for modeling the aluminum equilibrium system is primarily that reasonable titration curves can be derived with this aquatic chemistry model.

The complete set of equilibrium equations necessary to solve equation 4.2.2 is:

$$[OH^-] = \frac{K_W}{[H^+]} \quad (4.12)$$

$$[HCO_3^-] = \frac{K_{H_2CO_3} \cdot K_{Henry} \cdot P_{CO_2}}{[H^+]} \quad (4.13)$$

$$[CO_3^{2-}] = [HCO_3^-] \cdot \frac{K_{HCO_3^-}}{[H^+]} \quad (4.14)$$

$$[R^-] = 1 \cdot 10^{-6} \cdot [DOC] \cdot \frac{K_{org}}{K_{org} + [H^+]} \quad (4.15)$$

$$[Al^{3+}] = K_G \cdot [H^+]^3 \quad (4.16)$$

$$[Al(OH)^{2+}] = K_{Al(OH)^{2+}} \cdot K_G \cdot [H^+]^2 \quad (4.17)$$

$$[Al(OH)_2^+] = K_{Al(OH)_2^+} \cdot K_G \cdot [H^+] \quad (4.18)$$

where P_{CO_2} = CO₂ partial pressure (atm)
 DOC = dissolved organic carbon in solution (mg L⁻¹)
 K_W etc = Aqueous equilibrium coefficients as specified in Table 4.1

The constant $1 \cdot 10^{-6}$ that appears in the expression for $[R^-]$ is an empirical factor that converts DOC expressed in mg L⁻¹ to carboxyl groups expressed in keq m⁻³ [Ågren and Jacks, 1990]. Default have been used for the gibbsite coefficient, pK_G set to 6.5, 7.5, 8.5 and 9.2 for the O, E, B and C horizons respectively.

Table 4.1: Equilibrium equations and corresponding coefficients included in SAFE and PROFILE. Units applied are keq, m³, K and atmospheres. References are made to: 1: [Stumm and Morgan, 1983], 2: [Oliver *et al.*, 1983], 3: [Schecher and Driscoll, 1987].

Equilibrium Reaction	Equ. coeff.	Value/function	Ref.
$H_2O \rightleftharpoons H^+ + OH^-$	K_W	$\exp - \ln(10) \cdot (-6.09 + 4471/T + 0.0171 \cdot T)$	1
$CO_2(g) \rightleftharpoons H_2CO_3(aq)$	K_{Henry}	$\exp - \ln(10) \cdot (12.59 - 2198/T - 0.0126 \cdot T)$	1
$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$	$K_{H_2CO_3}$	$\exp - \ln(10) \cdot (-14.82 + 3401/T + 0.0327 \cdot T)$	1
$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$	$K_{HCO_3^-}$	$\exp - \ln(10) \cdot (-6.53 + 2906/T + 0.0238 \cdot T)$	1
$RH + H_2O \rightleftharpoons R^- + H_3O^+$	K_{org}	$\exp - \ln(10) \cdot (0.96 + pH - 0.001 \cdot pH^2)$	2
$Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$	K_G	User specified	
$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + 2H^+$	$K_{Al(OH)_2^+}$	$5 \cdot 10^{-10}$	3
$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$	$K_{Al(OH)^{2+}}$	$1 \cdot 10^{-5}$	3

4.2.3 Weathering rate model

In many types of soil systems, weathering of primary minerals provides the long-term neutralization capacity [Reuss *et al.*, 1986]. PROFILE has many elements in common with other contemporary soil acidification models [Sverdrup *et al.*, 1990, de Vries *et al.*, 1989]. Regarding weathering reactions, however, PROFILE allows the weathering rate to be calculated explicitly from independent soil properties [Sverdrup and Warfvinge, 1988], rather than being an input to the model. In this context, weathering refers to the release of alkalinity and base cations, rather than the actual dissociation of the silicate structure. The weathering rate constants used in the model are therefore not comparable with rate coefficients determined from Si and Al production experiments.

Several chemical reactions between the mineral and the constituents in the liquid solution contribute to the base cation release rate from chemical weathering of silicate minerals. The total weathering rate will be the sum of the rates of the individual elementary reactions. For most minerals several dissolution reactions have been experimentally identified [Sverdrup, 1990]. These involve many components in the liquid phase; H^+ , H_2O , OH^- and dissolved CO_2 , as well as Al, cations of the parent mineral and strongly complexing organic ligands.

The total base cation release rate is taken to be the sum of the rates of all the chemical reactions taking place to dissolve the mineral minus the rate of precipitation of secondary solid phases. The rate is proportional to the exposed surface area of the mineral. By inserting the expression for the concentration of activated complex in the rate equation, based on the transition state theory, a general equation for the weathering rate at constant temperature may be derived. Under the conditions prevailing in the natural soil environment, the base cation release rate for a single mineral, r , may be approximated by:

$$r = k_{H^+} \cdot \frac{[H^+]^{n_H}}{f_H} + \frac{k_{H_2O}}{f_{H_2O}} + k_{CO_2} \cdot P_{CO_2}^{n_{CO_2}} + k_{org} \cdot \frac{a_{org}^{0.5}}{\kappa_{org} + a_{org}^{0.5}} \quad (4.19)$$

where k_{H^+} = rate coefficient for H^+ reaction ($m \ s^{-1}$)
 k_{H_2O} = rate coefficient for H_2O reaction ($keq \ m^{-2} \ s^{-1}$)
 k_{CO_2} = rate coefficient for CO_2 reaction ($keq \ atm^{-1} \ m^{-2} \ s^{-1}$)
 k_{org} = rate coefficient for organic acid reaction ($keq \ m^{-2} \ s^{-1}$)
 n_H, n_{CO_2} = reaction order of individual reactions
 f_H, f_{H_2O} = rate reduction factors for product inhibition
 a_{org} = activity of organic ligands in solution

Numerical values for all the coefficients of the minerals at present considered in PROFILE are given in Table 4.2. Reactions with organic ligands have been lumped with the rate of the reaction with water. The two factors reducing the rate of base cation production due to increased concentrations of weathering products, f_H , f_{H_2O} are defined as:

$$f_H = \left(1 + \frac{[Al^{3+}]}{k_{Al}}\right)^{x_{Al}} \cdot \left(1 + \frac{[BC^{2+}]}{k_{BC}}\right)^{x_{BC}} \quad (4.20)$$

$$f_{H_2O} = \left(1 + \frac{[Al^{3+}]}{k_{Al}}\right)^{z_{Al}} \cdot \left(1 + \frac{[BC^{2+}]}{k_{BC}}\right)^{z_{BC}} \quad (4.21)$$

where k_{Al}, k_{BC} = dissolution reduction saturation coeff. (keq m^{-3})
 x_{Al}, z_{Al} etc. = reaction orders

The rate of weathering reactions in soils are kinetically limited, and hence temperature dependent. The temperature effect is quantified through the Arrhenius equation, stating that the reaction rate coefficient is function of the activation energy on the activated surface complex. In PROFILE, the rate coefficient for a given temperature is calculated as.

$$k_T = k_8 \cdot \exp\left(\frac{E_A}{R} \cdot \log_{10} \cdot \left(\frac{1}{T} - \frac{1}{273.2 + 8}\right)\right) \quad (4.22)$$

where k_T = rate coefficient at temperature T
 k_8 = rate coefficient at 8 °C (Table 4.1)
 E_A = activation energy (kJ keq^{-1})
 R = universal gas constant ($\text{kJ keq}^{-1} \text{K}^{-1}$)

Values for E_A/R been derived for the minerals in PROFILE and SAFE [Sverdrup, 1990], and are given in Table 4.2.3. The effect of the temperature on model output is often quite large. Typically, a change by 4°C results in a change in weathering rate by 30%.

In soils the availability of moisture may be limited causing the activity of the exposed mineral surface to be less than unity. The reactions will only take place on wetted surfaces, and the degree of surface wetting is taken to be proportional to the soil moisture saturation. All surfaces to participate in reaction must be wetted, but there must also be sufficient soil solution present for the weathering process to communicate with other soil processes. In PROFILE the soil moisture saturation is assumed to be proportional to the activity of the reacting surface. For dissolution in the natural soil environment, the rate equation for each soil horizon is:

$$R_W = \sum_i^{\text{minerals}} (1 - y_{Na}) \cdot r_i \cdot A_{exp} \cdot x_i \cdot \theta \cdot z \quad (4.23)$$

where r_i = rate of base cation production of mineral i ($\text{keq m}^{-2} \text{s}^{-1}$)
 y_{Na} = fraction of Na released during weathering of mineral i
 A_{exp} = exposed surface of the mineral matrix ($\text{m}^2 \text{m}_s^{-3}$)
 θ = the soil moisture saturation
 x_i = fraction of mineral i in the mineral matrix of the soil horizon

The exposed surface area can be in the soil horizon as approximated from a BET analysis or a particle size distribution and the mineralogy [Sverdrup *et al.*, 1990]. The soil moisture saturation is calculated by combining the densities of a solid phase (2700 kg m^{-3}) an aqueous phase (1000 kg m^{-3}), and a gaseous phase (0.010 kg/m^{-3}), with the bulk soil density ρ_{soil} and the volumetric water content Θ :

$$\theta = \frac{2700 \cdot \Theta}{2700 + 1000 \cdot \Theta - \rho_{soil}} \quad (4.24)$$

Table 4.2: Rate coefficients for the base cation release from weathering reactions at a temperature of 8 °C.

Mineral	pK_H	n_H	pK_{H_2O}	pK_{CO_2}	n_{CO_2}	k_{Al}	x_{Al}	z_{Al}	k_{Ca}	x_{Ca}	z_{Ca}
K-Feldspar	16.0	0.5	17.2	17.2	0.6	$1 \cdot 10^{-5}$	0.4	0.14	$5 \cdot 10^{-4}$	0.15	0.15
Oligoclase	15.9	0.5	17.0	15.8	0.6	$2 \cdot 10^{-5}$	0.4	0.14	$1 \cdot 10^{-3}$	0.2	0.15
Albite	15.4	0.5	17.0	15.9	0.6	$1 \cdot 10^{-5}$	0.4	0.14	$5 \cdot 10^{-4}$	0.2	0.15
Hornblende	15.4	0.7	17.0	15.9	0.6	$5 \cdot 10^{-5}$	0.3	0.3	$2.5 \cdot 10^{-3}$	0.3	0.3
Pyroxene	13.8	0.7	17.5	15.8	0.6	$5 \cdot 10^{-4}$	0.2	0.1	$2.5 \cdot 10^{-2}$	0.3	0.3
Epidote	12.6	0.8	16.8	15.8	0.6	$5 \cdot 10^{-4}$	0.3	0.2	$2.5 \cdot 10^{-2}$	0.2	0.2
Garnet	12.4	1.0	16.9	15.8	0.6	$1 \cdot 10^{-3}$	0.4	0.2	$5 \cdot 10^{-2}$	0.2	0.2
Biotite	15.3	0.6	17.6	15.8	0.5	$1 \cdot 10^{-5}$	0.3	0.2	$5 \cdot 10^{-4}$	0.2	0.2
Muscovite	15.2	0.5	17.5	16.5	0.5	$1 \cdot 10^{-6}$	0.4	0.2	$5 \cdot 10^{-5}$	0.1	0.1
Chlorite	15.3	0.7	16.7	15.8	0.5	$5 \cdot 10^{-5}$	0.2	0.1	$2.5 \cdot 10^{-3}$	0.2	0.1
Vermiculite	14.8	0.6	17.6	16.5	0.5	$1 \cdot 10^{-6}$	0.4	0.1	$5 \cdot 10^{-5}$	0.2	0.1
Apatite	12.8	0.7	15.8	—	—	—	—	—	$3 \cdot 10^{-4}$	0.4	0.2

Table 4.3: Lumped activation energies used to calculate the weathering rate coefficient from 8 C to the temperature T, by means of equation 4.22, and stoichiometric coefficients representing the relative release of base cations. Source: [Sverdrup, 1990]

Mineral	$E_A \cdot R^{-1}$			Base cation content			
	pK_H	pK_{H_2O}	pK_{CO_2}	y_{Na}	y_K	y_{Mg}	y_{Ca}
K-Feldspar	3500	2000	1700	0.0	0.90	—	—
Oligoclase	4200	2500	1700	0.45	—	—	0.55
Albite	3800	2500	1700	0.9	—	—	0.1
Hornblende	4300	3800	1700	—	—	0.67	0.33
Pyroxene	2700	3800	1700	—	—	0.50	0.50
Epidote	2500	3800	1700	—	—	—	1.0
Garnet	2500	3500	1700	—	—	0.25	0.75
Biotite	4500	3800	1700	—	0.20	0.80	—
Muscovite	4500	3800	1700	—	0.80	0.20	—
Chlorite	4500	3800	1700	—	—	1.0	—
Vermiculite	4300	3800	1700	—	0.50	0.50	—
Apatite	3500	4000	1700	—	—	—	1.0

4.2.4 Nitrogen reactions

In PROFILE, we have not attempted to model the processes that govern the flow of nutrient cations, nitrogen compounds and ANC between the soil solution and the roots of the growing plants. PROFILE relies on input data to specify the maximum rates of uptake of different compounds of the vegetation.

Nitrogen reactions are included as sources or sinks of acidity in the soil [Galloway and Dillon, 1983]. The connection to the acidity-alkalinity balance is clear from equation 4.2.2, where the net production is quantified by the term R_N . Considering only uptake of NH_4^+ and NO_3^- as well as nitrification, the net production of ANC from these reactions is:

$$R_N = R_{NO_3^-} - R_{NH_4^+} - 2 \cdot R_{nitr} \quad (4.25)$$

Regarding N-uptake, PROFILE relies on input data that specifies the the maximum yearly uptake, distributed vertically in the horizon. For each soil layer, the constraint for N-uptake can be defined as:

$$R_{NO_3^-} + R_{NH_4^+} \leq R_{Nmax} \quad (4.26)$$

where $R_{Nmax} = \max \text{ N uptake from solution in a layer (keq m}^{-3} \text{ yr}^{-1})$

In SAFE/PROFILE, the assumption is that ammonia and nitrate are taken up in fixed proportions, provided that both components are in supply. This fixed ratio is referred to as $x_{NH_4^+}$. The only biological process that is modelled in terms of a kinetic rate expression is nitrification. The rate of nitrification is governed by a kinetic expression:

$$R_{nitr} = \frac{k_{nitr} \cdot [NH_4^+]}{K_{nitr} + [NH_4^+]} \quad (4.27)$$

The values of the kinetic rate coefficient k_{nitr} and the Michaelis-Menten saturation constant K_{nitr} are discussed in 'Mapping Critical Loads' [Sverdrup *et al.*, 1990].

Steady-state conditions

In a steady-state situation, it is possible to solve for $[NH_4^+]$ by combining equation 4.4 with equation 4.27 and the condition that $R_{NH_4^+} = x_{NH_4^+} \cdot R_{Nmax}$. The ammonia concentration is then given as the solution to an ordinary second-order equation:

$$[NH_4^+] = \frac{K_{nit} - \alpha}{2} + \sqrt{\left(\frac{K_{nit} - \alpha}{2}\right)^2 + K_{nit} \cdot \left(\alpha + \frac{k_{nit}\Theta z}{Q}\right)} \quad (4.28)$$

where

$$\alpha = \frac{[NH_4^+]_0 \cdot Q_0}{Q} - (k_{nit} + x_{NH_4^+} \cdot R_{Nmax}) \cdot \frac{\Theta z}{Q}$$

If the ammonia entering a soil layer is sufficient to meet the demand for nitrogen we therefore get the following result to enter into the mass balances:

$$[NH_4^+] > 0 \left\{ \begin{array}{l} R_{NH_4} = \frac{Q_0[NH_4^+]_0 - Q[NH_4^+]}{z \cdot \Theta} - R_{nit} \\ R_{NO_3} = \min \left\{ \begin{array}{l} \frac{Q_0[NO_3^-]}{z \cdot \Theta} + R_{nit} \\ (1 - x_{NH_4^+}) \cdot R_{Nmax} \end{array} \right. \\ R_{nit} = \frac{k_{nitr} \cdot [NH_4^+]}{K_{nitr} + [NH_4^+]} \end{array} \right. \quad (4.29)$$

If the supply of NH_4 does not meet the total nitrogen uptake demand, however, the solution to equation 4.28 becomes 0. We then get:

$$[NH_4^+] = 0 \left\{ \begin{array}{l} R_{NH_4} = \frac{Q_0[NH_4^+]_0}{z \cdot \Theta} \\ R_{NO_3} = \min \left\{ \begin{array}{l} \frac{Q_0[NO_3^-]}{z \cdot \Theta} \\ R_{Nmax} - R_{NH_4} \end{array} \right. \\ R_{nit} = 0 \end{array} \right. \quad (4.30)$$

The "min" operator means that the lowest value of the two argument in the paranthesis is choosen. This condition prevents uptake of nitrate to exceed the input to the soil layer, which would result in negative concentrations in the calculations.

4.2.5 Base cation uptake

As the nitrogen uptake, base cation uptake is represented by a forcing function rather than a process. Furthermore, there is no constraint in the model that base cation uptake should occur in a certain proportion to the nitrogen uptake. The only condition is that the uptake cannot be larger than the supply from internal or external sources within a soil layer.

Based on the steady-state mass balance (equation 4.7), the uptake expressed per unit soil solution is given as:

$$R_{BC} = \min \left\{ \frac{Q_0[BC]_0}{z \cdot \Theta} + R_w, R_{BCmax} \right\} \quad (4.31)$$

where R_{BCmax} = maximum base cation uptake in a layer ($\text{keq m}^{-3} \text{ yr}^{-1}$)

In this case, the "min" operator puts a constraint on the uptake to be lower than the sum of what enters the soil layer by convective flow and what is produced by chemical weathering.

Temporal distribution

In the dynamic modelling, it is necessary to reproduce the temporal variation in base cation and nitrogen uptake. Such variations have been well documented within Swedish forestry research [Ågren *et al.*, 1989]. The necessity of taking the temporal aspect into account is clear from two general observations. If the uptake process is allowed to continue when the soil is frozen and no base cations are supplied from the above layer, the uppermost soil layers become totally depleted. As a consequence, the model simply crashes as concentrations go below zero. Another effect of assuming constant uptake rate is that the concentrations increase tremendously in the summer due to reduced water content in the soil.

In SAFE, the uptake is a function of the annual temperature sum:

$$R_{BC}(day) = \sum_{days} R_{BC} \cdot \frac{T(day) - 5^{\circ}}{\sum_{days} T} \quad (4.32)$$

There is also a limitation that stops uptake if the concentration of base cations is less than 8 meq m^{-3} .

As shown in Figure 4.3, these constraints generate an uptake pattern that is close to observed patterns, although the rate photosynthesis primarily is correlated to the radiation [Linder and Troeng, 1989]. The agreement tends to be better using the soil temperature than if the same approach is taken with the air temperature. the soil temperature is, however a model variable, based on air temperature data (see Chapter 3).

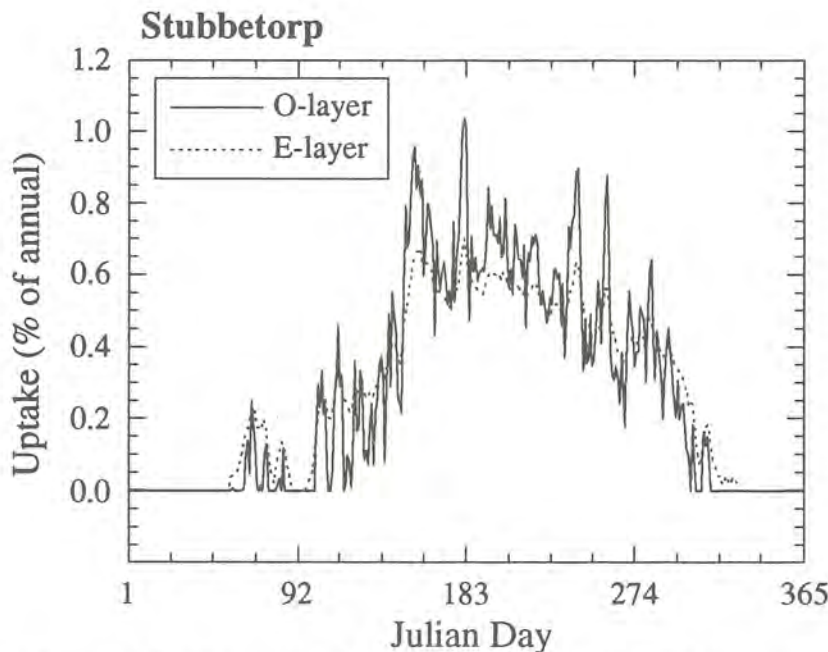


Figure 4.3: Example of temporal distribution of the annual uptake

4.2.6 The cation exchange reaction

Traditionally, soil cation-exchange has been modeled as an equilibrium reaction. In a thorough review by Harmsen (1982), the principles and assumptions behind the commonly used equilibrium exchange equations, such as those developed by Gaines and Thomas, Vanselow and Gapon, are discussed. In at least one case [Robbins *et al.*, 1980], the Gapon exchange equation has been successfully integrated into a dynamic soil chemistry and solute transport model, and verified under controlled conditions. In soil systems that are subject to episodic variations in flow intensity and soil solution composition however, there is no justification for assuming equilibrium between the liquid phase and the exchanger matrix *a priori*. If equilibrium is erroneously assumed in a hydrochemical model, an unreasonably strong buffering mechanism is introduced, short term dynamics are lost, and long term trends are led onto an incorrect path.

As the intrinsic rate of the cation exchange reaction is considered to be infinite, the exchange reaction between exchangeable calcium and acidity is modeled as a perfectly reversible chemical reaction, limited in rate by the transport of BC^{2+} -ions between the bulk of the soil solution and active sites on the exchanger surface. The pseudo-steady state rate equation for such a process can be derived from Fick's first law, and since the change in exchangeable calcium, $\bar{X}_{BC}$, will be proportional to the flux of BC^{2+} to the exchanger, the rate equation becomes:

$$\frac{d\bar{X}_{BC}}{dt} \propto \frac{D_{BC}}{l} \cdot ([BC^{2+}]_s - [BC^{2+}]_{ex}) \quad (4.33)$$

where D_{BC} is the diffusivity of the BC^{2+} - in solution, and l is a characteristic diffusion distance, the magnitude of which generally is difficult to assess explicitly. Therefore, a lumped mass transfer coefficient k_x must be introduced to yield:

$$\frac{d\bar{X}_{BC}}{dt} = k_x \cdot ([BC^{2+}]_s - [BC^{2+}]_{ex}) \quad (4.34)$$

The BC^{2+} concentration at the soil liquid-solid interface will be given by an appropriate equilibrium model. If it is assumed that all exchangeable acidity is present as exchangeable H, $[BC^{2+}]_{ex}$ can be calculated from the Gapon exchange equation [Sposito, 1992] as:

$$[BC^{2+}]_{ex} = \frac{[H^+]_{ex}^2 \cdot \bar{X}_{BC}^2}{K_{H/Ca}^2 \cdot (1 - \bar{X}_{BC})^2} \quad (4.35)$$

Thus, calculating $[BC^{2+}]_{ex}$ will require computation of the pH at the exchanger phase surface, and one equation in addition to an exchange equilibrium equation is needed. The additional relationship required can be derived from the charge balance evaluated at the surface as well as for the soil solution, combined with the Gapon selectivity equation for heterovalent exchange. One can then solve for $[H^+]_{ex}$:

$$[H^+]_{ex} = \frac{K_{H/Ca} \cdot (1 - \bar{X}_{BC})}{\bar{X}_{BC}} \cdot \sqrt{[BC^{2+}]_s - 2[ANC]_s + 2[ANC]_{ex}} \quad (4.36)$$

Since $[ANC]_{ex}$ is a unique function of the liquid-solid interface H^+ -concentration, this equation must be solved iteratively, and the result inserted into equation (4.34) to form the final differential equation:

$$\frac{d\bar{X}_{BC}}{dt} = k_x \cdot ([BC^{2+}]_s - \frac{[H^+]_{ex}^2 \cdot \bar{X}_{BC}^2}{K_{H/Ca}^2 \cdot (1 - \bar{X}_{BC})^2}) \quad (4.37)$$

If exchangeable aluminum is dominating, however, the interface BC^{2+} -concentration is calculated from an Al-BC exchange isotherm:

$$[BC^{2+}]_{ex} = \frac{[Al^{3+}]_{ex}^{\frac{2}{3}} \cdot \bar{X}_{BC}^2}{K_{Al/BC}^2 \cdot (1 - \bar{X}_{BC})^2} \quad (4.38)$$

Combining this expression with the assumption that $[Al^{3+}]$ is given by a simple gibbsite equilibrium, such that:

$$[Al^{3+}]_{ex} = K_G \cdot [H^+]_{ex}^3 \quad (4.39)$$

it becomes evident that it is indifferent whether H^+ or Al^{3+} cation exchange is assumed, provided that the Gapon exchange equation is applied. Since the mass transfer coefficient quantifies a thoroughly investigated physical process, it would be possible to derive theoretical relationships for calculating k_x for perfectly characterized soil systems. Since capacity factors such as the cation exchange capacity (CEC) and soil density (ρ_s) will exhibit considerable spatial variability, k_x should therefore be given by a distribution of values, while the model calculations presented in this paper are performed with on single value. With the present status of the model, the numerical value of the over-all cation exchange rate coefficient k_x , had to be selected based on data from soil liming experiments [Warfvinge, 1988].

As an increase in base cation saturation corresponds to withdrawal of acid neutralizing capacity from the soil solution, the rate of which is calculated as:

$$R_x = -\frac{CEC \cdot \rho_s}{\Theta} \cdot \frac{d\bar{X}_{BC}}{dt} \quad (4.40)$$

Steady-state conditions

As obvious from the mass balance for ANC, a steady-state solution to the equation equation 4.1 for:

$$\frac{d[ANC]}{dt} = 0 \quad (4.41)$$

may be obtained even if the cation exchange phase has not reached a steady state in terms of base saturation. For a soil system to be in true equilibrium however, it is a necessary constraint that the distribution of cations on the solid phase should not vary in time. Mathematically, this corresponds to a situation where:

$$R_{exc} \propto \frac{d}{dt}(CEC \cdot (\bar{X}_{BC} - \bar{X}_H - \bar{X}_{Al})) = 0 \quad (4.42)$$

where CEC = cation exchange capacity in the horizon, arbitrary units
 $\bar{X}_i$ = exchangeable fraction of element i

It is then also very important to recognize that the cation exchange capacity is assumed to remain constant, i. e. $dCEC/dt = 0$.

In PROFILE, the soil solution composition is thus calculated without considering cation exchange. With the concentrations of all liquid phase components computed, the composition of the exchanger phase may be determined. Three equations are necessary to calculate the charge fractions; two selectivity equations and one total condition. With the Gapon exchange model, the activity of exchangeable elements are expressed in terms of charge fractions, and we get:

$$K_{H/Al} = \frac{[H^+]^3 \cdot \bar{X}_{Al}^3}{[Al^{3+}] \cdot \bar{X}_H^3} \quad (4.43)$$

$$K_{H/BC} = \frac{[H^+]^2 \cdot \bar{X}_{BC}^2}{[BC^{2+}] \cdot \bar{X}_H^2} \quad (4.44)$$

$$1 = \bar{X}_H + \bar{X}_{Al} + \bar{X}_{BC} \quad (4.45)$$

where $\bar{X}_H, \bar{X}_{BC}, \bar{X}_{Al}$ = charge fractions on cation exchange matrix
 $K_{H/Al}$ = Gapon selectivity coefficient for H-Al exchange
 $K_{H/BC}$ = Gapon selectivity coefficient for H-BC exchange

Solving for $\bar{X}_{Al}$ and $\bar{X}_{BC}$ in equation 4.43 and equation 4.44 respectively, and substituting these quantities into equation 4.45 makes it possible to solve for $\bar{X}_H$ explicitly as:

$$\bar{X}_H = \left(1 + \frac{K_{H/Al}^{\frac{1}{3}} \cdot [Al^{3+}]^{\frac{1}{3}}}{[H^+]} + \frac{K_{H/BC}^{\frac{1}{2}} \cdot [BC^{2+}]^{\frac{1}{2}}}{[H^+]}\right)^{-1} \quad (4.46)$$

The calculated value of $\bar{X}_H$ can now be used with the selectivity equation in order to characterize the exchanger phase completely.

4.3 IMPLEMENTATION AND USE

4.3.1 PROFILE

The equations in the PROFILE model are solved according to the flow sheet in Figure 4.4. Since the ANC production is a function of the ANC itself, an iterative procedure has to be used. ANC is the only variable that can be solved for, with confidence that there is only one solution. In principle, the iteration could have been carried out based on Al or base cations, but due to the inhibiting effects on weathering that these components have, there may very well be many solution to the mass balances of these components. The nitrogen chemistry could also have been solved using iterations, but the possibility to use the analytical solutions available were used. The iterations are carried out with a Regula-Falsi iteration procedure in order to avoid the hazards involved in applying Newton-Raphsons method on these systems of equations.

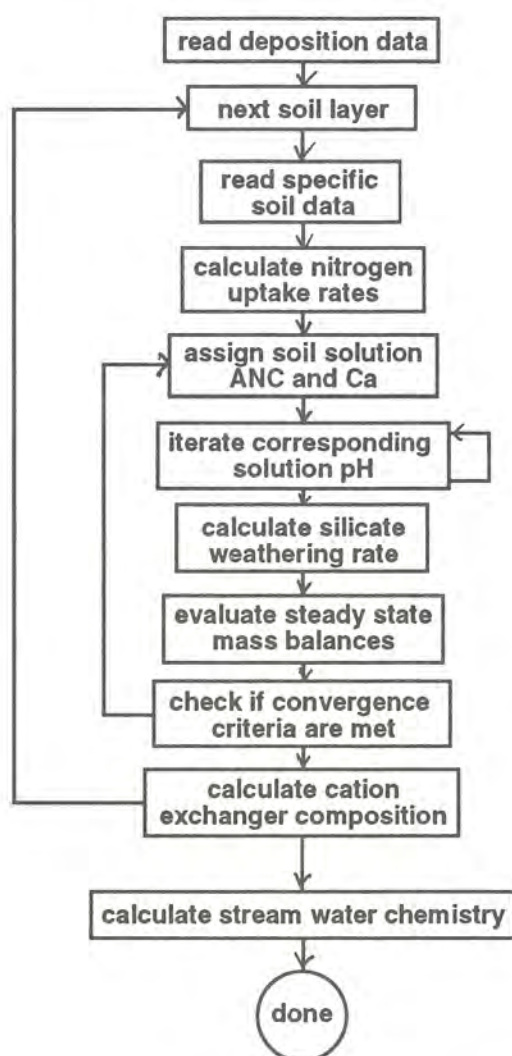


Figure 4.4: Calculation sequence in the PROFILE model.

HD80:PROFILE:BlankStack/v2.3

Stack: BlankStack/v2.3		☒ Do Stream Water	
Run ID: Created: 90-10-18		Soil temperature (C):	
Number of soil layers		Nitrification rate	☐ high
Precipitation rate (m/yr)			☐ medium
Runoff rate (m/yr)			☐ low
Deposition (kEq/ha/yr):			☒ none
SO4 deposition		Go To Card	?
NO3 deposition		Check Input	
NH4 deposition		Import Data	
Total Mg+Ca+K deposition		Run PROFILE	
Non-marine fraction (%)			
Maximum uptake (kEq/ha/yr)			
Mg+Ca+K			
Nitrogen			

HD80:PROFILE:BlankStack/v2.3

Soil layer no:

Soil layer height (m)		☐ K-feldspar	
Moisture content (m3/m3)		☐ Oligoclase	
Soil bulk density (kg/m3)		☐ Albite	
Surface area (m2/m3)		☐ Hornblende	
CO2 pressure (k atm)		☐ Pyroxene	
% of precipitation entering layer		☐ Epidote	
leaving layer		☐ Garnet	
Mg+Ca+K uptake (% of max)		☐ Biotite	
N-uptake (% of max)		☐ Muscovite	
DOC (mg/L)		☐ Chlorite	
log K gibbsite		☐ Vermiculite	
pK H/Al exchange		☐ Apatite	
pK H/Ca exchange			

Figure 4.5: The input data 'forms', as displayed to the user of the PROFILE application for Apple computers.

PROFILE is available as a computer application for Apple Macintosh computers, and requires fractions of a second of computer time. Input data for soil chemistry calculations are entered interactively on two types of screens. On one screen, general data is entered, as shown in the upper part of Figure 4.5. The nitrification rate is selected according to different classes [Sverdrup *et al.*, 1990].

On additional screens, data specific for each soil horizon is given. Mineralogy is chosen from a selection of twelve common groups of minerals. A user's manual with cross-references to the 'Mapping Critical Loads' document further facilitates model use. The computer implementation of the model is available through the authors, easy to use and available free of charge for non-commercial use.

Besides calculating soil and stream water chemistry, the model calculates the BC to Al ratio in the soil solution. This BC:Al ratio is known to serve as an indicator of the potential for forest growth. Also, the model summarizes general results such as total weathering rate in the profile, total uptake of N and base

cations, acidity produced by N cycling and deposition rates expressed according to different conventions.

4.3.2 SAFE

While PROFILE is a very user-friendly, fast-running model, SAFE is rather the opposite. The problem with applying the SAFE model is the execution time, several hours even on the fastest Apple computer. This is mainly because the ion-exchange submodel requires very many iteration steps. Also, the daily hydrological data requires a short time step. For future applications, it will be considered if the diffusion control exchange model can be solved in a more efficient manner. That, together with weekly hydrological data would bring the simulation times down to several minutes rather than hours. Recent test with RISC-processor computers have brought the execution time by a factor 10, implying 30–40 minutes to make a run covering 200 years and 4 layers.

It is very important to make models available to others to test the model further. PROFILE has been distributed to numerous colleges within the time period of the project. SAFE has not been used by others, mainly because the model development has been going on during the whole project period.

4.3.3 Numerical methods

The set of differential equations in SAFE is solved with a set of initial values using a Runge-Kutta-Fehlberg method. This method allows the time-step to be maximized for a desired calculation accuracy and required stability. A fixed time-step would require unnecessary consumption of computation time during periods with little difference between input and output chemistry. The upper limit of the time step would be limited by periods with large values for the differentials, such as when the change in soil moisture content is high. The maximum time-step used can be set by the user, but naturally, it should not be greater than the resolution in input from time series. In many applications, daily hydrological input is used.

One extremely time consuming operation in the models is iteration of the pH-ANC relationship. As pointed out by Schecher and Driscoll (1987), they are not readily solved with normally very efficient root-evaluation methods such as Newton-Rapsons method, which tends to create oscillating solutions. The most reliable method is bisection, where the solution is sought within a predefined interval. In SAFE and PROFILE, the ANC-pH iterations are performed with a modified Regula-Falsi method, which brings the typical number of iterations down to 3 for a relative accuracy of 10^{-6} in H^+ -ion concentration. In the solution strategy, the previous H^+ value is used as the upper limit when the mass balances show that the ANC decreases.

4.4 MODEL TEST

4.4.1 PROFILE

PROFILE was applied to the research site at Gårdsjön in SW Sweden [Olsson *et al.*, 1985]. The model was used to calculate the critical loads of two very similar subcatchments by Lake Gårdsjön, F1 and F3. Input data used for soil chemistry calculations are shown in Table 4.4. At present, the total deposition of all acid precursors, the potential acidity, amounts to $2.44 \text{ keq ha}^{-1} \text{ yr}^{-1}$ [Lövblad *et al.*, 1992]. The contribution of total acidity deposited with SO_4^{2-} is 1.27, NO_3^- is 0.71 while NH_4^+ contribute $0.74 \text{ keq ha}^{-1} \text{ yr}^{-1}$. The total atmospheric base cation input is $0.57 \text{ keq ha}^{-1} \text{ yr}^{-1}$, of which the non-marine part contributes with a net alkalinity input of $0.28 \text{ keq ha}^{-1} \text{ yr}^{-1}$.

Figure 4.6 shows PROFILE calculations performed for the F1 subcatchment. Soil solution data was taken from Giesler and Lundström (1991). For comparison, pH measured in water suspension [Melkerud, 1983] was included in Figure 4.6. While the model calculates a long term value for the soil solution, the measurements represent temporal point data. Therefore the model can be said to describe the annual average conditions in the profile. It is clear, however, that the model exhibits the same spatial pattern as the data with lower pH values in the upper soil layers. The internal acidity input in the O horizon is nitrification and NH_4^+ immobilization, while weathering and NO_3^- are sources of alkalinity in the lower layers. While H and Al are strongly coupled via the pH-ANC relationship and the Al equilibrium system. The value of K_G is therefore an immediate link between pH and calculated Al concentration. To obtain the best values for K_G these were actually calculated from the data. The capability of the model to reproduce pH and Al data is therefore dependent on how well it calculates the ANC.

At present PROFILE cannot present the calculations of different base cations separately because the vertical distribution of the uptake and regeneration of different base cations are not known. The internal circulation is especially important for K. Comparison of calculated BC concentration with measured Ca (Figure 4.6) shows that the two quantities follow the same pattern down through the soil.

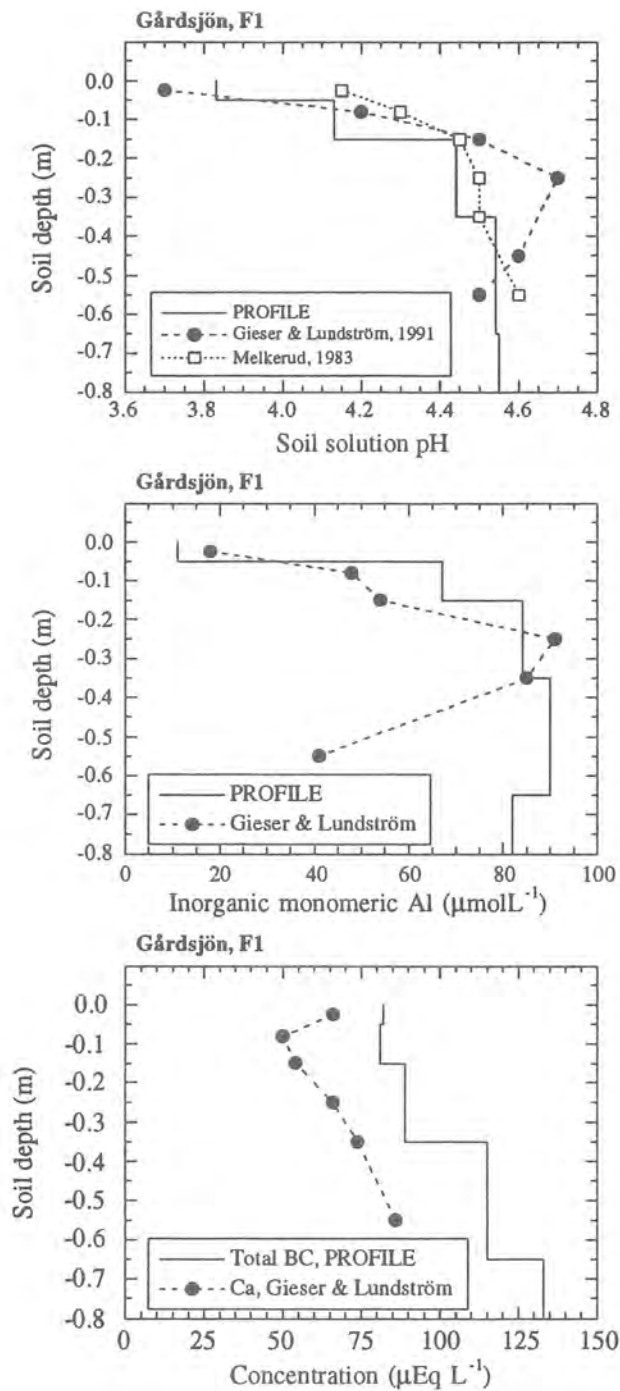


Figure 4.6: Calculated soil solution pH, Al and base cation concentrations compared with data .

Table 4.4: Input data for the Gårdsjön case study. Data sources are 1: [Melkerud, 1983], 2: [Lundin, 1982], 3: [Castelle and Galloway, 1990], 4: [Jacks and Norrström, 1986], 5: [Raben, 1988], 6: [Persson and Broberg, 1985], 7: [Giesler and Lundström, 1991]

Parameter	Unit	Soil layer					Ref
		1	2	3	4	5	
Soil layer height	m	0.05	0.10	0.20	0.30	0.15	1
Moisture content	$\text{m}^3 \text{m}^{-3}$	0.2	0.2	0.2	0.2	0.2	2
Soil bulk density	kg m^{-3}	800	1200	1400	1600	1600	1
Specific surface area	$\text{m}^2 \text{m}^{-3}$	$5 \cdot 10^5$	$1 \cdot 10^6$	$1.5 \cdot 10^6$	$1.7 \cdot 10^6$	$1.7 \cdot 10^6$	1
CO ₂ pressure	times ambient	3	5	10	15	20	3, 4
Inflow	% of precip.	100	90	80	70	61	†
Percolation	% of precip.	90	80	70	61	61	†
Mg+Ca+K uptake	% of total max	20	20	30	30	0	5
N uptake	% of total max	20	20	30	30	0	5
DOC	mg/L	34	76	8	5.9	5.9	5
log Gibbsite const.	$\text{kmol}^2 \text{m}^{-3}$	6.5	8.12	9.05	9.27	9.27	6
Mineral		% of total					
K-feldspar		15	15	18	13	19	
Oligoclase		14	14	12	16	14	
Hornblende		0.1	0.5	0.5	1.5	0.5	
Epidote		0.1	0.5	0.5	1.5	0.5	
Garnet		0	0.1	0.1	0.1	0.1	
Biotite		0	0.1	0.5	0.5	0.5	
Chlorite		0	0.4	0.4	0.4	0.4	
Vermiculite		0	3.0	5.0	0	0	
Quartz		70.9	69.0	65.0	63.0	65.0	

† Pure guess



Figure 4.7: The location of the European sites for testing PROFILE.

4.4.2 Weathering submodel

This section demonstrates the performance of the weathering part of the model, and the results are compared with weathering rates determined with other models and methods. It should be kept in mind that the weathering rates is the output of the PROFILE model, which calculates the concentrations in the solution. The concentrations are then used in the kinetic equations to drive the weathering reactions. This means that the values refer to a state where the mineral matrix has reached a steady-state with the surrounding solution. The dynamic aspect of weathering that the SAFE model implies, is therefore not shown in the calculations. Colleagues in Sweden and other European countries have contributed to this model test, by supplying data for the model, and results from weathering rate determinations done with other methods and models. As many of the data sets are still unpublished, the references to the data sources are given below, rather than in the data section of this report. The location of the sites have been indicated in Figure 4.7.

Test sites and data sources

The input data requirements for a model calculation of the weathering rate in the watersheds at Gårdsjön was available in the literature [Olsson *et al.*, 1985, Hultberg, 1985], and has been described in the test of an earlier version of PROFILE [Sverdrup and Warfvinge, 1988]. The soil matrix particle size distribution was determined at different levels in the soil profile at three locations, in all 26 samples [Melkerud, 1983], and from this material the surface area was calculated according to the procedure in Chapter 8. The present base cation release rate was calculated for the Gårdsjön watersheds using the the PROFILE model based on observed particle size distributions, soil pH values, soil texture, water content and weathering rate coefficients determined in laboratory studies. The average depth of the soil layer is 0.8 meter.

Data from Svartberget in Northern Sweden was supplied by Dr. Kevin Bishop of the Swedish University of Agricultural Sciences at Umeå as well as from the literature [Giesler and Lundström, 1991, Miskovsky, 1987]. Svartberget is located in the province of Västerbotten in northern Sweden, the catchment is covered by a Scots Pine forest. The annual average temperature at the site is 1.8 °C. The weathering rate has been estimated with two methods; the Sr-isotope method developed by Jacks and Åberg (1987), and by estimation of the depletion of Zr and Ti in the soil profile as a measure of the historical weathering rate, and finally by mass balance budget studies [Lundström, 1990]

Data for Høylandet, western Norway, was supplied by Dr. Tore Frogner at the Norwegian University of Agricultural Sciences. The site is located in the mountainous western part of the country, close to the North Atlantic, and has a mountain birch forest. The annual average temperature is 1.5 °C.

Data for Nordmoen was taken from Teveldal *et al.* (1990), Teveldal, (1991) and Wright *et al.* (1991) as well as supplied by Dr. Tore Frogner. The site is situated on a thick glaciofluvial sand deposit formed as a terminal moraine. The site is located north of Oslo in Norway. The vegetation is dominated by Norway Spruce and Blueberry heather in the understory. The site has never been cultivated, and the soil type is an iron-humus podzol or Udipsamment. The weathering rate was estimated based on mineral depletion in the upper 0.25 meter using quartz as the internal tracer.

Data for the catchment at Most, Czechoslovakia was supplied by Dr. Tomas Pačes, Czech Geological Survey at Praha. The site is located in the Erzgebirge, overlooking the Most valley. The site is extremely heavily polluted, and the acid deposition has killed the forest. Today the catchment is covered with dead decomposing trees, faulty grass and stone rubble. Pačes (1985) measured the weathering rate for Na, K and Si in the X-14 catchment, by mass balancing. The weathering of Ca and Mg was estimated from the soil mineralogy and plagioclase composition at the site, to be in the range 0.50-0.70 keq Ca ha⁻¹ yr⁻¹ and 0.10-0.20 keq Mg ha⁻¹ yr⁻¹ respectively. Three points are entered in the diagram for this site, the weathering rate of Na, K and total rate.

Data for Aubure, in Alsace, France was supplied by Dr. Etienne Dambrine, of the Institute for Forest Research at Nancy, France. The site is located on the southwestern slope of the Vosges mountains in Alsace, and covered by a Spruce forest.

Data for the geophysical properties of the rock-carving in Bohuslän, southwestern Sweden were supplied from unpublished notes by Dr. Gunnar Jacks of the Department of Land and Water Resources at The Royal Institute of Technology at Stockholm. The rock-carving, located in the Province of Bohuslän in Sweden, dating from the Middle Bronze Age, the carvings are estimated to be approximately 3.200 years old. The carving studied was investigated for increased weathering due to exposure to rain of increasing acidity. The carving is located on a flat polished sloping side of exposed bedrock, facing southwest, depicting ships, people, cupmarks and different objects and symbols of the Bronze Age cult. The rock is a gneiss, composed of feldspar, plagioclase and biotite. Water is running over the rock from the top.

Data for Risfallet and Masbybyn was supplied from the results of the field activities of this project. Two points are entered for the Risfallet site, representing

measurement of the rate at two different depths, 1.0 and 2.0 meter [Sverdrup and Warfvinge, 1991].

Data for the site at Mharcaidh in the Scottish uplands was supplied by Dr. Derek Bain of the Macaulay Institute in Scotland [Bain *et al.*, 1990]. Data for Woods Lake in the Adirondack Park was taken from the literature published in the ILWAS study [Chen *et al.*, 1983, Cronan, 1984, April, 1984, April *et al.*, 1986]. At Woods lake the weathering rate was measured by studying the depletion of minerals in the soil profile, and the present weathering rate was estimated to be close to the historic rate [Cronan, 1984].

Data for the Maryland sites were taken from the Maryland Critical loads Mapping Project [Sverdrup *et al.*, 1992]. The weathering rate was estimated from mass balances and the assumption that the sites were at steady state with the present deposition input of acidity and base cations. The weathering rates in large excess of the present acid deposition rate.

A summary of the mineralogy at the sites are shown in Table 4.5, the texture is in 4.6, and climatical and vegetation input data has been listed in Table 4.7.

Table 4.5: The mineralogy of the soils used in the test of the model.

Legend:

Kf: K-feldspar; Pl: Plagioclase; Al: Albite; Ho: Hornblende;

Py: Pyroxene; Ep: Epidote; Ga: Garnet; Bi: Biotite;

Mu: Muscovite; Ch: Chlorite; Ve: Vermiculite; Ap; Apatite

Location	Kf	Pl	Al	Ho	Py	Ep	Ga	Bi	Mu	Ch	Ve	Ap
Gårdsjön F1,F2, S	18	12	-	0.5	-	0.5	0.1	0.5	-	0.4	5	0.35
Gårdsjön F3, S	18	12	-	0.5	-	1.5	0.1	0.5	-	0.4	5	0.35
Svartberget, S	7.6	16	-	7.7	-	2	-	-	-	2	4	0.4
Rock carving, S	30	59	-	-	-	-	-	-	1	-	-	-
Risfallet, S	25	26	-	3.5	-	-	-	-	-	0.5	-	0.1
Masbyn, S	27	23	-	1.1	-	-	-	-	-	1.1	-	0.4
Fårahall, S	29	28	-	4	-	-	-	3	-	-	5	0.3
Höylandet, West N	3.5	20	-	0.6	8.6	2.9	-	-	-	3.5	-	-
Nordmoen, East N	7.7	12.8	-	4.0	-	-	-	-	21.3	15.4	10	0.1
Aubure, France	8.0	-	4.0	-	-	-	-	-	4.0	-	-	0.1
Marchaidh, Scotland	25	40	-	-	-	-	-	-	-	-	5	-
x-14, Most, CS	9	20	-	-	-	-	-	2.5	5	2.5	7	-
Woods lake, NY	31	10	-	2	0.4	0.5	0.6	3.6	-	-	-	-
Anne Arundel C'ty,MD	2.1	2.9	-	0.01	-	0.02	-	-	12.4	-	-	9.5
Queen Anne C'ty,MD	6.0	7.0	-	0.12	0.03	0.01	-	-	7.4	-	-	7.6
Washington C'ty,MD	2.2	14	-	0.25	-	10.2	-	-	4.7	-	-	16.7
Wicomico C'ty,MD	4.1	3.6	-	0.06	0.02	0.01	-	-	7.2	-	-	10.0

Table 4.6: The texture of the soils, expressed as million m² per m³ soil.

Location	O-layer	E-layer	B-layer	C-layer
	10 ⁶ m ² /m ³ soil			
Gårdsjön F1,F2, F3 Sweden	0.08	1.0	1.5	1.7
Svartberget	0.03	0.8	0.9	1.2
Rockcarving, Bohuslän	0.01	-	-	-
Risfallet	0.04	0.2	0.66	0.66
Masbyn	0.36	0.6	0.7	0.8
Fårahall	0.47	0.71	0.88	0.9
Höylandet	1.7	1.7	2.1	2.2
Nordmoen	0.13	1.3	1.0	1.0
Aubure, France	0.01	1.9	2.6	3.1
Mharcaidh, Scotland	0.5	0.7	0.64	0.56
x-14, Most, Czechoslovakia	0.5	2.0	2.0	1.5
Woods lake, NY	0.5	1.5	2.0	1.5
Queen Anne County, Maryland	0.5	3.7	5.2	3.0
Anne Arundel County, Maryland	1.0	4.0	5.8	5.0
Washington County, Maryland	0.5	3.9	4.3	2.7
Wicomico County, Maryland	0.3	3.0	4.4	2.8
Aubure, France	0.01	1.9	2.6	3.1
Mharcaidh, Scotland	0.5	0.7	0.64	0.56

Table 4.7: Climatic and vegetation input data.

Location	Precip.	Runoff	S	NO ₃	NH ₄	BC	BC	N	Temp.
	m/yr			Deposition		Uptake			°C
				keq ha ⁻¹ yr ⁻¹		keq ha ⁻¹ yr ⁻¹			
Gårdsjön F1,F2, F3, S	0.9	0.55	1.5	0.6	0.6	0.75	0.5	0.7	6.0
Svartberget	0.72	0.37	0.37	0.13	0.13	0.13	0.08	0.15	1.8
Rock carving, Bohuslän	0.9	0.55	1.5	0.6	0.6	0.75	0.5	0.7	6.0
Risfallet	0.55	0.22	0.58	0.25	0.22	0.14	0.2	0.5	4.8
Masbyn	0.55	0.22	0.7	0.21	0.22	0.14	0.18	0.41	4.8
Fårahall	1.05	0.45	1.82	0.71	0.56	0.67	0.4	0.5	6.5
Höylandet	1.6	1.3	0.17	0.12	0.14	0.83	0.15	0.25	1.5
Nordmoen	0.78	0.41	0.8	0.31	0.31	0.19	0.4	0.61	4.3
Aubure, France	0.86	0.66	1.44	1.98	1.6	2.1	1.58	2.56	6.0
Mharcaidh, Scotland	0.92	0.86	0.7	0.16	0.10	0.55	0	0	5.5
x-14, Most, CS	1.0	0.43	7.5	1.0	1.0	0.7	0.3	0.2	10.0
Woods lake, NY	1.2	0.75	1.4	0.28	0.21	0.31	0.5	0.55	6.5
Queen Anne C'ty, MD	0.97	0.35	0.89	0.31	0.18	0.24	0.1	0.2	13.3
Anne Arundel C'ty, MD	0.97	0.35	0.85	0.32	0.19	0.22	0.61	1.1	11.0
Washington C'ny, MD	0.98	0.33	1.01	0.35	0.17	0.14	0.88	0.65	11.4
Wicomico C'ty, MD	0.9	0.35	0.69	0.26	0.21	0.27	-0.78	0.35	12.4

Results

The results of the calculation for the catchments at Gårdsjön are shown in Table 4.8. We have compared the total base cation weathering rates as calculated with the model with the rates obtained using the conventional mass balance approach. The calculated rate values correlate well with the observed values, and the observed difference is within the limits caused by uncertainty in input data. In addition, Table 4.9 gives the weathering rate calculated for each base cation separately.

The results of the calculation made for the different sites are shown in Figure 4.8. It can be seen that the correlation between the calculated values and the values estimated by other independent method is excellent. In general the agreement is within $\pm 0.1 \text{ keq ha}^{-1} \text{ yr}^{-1}$. There is a bias toward a slight over-estimation at high weathering rates. We believe this to be a result of the uncertainty in the kinetic information available for epidote and phosphorous minerals in the soil. In the model, all phosphate in the soil is assigned to apatite, and obvious simplification. The field weathering estimates along with the method of estimation has been summarized in Table 4.4.2. For several of the sites, multiple estimates by independent methods exists.

The Maryland site with the highest rate, $15.8 \text{ keq ha}^{-1} \text{ yr}^{-1}$ is not included in Figure 4.8. Here, a rate of $18.2 \text{ keq ha}^{-1} \text{ yr}^{-1}$ is calculated. The mineralogy at this site is dominated by epidote, and the observed discrepancy could be due to errors in the rate coefficients for epidote weathering kinetics.

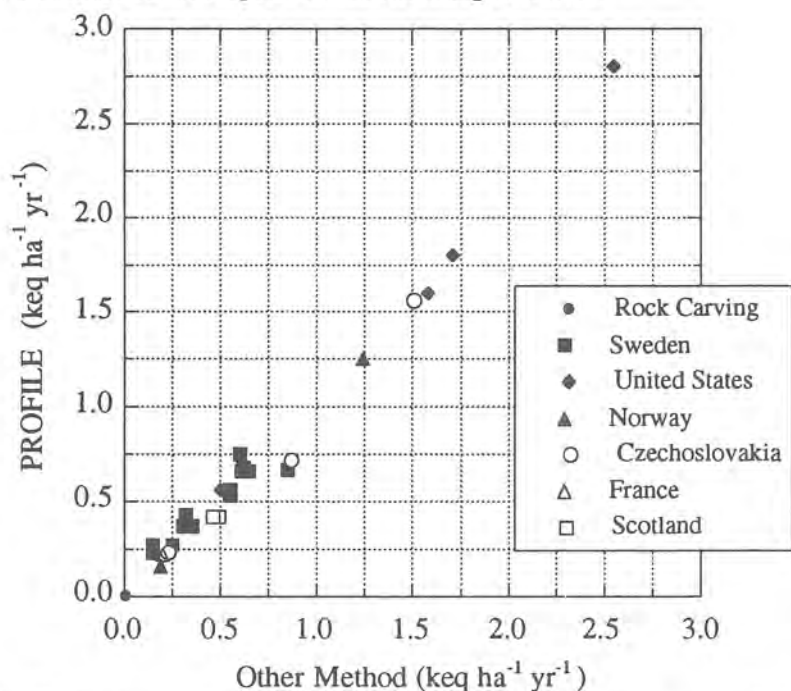


Figure 4.8: The comparison between the weathering rate calculated for 15 European and American sites as compared to the estimated weathering rate using other methods.

Table 4.8: Model calculation of base cation release due to chemical weathering in catchment F3 in the Gårdsjön area. The figures reflect the total flux produced. The average depth of the soil layer is 0.6-0.8 meter, and the maximum depth 2.1 meter.

Minerals	Base cation production			Catchment rate keq ha ⁻¹ yr ⁻¹	Base cations
	0-30 cm	30-60 cm	60-90 cm		
	keq ha ⁻¹ yr ⁻¹				
Microcline	0.02-0.04	0.04-0.08	0-0.01	0.03-0.05	K
Plagioclase	0.12-0.17	0.13-0.28	0.10-0.14	0.12-0.24	Na,Ca
Hornblende	0.20-0.34	0.15-0.20	0.06-0.08	0.17-0.26	Ca,Mg
Epidote	0.14-0.16	0.10-0.15	0.06-0.08	0.12-0.19	Ca
Sum	0.38-0.71	0.42-0.71	0.22-0.31	0.44-0.75	Na, Ca, Mg, K

Table 4.9: Base cation release rates from budget studies compared chemical weathering rate calculated with the PROFILE and total-analysis correlation model [Olsson and Melkerud, 1990, Sverdrup *et al.*, 1990].

Catchment	Ca	Mg	K	Na	Sum	Method
			keq ha ⁻¹ yr ⁻¹			
Catchment F1	0.21-0.46	0.42-0.46	0.02-0.11	0.03	0.64-1.06	Budget study
	0.22	0.22	0.25	0.12	0.81	Zr depletion
	0.27	0.17	0.10	0.05	0.59	TA-correlation
	0.18	0.32	0.12	0.04	0.66	PROFIL model
Catchment F2	0.18-0.43	0.21-0.27	0-0.07	0.03	0.43-0.80	Budget study
	0.32	0.14	0.11	0.07	0.64	TA-correlation
	0.24	0.30	0.10	0.04	0.68	PROFILE model
Catchment F3	0.19-0.44	0.19-0.25	0-0.07	0.03	0.40-0.79	Budget study
	0.32	0.23	0.10	0.02	0.67	TA-correlation
	0.40	0.20	0.11	0.04	0.75	PROFILE model

Table 4.10: The observed weathering rates and the methods used for determination.

Site	Method	Rate observed keq ha ⁻¹ yr ⁻¹	Soil depth meter	Normalized rate to 1 m keq ha ⁻¹ yr ⁻¹
Gårdsjön	Al-budget study	0.65	0.8	0.81
Gårdsjön	Budget, steady state	0.49-0.88	0.8	0.61-1.10
Gårdsjön	TOTAL model	0.63	0.8	0.80
Gårdsjön	Historic rate, Zr enrich.	0.85	0.8	1.0
Gårdsjön	Historic rate, Zr enrich.	0.81	0.8	1.00
Gårdsjön	Historic rate, Quartz enrich.	0.16-0.32	0.4	0.04-0.8
Gårdsjön	Base mineral index	0.34-0.90	0.8	0.44-1.13
Gårdsjön	Mineralogy correlation	0.40-0.80	0.8	0.50-1.0
Gårdsjön	Henriksen model	0.09-0.69	0.8	0.01-0.86
Svartberget	Historic rate, Zr enrich.	0.31	0.80	0.39
Svartberget	Ca budget study	0.85	0.80	1.00
Svartberget	Sr isotope	0.35	0.80	0.44
Rockcarving	Mass balance, steady state	0.007	-	-
Risfallet	Sr-isotope	0.25	1.00	0.25
Risfallet	Si-Budget study	0.55	2.00	0.27
Risfallet	Historic rate, Zr enrich.	0.15	1.35	0.11
Masbyn	Si-Budget study	0.55	2.00	0.27
Masbyn	Historic rate, Zr enrich.	0.15	1.35	0.11
Fårahall	Historic rate, Sr-isotope	0.60	1.1	0.54
Höylandet	Sr-Isotope	1.24	1.00	1.24
Nordmoen	Historic rate, Quartz enrich.	0.19	0.25	0.76
Aubure	Historic rate, Quartz enrich.	0.20	0.50	0.40
Mharcaidh	Zr-enrich.	0.46	1.0	0.46
Mhardaidh	Sr-isotope	0.49	1.0	0.49
Most, x-14	Mass balance Na	0.87	1.40	0.62
Most, x-14	Mass balance K	0.20	1.40	0.14
Most, x-14	Ca+Mg+Na+K mass bal.	1.51	1.40	1.08
Woods Lake	Historic rate, mineral depl.	0.50	1.00	0.50
Washington C'ty, B-007	Mass balance, steady state	18.5	2.26	8.19
Queen Anne C'ty, N-009	Mass balance, steady state	2.55	2.05	1.24
Anne Arundel C'ty, N-020	Mass balance, steady state	1.58	1.32	1.20
Wicomico County, S-004	Mass balance, steady state	1.71	1.60	1.07

Discussion

The weathering rate in nature is determined by the abundance of weatherable minerals and their texture in the soil. The PROFILE model represents the first tool available for estimation of the weathering rate from independent data on geochemistry and soil conditions. It can also be applied on a regional scale simply by collecting data from as many sites within a region that is necessary to represent the areal distribution of soil mineralogy, texture other key parameters such as soil moisture conditions. A few minerals in the soil are of major controlling importance for the weathering rate in the field, as compared to other minerals;

- Epidote
- Hornblende
- Plagioclase feldspars

In non-glaciated, old soils, primary minerals such as pyroxene and biotite may sometimes play a minor role. Secondary minerals of some importance are vermiculite, chlorite and illite. It is our experience from surveying the mineralogy in both glaciated regions (Denmark, Sweden, Norway) and unglaciated regions (Maryland) that epidote is present everywhere, but almost always in small amounts. Often it can be shown that the three mineral listed above account for 75% or more of the observed weathering rate in any type of soil. Biotite and vermiculite, on which much effort has been spent, is of little or no significance for the weathering rate at a vast majority of the sites, a fact that stand out beyond any doubt. This should perhaps lead to some reconsideration of all the research resources spent on biotite, chlorite and vermiculite as well as the already well documented feldspars, while the significantly more important minerals epidote and hornblende, have received little attention so far.

The different weathering reactions depend on state variables such as soil solution concentrations of Al, base cations, pH, dissolved inorganic carbon and dissolved organic carbon. These solution concentration effects can be summarized as:

Substance	Effect
H ⁺	Increase
Al ³⁺	Decrease
Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺	Decrease
CO ₂	Increase
Organic acids	Increase

Quantitatively the effects are different for different types of minerals [Sverdrup, 1990], minerals rich in aluminium react stronger to dissolved Al than those poor in Al, and the same applies to base cations. However these factors will all interact in the natural environment, and the net result of for instance the pH dependence may not be the same as in the laboratory. In the field the effect of pH may be

pronounced, but this may also be overwhelmed by the effects of other factors such as Al or organic acids. Under certain circumstances where much aluminium or base cations are produced in the soil, this may overrule the effect of pH and the weathering rate may decrease.

The whole question of the dependence of the weathering rate on soil pH must be carefully handled when such a relationship is sought for in field data, since the two are not independent of each other. The soil pH is a result of the balance between sources of acidity and sources of alkalinity in the soil, where weathering is a major part of the alkalinity source. Accordingly the pH of the soil may be dependent on the weathering rate as well as the weathering rate depending on the soil pH. This implies that if the observed field rate, incorporating different textures and mineralogies are plotted versus soil pH, we would find an increase in weathering with increasing soil pH.

The rate coefficients published here are not consistent with most rate coefficient values found in the literature. By rephrasing published rate equations, it has been possible to develop rate equations that are more general, so that the influence of many factors can be modeled simultaneously. Due to the complexity of weathering kinetics, certain assumptions have led to premature conclusions. For example, in several earlier theories and earlier experimental studies, it was not recognized that CO_2 reacts with minerals in a separate and independent chemical reaction with the mineral. For some minerals this will make a difference on the rate of more than one order of magnitude. The earlier studies were at times inconsistent, comparing the dissolution rates of minerals with the same geological classification, but with significantly different chemical composition. Inconsistencies concerning the use of dry sieved mineral samples, washed samples, non-sieved crushed minerals as compared to rates based on the total exposed surface area as measured by the BET method, has muddled the comparative studies significantly, prohibiting proper rate coefficient evaluation, or their usefulness in comparison with rates observed in the field [Paçes, 1983, Velbel, 1985] as rate coefficients obtained under conditions not applicable to field conditions were used. It was not always recognized that several organic ligands used to keep the pH value constant during experiments, react with the minerals. If different buffers are used in a series of dissolution experiments, then each organic ligand will react differently with the mineral, and no clear interpretation can be made of the results. Several studies were never carried all the way to long term steady state dissolution.

In summary the discrepancy between the face value of the laboratory rate and the field rate may add up as shown in Table 4.4.2. Multiplying the difference factors for the typical case would when compared at face value, give a ratio between experimental laboratory rate and field rate of 96–80 000, 2–5 orders of magnitude, depending on the conditions.

Table 4.11: The effect of different conditions on the weathering rate in the laboratory as compared to apparent field rates.

Factor	Effect on weathering rate	Cumulative effect on weathering rate
Buffers	1-10 times increase	1-10
Freshly ground	2-5 times increase	2-50
Temperature	1-15 times increase	2-750
Partial wetting	4-7 times increase	8-5.000
CO ₂ overpressure	1-15 times increase	8-80.000

Conclusions

Several conclusions may be made from the present study, and some with consequence for further research efforts in the field. From the present analysis of kinetic data, field data and model assessment it may be concluded that:

- The PROFILE model can be used to calculate the weathering rate from independent geophysical and geochemical input data with an accuracy of $\pm 15\%$.
- There is full consistency between field rate and laboratory weathering rates when the differences between field and laboratory in chemical and physical conditions are properly accounted for.
- Plagioclase feldspar, hornblende and epidote weathering account for 85% of the rate observed in most soils, and apatite play an important role at certain sites.
- In soil mineral weathering models it is necessary to incorporate the weathering rate as dependent on the chemical and physical conditions, in order to take the interaction with other processes into account.
- Mechanistic models are necessary for interpreting the significance of observed field weathering rates in relation to different hypothesizes concerning single processes and mechanisms.

It is also a consequence of our observations and conclusions, that future kinetic research on silicate minerals should emphasize hornblende and epidote, and that minerals like biotite, chlorite and feldspars are given less attention, as they are either already well documented (feldspar) or without significant importance for weathering in the natural soil.

4.4.3 SAFE

In order to test the performance of SAFE, the model was applied to sites on Linderödsåsen (see Chapter 2) in southern Sweden where historical data for exchangeable bases is available. Two podzol sites and one cambisol site were selected from the ten profiles studied earlier in 1949 and 1984 [Falkengren-Grerup *et al.*, 1987]. The selected sites were those where available data with high confidence could be related to different soil layers, thereby lending themselves to a modelling exercise. All details covering site description, input data and assumptions have been given in 'Modeling Long-Term Base Supply to Acidified Forest Stands' [Warfvinge *et al.*, 1992].

Site Skåne 2

The data for this site indicate that more than 50% of the exchangeable bases were depleted between the soil samplings in 1949 and 1984. The data exhibit consistent changes down through the soil profile. As shown in the model output diagrams (Figure 4.9), the changes are reproduced in detail by SAFE, following calibration by means of adjusting the base saturation value for 1840. The calculations suggest a decrease reflecting the depletion of base cations caused by the increased acid deposition. Following the clear cutting in 1985, the nutrient supply in the O-layer will be regenerated due to mineralization of biomass. In the model, mineralization leads to production of Ca, Mg and K. The basic assumption, however, is still that all nitrogen is immobilized, and therefore no acidity is produced from nitrogen mineralization. In lower soil layers SAFE predicts that the base saturation will continue to decrease. This will lead to almost complete depletion of nutrient base cations in the lower parts of the root zone. During the end of simulation period, the system enters into a phase with rather stable conditions, as the deposition is constant since 1985, and the stand begins to mature.

Based on measured mineral surface area, mineral composition and the calculated soil solution chemistry, SAFE calculates the total production of Ca, Mg and K from mineral weathering to be within 0.55 and 0.60 keq ha⁻¹ yr⁻¹ (55–60 mEq m⁻¹ yr⁻¹) during the simulation period. The production of ANC from weathering is higher, 0.75 keq ha⁻¹ yr⁻¹. The difference is due to weathering of Na rich minerals, primarily oligoclase. The only significant increase in weathering rate occurs during the period with a drop in soil solution pH during the 70's and 80's, prior to the clear cutting in 1984. The weathering rate at Site 2 is thus quite insensitive to changes in soil chemistry. After the removal of the forest cover, the deposition rate decreases allowing a recovery in base saturation to occur because of the base cations released from mineralization of root and soil biomass.

Figure 4.10 shows the whole profile base saturation, calculated as a weighted mean value:

$$\bar{X}_{BC} = \frac{1}{\sum_i^{layers} CEC_i \cdot z_i} \cdot \sum_i^{layers} CEC_i \cdot z_i \cdot \bar{X}_{BC,i} \quad (4.47)$$

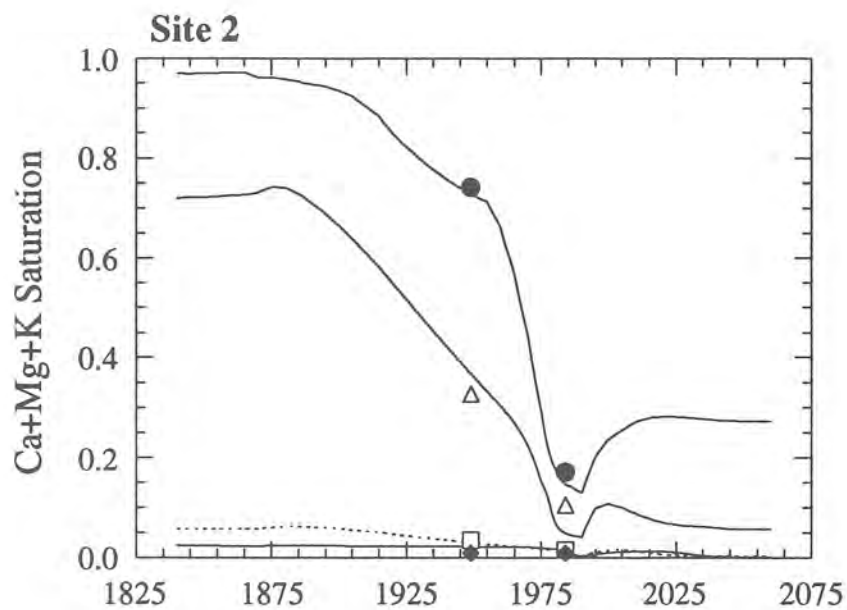


Figure 4.9: Simulated and measured Ca+Mg+K saturation at Site 2 for 4 soil horizons.

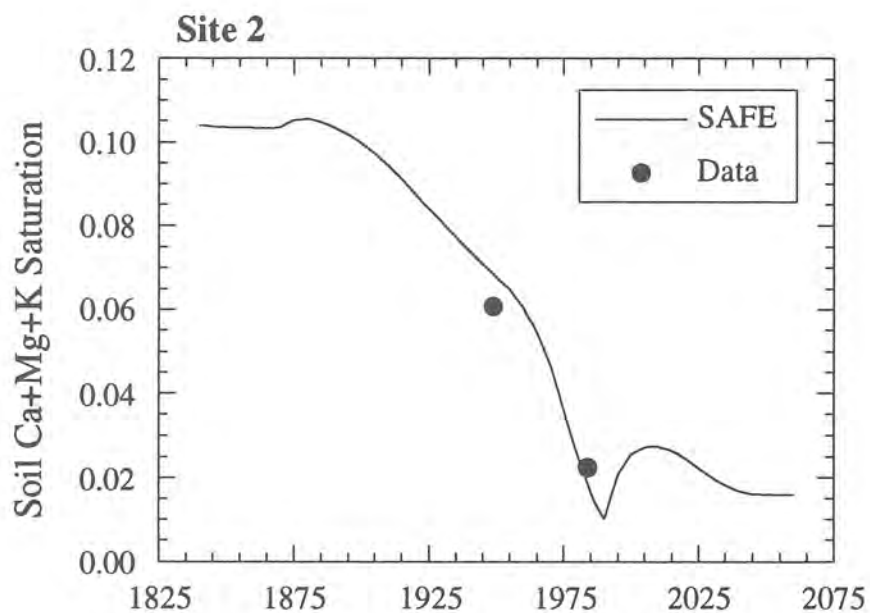


Figure 4.10: Weighted simulated and measured Ca+Mg+K saturation at Site 2.

Site Skåne 4

Skåne 4 is a heathland site on a poor soil with respect to mineral composition. Starting at a moderate level, a decline in Mg+Ca+K saturation by 40% was recorded over 35 years, between 1949 and 1984 (Figure 4.11).

One problem with applying SAFE to this site was the lack of data for the upper soil layer. A top, 10 cm layer was added on to the documented part of the soil profile. It was given the same characteristics as the second layer with respect to total exchangeable pool size. Since the pool size of exchangeables in the upper layers was very low as compared to the total amount of base cations, this does not have an important impact on the development in total base saturation in the profile.

As shown in Figure 4.11, SAFE reproduces the general trend in base saturation, but the model overpredicts base saturation in 1949 while 1984 values are underpredicted. This is due to the observed change for the third soil layer. Data suggests that the base saturation actually increases slightly, a phenomena that cannot be given an interpretation with the SAFE model.

The weathering at the site is calculated to $0.41 \text{ keq ha}^{-1} \text{ yr}^{-1}$ with a slight increase during the most acidic conditions.

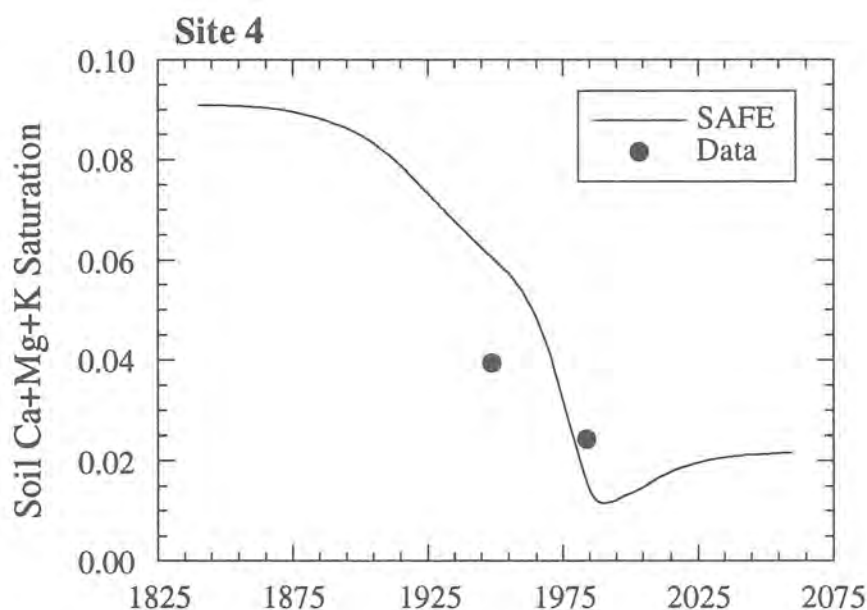


Figure 4.11: Calculated and simulated base cation status at Site 4.

Site Skåne 7

This spruce sites exhibits a significant drop in base cation saturation of 1949 to 1984 period, and the SAFE model results agree with the observed trend on a whole profile basis (Figure 4.12). The clear cutting in 1965 leads to a period of no acidification lasting less than 5 years, after which the deposition increases due to forest filtering. The calculations for all three sites clearly suggest that soil acidification is a phenomena dating back to the turn of the century, rather than a consequence of the accelerated industrialisation beginning in the 1930's.

The model predicts that the base saturation will continue to decline during the next spruce generation. After an assumed clearcutting in 2045, the base saturation may well start to increase again. The weathering rate for the soil column was calculated to $1.0 \text{ keq ha}^{-1} \text{ yr}^{-1}$, and the production of Ca, Mg and K to $0.78 \text{ keq ha}^{-1} \text{ yr}^{-1}$.

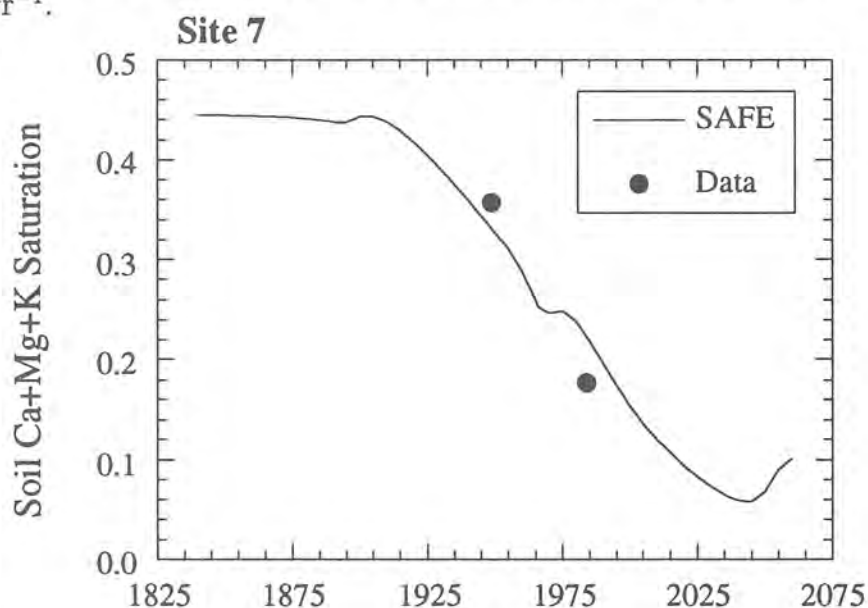


Figure 4.12: SAFE calculations and data for Site 7.

5 SENSITIVITY ANALYSIS

(P. Warfvinge and P. Sandén)

Analysis of model sensitivity is a very important component of a model development process. It helps keeping the model simple because it reveals model parameters with insignificant effect on the results. It is also a tool to identify interaction between model components and parameters. In this case, where two relatively complex models are integrated, the sensitivity analysis will help us to identify the stability of the results in relation to the uncertainty of our assumptions. It will also show how errors from one model is effecting the output of the other.

A major working hypothesis within the project has been that hydrological processes affect the rate of soil acidification, and hence the sensitivity of groundwater to acid deposition. Intuitively, it appears reasonable that the magnitude and temporal dynamics of the water flux should affect the fluxes and concentrations of species dissolved in water. Also, it is clear from surface water studies that temporal variations in stream chemistry can be explained to a large degree by hydrological variations [Whitehead *et al.*, 1984].

An additional objective with the sensitivity analysis is to examine the effect of resolution in the hydrological input on the hydrochemical predictions. Many acidification models operate with constant precipitation and temperature data. Examples of such models are MAGIC [Cosby *et al.*, 1985] and SMART [de Vries *et al.*, 1989], which have been developed with the specific objective of addressing regional aspects of acidification, rather than to be applied to particular sites. Others, ILWAS [Chen *et al.*, 1983], BIRKENES [Christoffersen *et al.*, 1982] and WAM [Booty, 1983], actually started as hydrological models to which hydrochemical modules were added. All these models were developed for specific sites, and a dynamic hydrological component was found necessary to reproduce available data. These models work with daily time steps and have been used to calculate seasonal variations as well as long term predictions under different deposition scenarios. These have the capacity of predicting ecological effects due to short-term variations in chemical conditions. Such models can therefore be used to give "early warning" informations for threatened ecosystems.

A sensitivity analysis can be performed in many ways. Model parameters may be varied one at a time, keeping all other parameters at a reference value, to single-out the effect of a single entity. Complete sets of model parameters can also be generated by random sampling from defined distributions [Downing *et al.*, 1985]. The advantage with the former strategy is that the effect of specific assumptions becomes quite clear, which is an asset in the model development process. However, a disadvantage is that the additive effect of all uncertainties involved is lost, which may lead to an underestimate in variance, depending on the distribution of model parameters. On the other hand, defining the distribution of parameters generally involves a significant amount of guess work under any conditions.

The hydrochemical calculations in this section are not identical to the calculations presented in Chapter 6 where more emphasis is put on predictions of groundwater acidification. This is a result of the experience from this sensitivity analysis.

5.1 SENSITIVITY OF THE HYDROLOGICAL MODEL

5.1.1 Range of variability of conditions

The basis for the sensitivity analysis was the determination of reasonable ranges of variability of the hydrological conditions. In order limit the amount of computations the ones that were considered to be most significant of these were selected and summarized in a scheme of 14 hydrological simulations. They are also used to study the sensitivity of the hydrological variables on the hydrochemical model.

There is only a limited number of parameters and input data in the hydrological model that can introduce uncertainty. The soil moisture routine of the modified PULSE model has only three parameters (field capacity, wilting point and the α -parameter in the exponential reduction of potential evapotranspiration). These parameters can be obtained from measured properties of the soil profile. Precipitation is the most important input data to the model.

Table 5.1 presents the chosen parameter set for the different simulations representing the Stubbetorp reseach site. The effect of the water below wilting point (WP) was tested by doubling and removing the parameter (Simulation 2 and 3). The effect of field capacity (FC) was analyzed by increasing and deceasing the plant available water (FC-WP) by 20 % (Simulation 4 and 5).

Table 5.1 Parameter values used in the different simulations for Stubbetorp. Simulation 1 is used as reference and in all instances where no value is presented, the values from simulation 1 are valid. FC, Σ FC, WP and Σ WP are all expressed in mm.

No.	FC				Σ FC	WP				Σ WP	CPREC	Distr. of evap.tr.	Soil temp. damp./lag
	O	E	B	C		O	E	B	C				
1	27	23	149	55	254	2	2	15	5	24	1.0	exp	$\alpha=6$
2	25	21	134	50	230	0	0	0	0				
3	29	25	164	60	278	4	4	30	10				
4	22	19	122	45	208								
5	32	27	176	65	300								
6												alt.	
7	26	19	149	88	282								
8											1.3		
9											0.7		
10													10 d forw.
11													10 d backw.
12													$\alpha = 3$ m
13													$\alpha = 12$ m
14													$\alpha = 1$ m

The exponential function that describes the decreasing potential evapotranspiration does not completely fit the literature data. It was therefore decided to test another function, which showed a better resemblance with the data on root density (Simulation 6). This function is of the same type as the one used for soil temperature:

$$PET_i = PET \cdot \frac{\left(1 - \frac{l_i}{\alpha \cdot l_i}\right) \cdot s_i}{\sum_{j=i}^n \left(1 - \frac{l_j}{\alpha \cdot l_j}\right) \cdot s_j} \quad (5.1)$$

where PET = monthly values of potential evapotranspiration

n = number of soil layers

l = depth to the middle of the soil layer

s = thickness of the soil layer

α = an empirical coefficient.

In the early stage of model testing the field capacity for each horizon were calculated using a fixed pF value (1.7) for all horizons. As the pF-value at field capacity depends on the distance to the groundwater, the top horizons reach field capacity at a higher pF than the bottom horizon. As an alternative, the field capacity was therefore calculated from a long term average of the groundwater levels, using different pF values at the different horizons (Simulation 7).

The sensitivity to precipitation was tested by changing the precipitation correction (CPREC) by $\pm 30\%$ (Simulation 8 and 9).

The sensitivity analysis of the temperature model is discussed in Chapter III.5 (Simulation 12 and 13). In addition to that analysis a 10 day shift of the temperature curve was tested (Simulation 9 and 10), and an extreme damping (Simulation 14)

5.1.2 Results

Figure 5.1 presents the results from changing plant available water by $\pm 20\%$ and using a more realistic pF value for the calculation of FC. These different ways of estimating FC only affect the level, while the variation pattern stays the same. Recalculation of FC using variable pF with depth have a large impact on the level in E and C horizons. The FC increase in the C horizon and decrease in the E horizon, which determines the maximum level of soil moisture content in the model. Changing the plant available water by $\pm 20\%$ has a fairly large effect on the level of soil moisture content. This change in FC represents a realistic level of uncertainty considering the laboratory estimates of pF, the fixed groundwater table and the heterogeneity on a basin wide scale.

Changing the precipitation volume by $\pm 30\%$ has a fairly small effect on the soil moisture content (Table 5.1). The largest difference can be seen during the dry summer 1988.

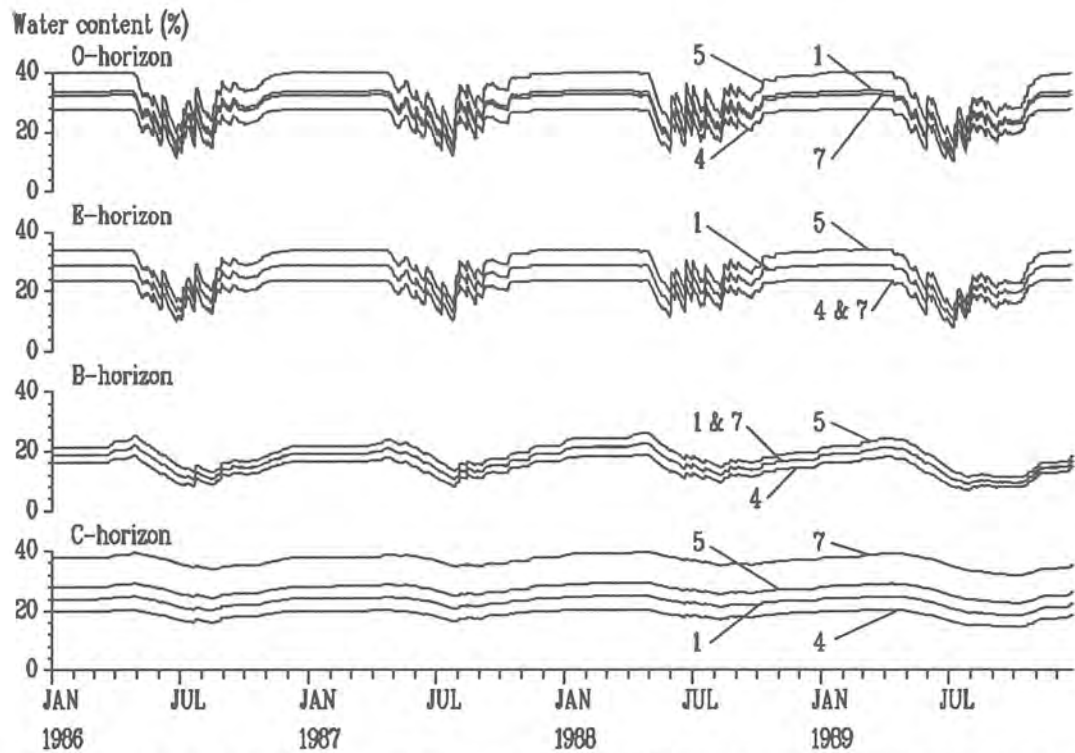


Figure 5.1 Model sensitivity to changes in the FC-parameter. Base simulation (1), -20% FC-WP (4), +20% FC-WP (5) and fixed groundwater table (7).

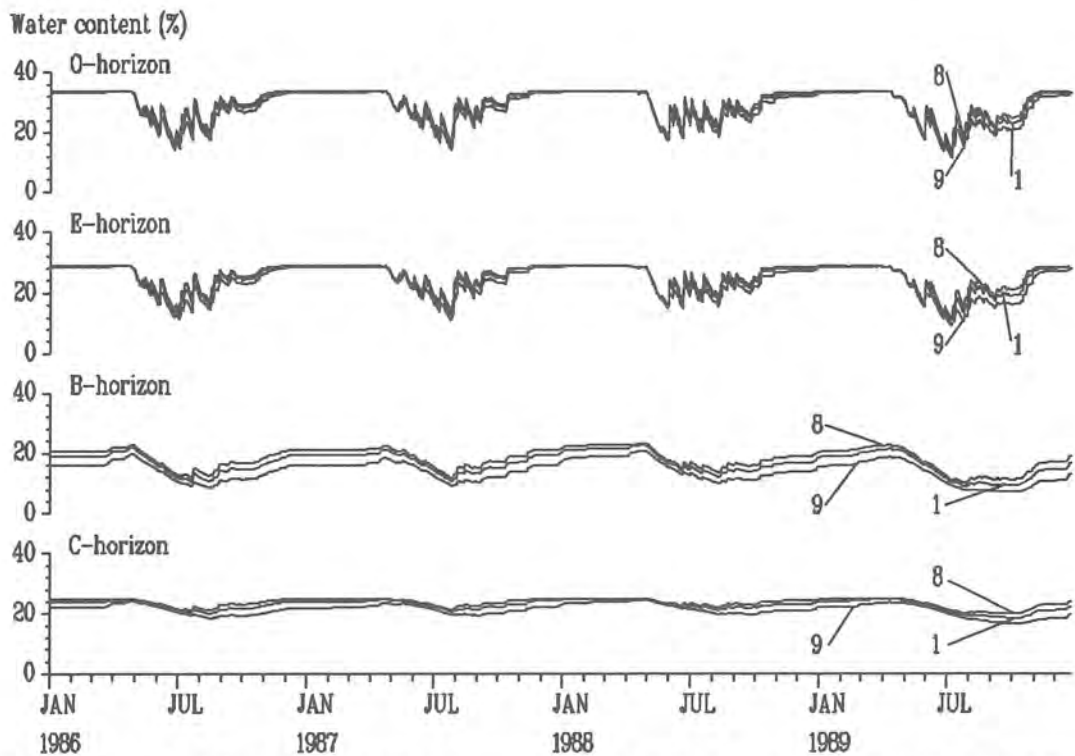


Figure 5.2 Model sensitivity to change in precipitation. Base (1), +30% precipitation (8) and -30% precipitation (9).

Using a different function for reducing evapotranspiration with depth have only a marginal effect on the soil moisture content (Figure 5.3). The major effect of changing WP is the change in FC (not shown). If FC had been held constant, the effect would have been marginal.

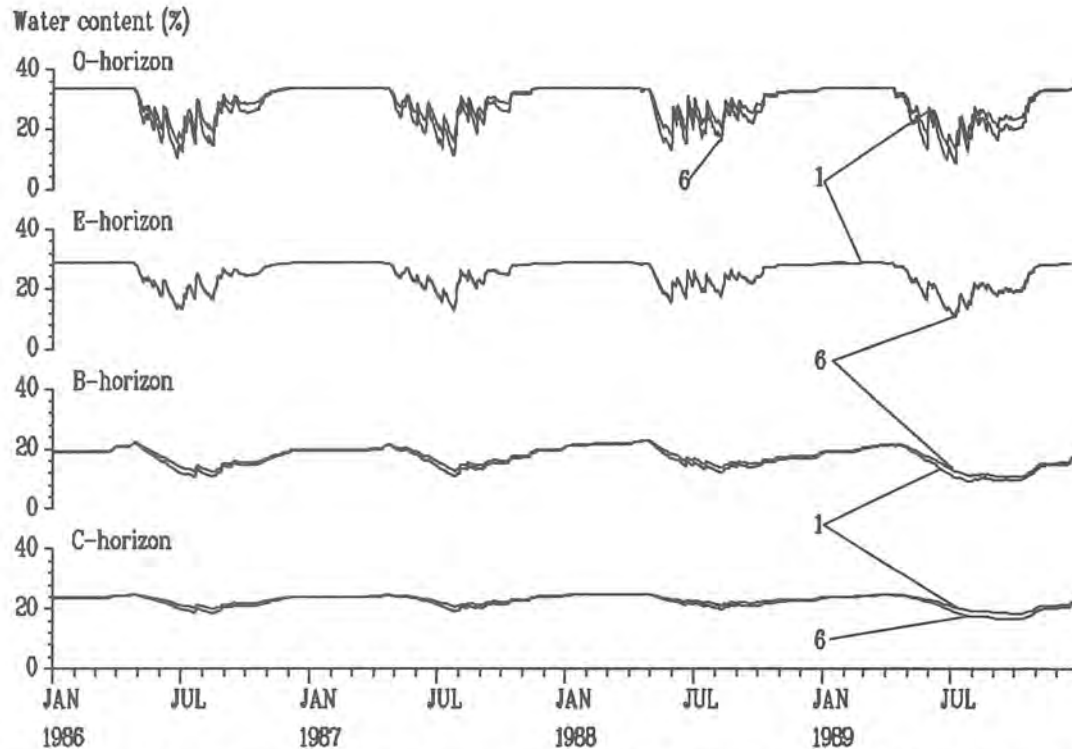


Figure 5.3 Model sensitivity to evapotranspiration function. Base (1) and alternate function (6).

5.1.3 Discussion and conclusion

The large effect found with different ways of estimating FC, lead to the use of variable pF in all simulations presented earlier.

The dynamic variation in soil moisture content is completely driven by model structure and input data. Changes in the parameters can only give small differences in the pattern. The absolute level of soil moisture content is, however, determined by the parameter FC, which varies with the pF-value. The pF-value is depending on the groundwater level, which varies in time and space, and the soil properties, which varies in space. The overall variation of FC-values within a basin or a region will therefore be large. For a regionalization of the results this uncertainty has to be taken into account for the forecast of acidification of groundwater.

5.2 HYDROCHEMICAL MODEL

All chemical models require that the environment in which the chemical reactions take place is defined. Thus, the SAFE and PROFILE models require a number of hydrological parameters as input, to define total volume in each soil compartment, water transit times and routing of water. For SAFE, which generates a time series of soil chemistry output, a corresponding time series is required for hydrological input. Such data can either be obtained from field measurements, or generated by a hydrological model, calibrated to fit field data. Only the latter option is feasible in practice. The conclusions in the previous section have resulted in estimates of the range of PULSE input parameters within which the 'true' values are believed to lie. The distribution of output from the hydrological model results in a range of estimations of the hydrochemistry. The uncertainty thereby introduced should then be added to the uncertainty in estimates due to chemical model formulation, and other data and parameters in the SAFE/PROFILE models.

The model sensitivity to the resolution in time is also addressed. Although predictions of long-term changes in groundwater quality is the primary objective with the modeling effort, time resolution in input data can be important. One can compare it to numerical integration of differential equations; the time step has no correlation whatsoever with the time period for which the simulation is carried out.

5.2.1 Sensitivity to hydrological input

Hydrology interacts with the SAFE model through three quantities, the flow through the profile, the soil moisture content and the soil temperature. The coupling between the models and processes are most easily described by referring to the equations of SAFE and PROFILE, which is done in later sections.

The sensitivity analysis was carried out for Site 2 at Stubbetorp, the poorest of the sites at the study area in terms of buffering capabilities. The model was calibrated to fit measured base saturation for 1987. With this done, the model is mathematically constrained and the path of key quantities such as pH, ANC and base cation concentration cannot be further manipulated.

Each SAFE run was triggered from a starting point in 1903. This value was chosen to represent a point in time when the area was in an early phase of acidification. As described in Chapter 4, each SAFE run is triggered from steady-state condition calculated with PROFILE. Different simulations with the hydrological result in different initial conditions, as expressed in terms of pH, ANC and solution base cation concentrations in 1903.

The hydrological time series have been developed for the period 1961 to 1989. Since the calculations must start at an earlier point in time, this time series was repeated several times. This results in a discontinuity each time the time series is restarted, which is reflected in a cyclic behavior in the results.

The results from the 'base case' run is shown in Figure 5.4. The graphs were constructed from volume-weighted annual mean values calculated from daily results. The results suggest that the ANC in the groundwater was already decreasing, albeit very slowly, early this century. The soil water in upper soil layers, the O and E horizons, have virtually always been acidic due to the deposition of ammonia in

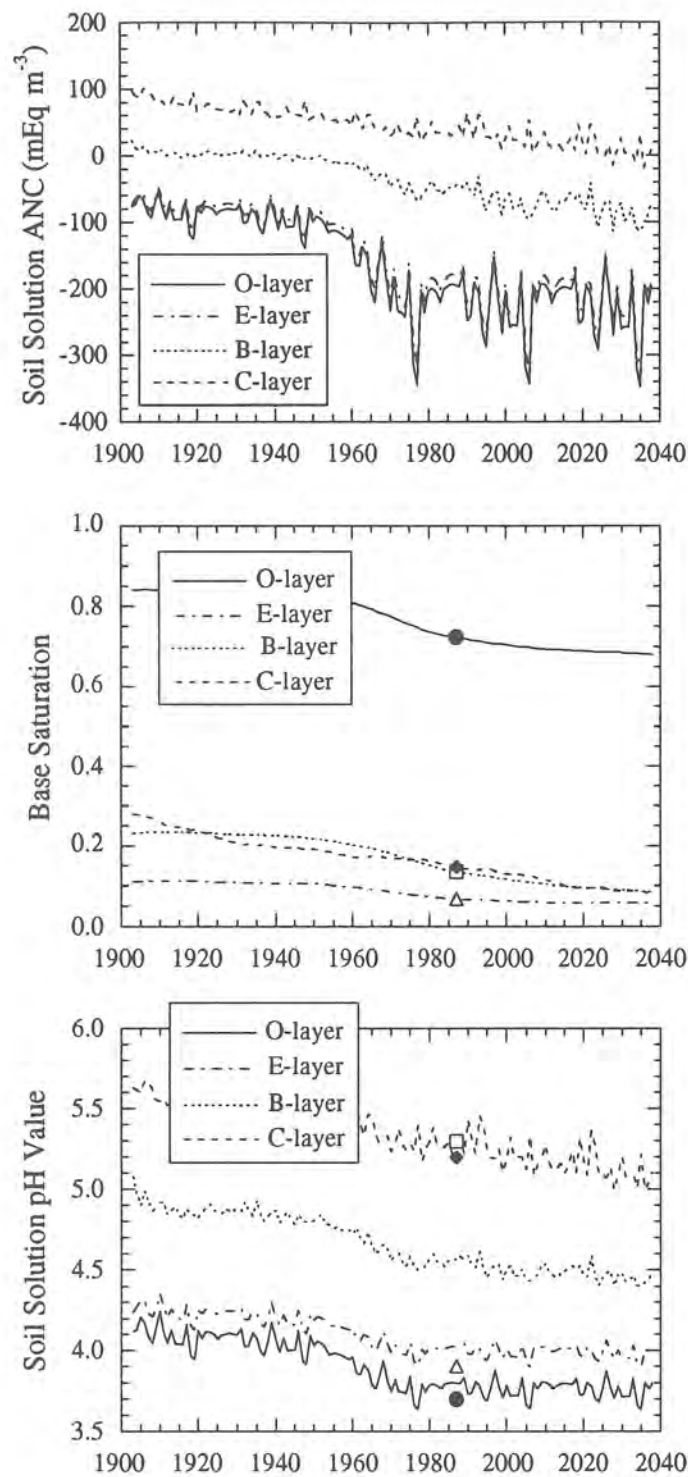


Figure 5.4: SAFE calculations for Stubbetorp using standard set of parameters. The base saturation has been calibrated to data by adjusting initial conditions. The pH and ANC has not been subject to calibration.

excess of the supply of alkalinity, deposited with non-marine Ca, Mg and K. The presence of organic acids in the organic layers further decrease the pH for given values of ANC. The model predicts the pH values in the soil solution within 0.1–0.2 units, the exception being the B horizon. As pointed out earlier, the calculated base saturation has been fit to data.

For the sensitivity analysis, 14 different runs were performed, with number 1 representing base case calculations. In Table 5.2, a summary of the effect of different changes in PULSE model parameters is shown. According to the influence on quantities relevant for SAFE/PROFILE, the runs fall into three groups. The first group include changes in parameters or model formulations that mainly affect the soil moisture content, either the general level or the seasonal variations. The second group, runs 8 and 9, represent extreme values in precipitation amounts, and thus in water flux. Finally, the effect of the submodel used in PULSE to calculate the soil temperature in different soil layers is examined. This is done in runs 10–14.

For each calculations, SAFE was triggered from PROFILE calculations using overall mean values for temperature, water flux and soil moisture content. From this starting point, the SAFE model takes over, using daily time steps for water fluxes, soil moisture content and temperature to calculate the soil chemistry as a function of time.

Table 5.2: Variations in hydrological conditions in the runs performed for the sensitivity analysis. The α means that 95% of the temperature oscillations are damped at the particular depth.

No:		Effect on		
		soil moist.	water flux	temp.
1	Base case			
2	Decreased Wilting Point	–	0	0
3	Increased Wilting Point	+	0	0
4	Decreased Field Capacity	–	–	0
5	Increased Field Capacity	++	+	0
6	Alternative Evaporation	+	–	0
7	FC Related to Groundwater Table	++	+	0
8	Increased Precipitation	0	++	0
9	Decreased Precipitation	0	–	0
10	Temperature Lag	0	0	+/-
11	Temperature Ahead	0	0	+/-
12	$\alpha=3m$	0	0	(+)
13	$\alpha=12m$	0	0	(-)
14	$\alpha=1m$	0	0	+
+	Increased soil moisture content, water flux or temperature			
0	No effect			
()	Minute effect			
–	Decreased soil moisture content, water flux or temperature			

Effect of moisture content

In the sensitivity analysis, 6 sets of parameters or formulations in the hydrological model resulting in different moisture saturations were used.

The soil moisture content appears in two contexts. It appears in all mass balances, such as the fundamental conservation equation for ANC:

$$\frac{d[ANC]}{dt} = \frac{1}{z \cdot \Theta} \cdot (Q_0[ANC]_0 - (Q + z \cdot \frac{d\Theta}{dt}) \cdot [ANC]) + R_w + R_{exc} - R_{BC} + R_N \quad (5.2)$$

The term $z \cdot \Theta$ is the volume of water in a layer with the height z , expressed as $m^3 m^{-2}$. It determines the effect on the concentration of a certain influx or outflux of ANC. The lower the moisture content, the higher the impact of a given magnitude of the flux on concentration within the volume of water in the layer.

Less obvious is the role of the differential $z \cdot \frac{d\Theta}{dt}$. It pops up when the mass balance for ANC is set up. The general equation states that:

$$\frac{d(z\Theta[ANC])}{dt} = z[ANC] \frac{d\Theta}{dt} + z\Theta \cdot \frac{d[ANC]}{dt} \quad (5.3)$$

Qualitatively, the $z \cdot \frac{d\Theta}{dt}$ part of the differential describes concentration or dilution of the soil solution when the soil moisture content changes. One effect of this is that the concentration of the soil solution tends to increase the pH if ANC is greater than 0, but tends to create more acid conditions if the ANC is negative. This phenomenon is, however, observed in nature, such as in arid carbonate soils and in canopy throughfall.

In the descriptions of other acidification models, ILWAS being the exception, the full differential is not developed. This automatically makes it impossible to assess the impact of changes in soil moisture content over the year. Just setting $Q_0 \neq Q$ is a good start, but leads to a formal error in the differentials.

The soil moisture content also has a very important role in determining the weathering rate. In the models, the weathering rate is proportional to the degree of soil moisture saturation. This is calculated from the moisture content, the soil bulk density and the density of the soil solids.

Runs 2 and 3 examine the effect of different assumptions regarding the fraction of water held below the wilting point. Run 2 then corresponds to no water below the wilting point. The calculations (Figure 5.5) show that SAFE generates different scenarios when this parameter is changes in PULSE. A major cause of the differences is however the change introduced in the field capacity by this change in the wilting point as the plant available water was kept constant.

Runs 4 and 5 deal with the uncertainty involved in estimating the field capacity. A high field capacity results in more soil water and also larger variations, since the flux from a layer depends on the inverse of the difference between the field capacity and the wilting point. The results are quite similar to the effects demonstrated in runs 2 and 3, an increase predicted ANC values when the moisture content is increased.

Finally, runs 6 and 7 were performed with alternative model formulations rather than just a change in parameters. In run 6, an alternate equation for the distribution of evapotranspiration with depth is used. This result in lower soil moisture in the

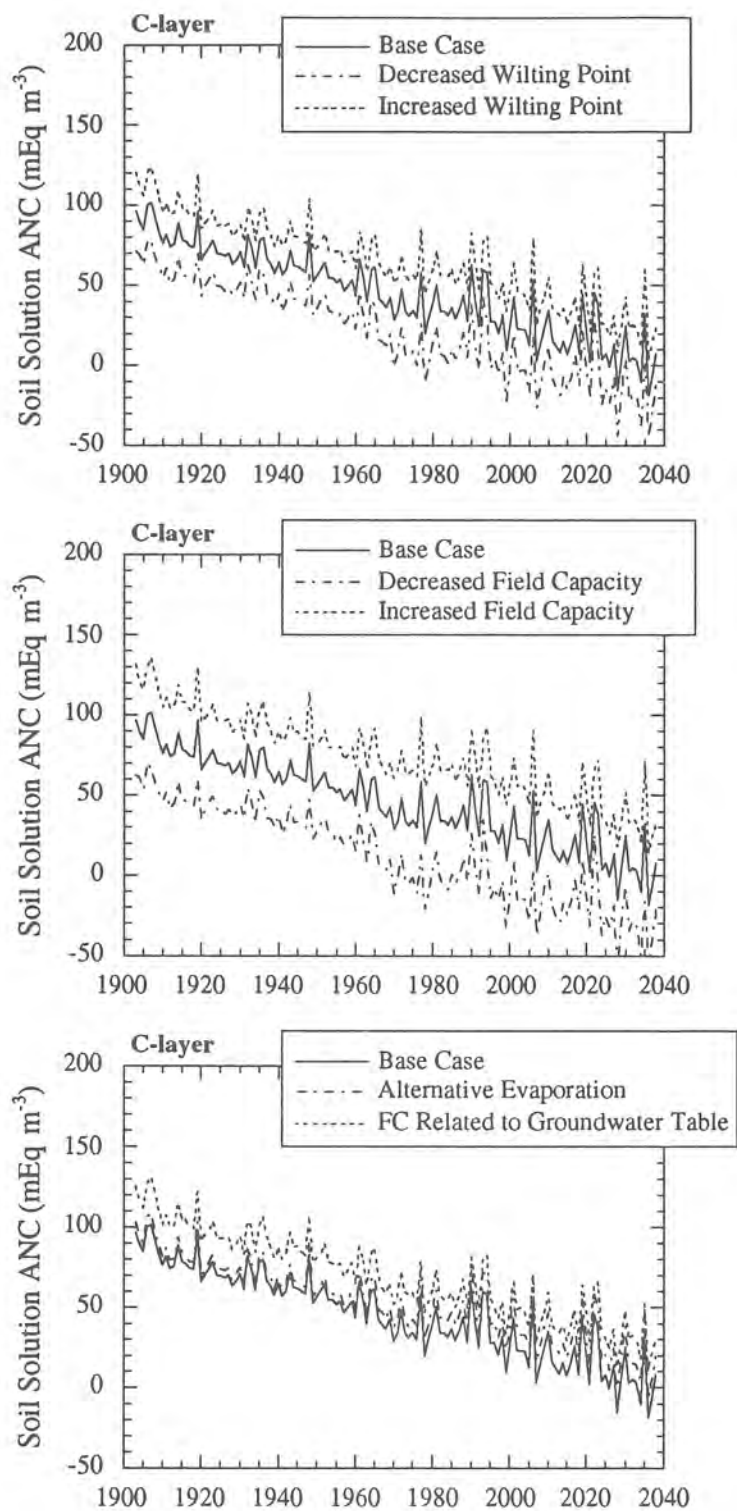


Figure 5.5: Simulations illustrating the sensitivity to parameters in the hydrological model mainly effecting the soil moisture content. Upper panel show simulations 2 and 3, Middle panel simulations 4 and 5, and bottom panel simulations 6 and 7.

top and bottom layer and lower in the B-layer during the summer. The calculations show that the differences between these two formulations are very small, but the deviation from the base case run tends to increase in time, rather than just being an offset.

Of significantly more importance is the difference between the two approaches taken for estimating the field capacity from field data. Using decreasing pF-values with depth result in decreasing field capacity in the top layers and increasing field capacity in the bottom layer. The B-layer remains more or less unchanged. As the field capacity change so does the soil moisture. It is clear from the lower diagram in Figure 5.5 that the more realistic calculation of field capacity has a profound effect on the simulated soil chemistry.

Water flux

In the chemical model, the water flux through the soil only appears in the mass balances. The larger the fluxes, the greater is the impact of differences between the concentration in the layer and the inflow in the chemistry of the layer. Another interesting aspect is that the deposition data is given as fluxes. That means that the acidity of the precipitation is lower in wet years than in dry, causing more acid conditions in the soil during dry years. This shows most clearly in the ANC of the O and E layers, shown for the base case in Figure 5.4.

In Figure 5.6, the ANC for the C-layer and the base saturation for the whole profile is shown. The model suggests that the ANC will be higher for the low precipitation rate, while the higher water flux gives a dilution of the ANC. If, however, the ANC would have been negative, the opposite effect would have been the case.

The effect on the base saturation is rather unexpected. One would normally expect that the higher flux would lead to a more rapid depletion of exchangeable bases. Here, however, the base case appears to represent the most rapid decrease in base saturation. The reason why the low precipitation rate, i.e. 70% of actual measurements, give lower rate of depletion is straight forward; a concentration of all dissolved constituents decreases H^+ and Al but increases BC in solution, both acting to keep base saturation up. The explanation for the less rapid decline suggested for 130% of base case precipitation is that the weathering rate becomes higher for this case. This is caused by an increase in soil moisture content, and also less reaction product retardation of the dissolution rates.

Many biological processes that affect the production of acidity in the soil are affected by the soil water conditions. These processes include nutrient uptake, biomass mineralization and denitrification. At present, these effect on soil moisture are not taken into account in the hydrochemical models, although these procesess have been studied and kinetic models have been developed in association to the project [Sverdrup *et al.*, 1991].

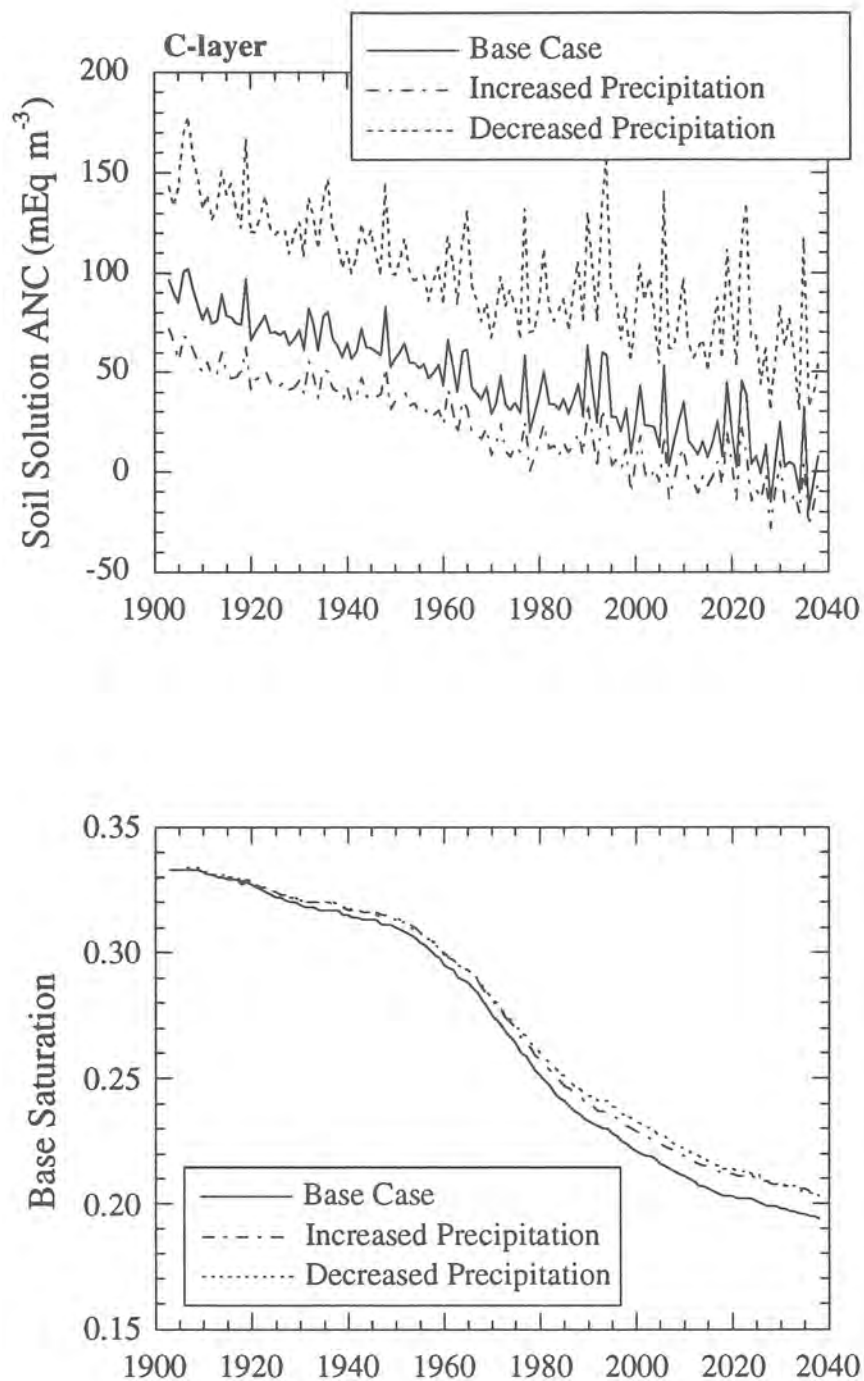


Figure 5.6: Simulations illustrating the sensitivity to parameters in the hydrological model parameters effecting the flow rate, but also the soil moisture content. The effects of dissolution and concentration of the soil solution as compared to the base case simulations results in very complex response on model output.

Temperature

Finally, the temperature affects three elements of the chemical model. It affects the soil solution speciation through temperature dependent equilibrium coefficients of the carbonate system. This buffer system is important primarily in the bottom part of the soil column at pH values ranging from slightly below 5 and up. Also, the weathering rate coefficients are temperature dependent through the Arrhenius relationships. The effect is that the rate of dissolution increases with increased temperature. As a rule of thumb, 4 degrees increase in temperature results in an increase in weathering rate by 30%.

Two features of the temperature calculations in the hydrological model were examined in the sensitivity analysis. First, the effect of changing the phase of the temperature variations by 10 days forward and backward was examined. Figure 5.7 shows the results from this exercise. From the time series, these runs look virtually identical.

Secondly, the effect of different values of the parameter α in the hydrological model was examined. This parameter sets the point below groundlevel where the oscillation in soil temperature amounts to about 5% of the oscillation in air temperature. The effect is that a lower value of α results in a higher annual average temperature, and thus a higher weathering rate. Figure 5.8 shows that α values of 3 m and 12 m give very similar results, while a value of 1 m gives a significant difference in ANC. As will be discussed later, the change in ANC is rather similar for all runs.

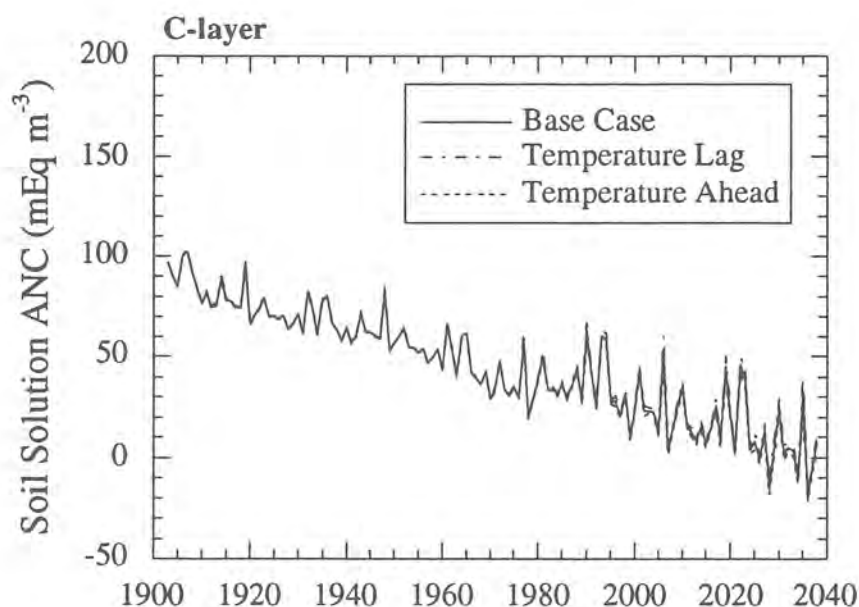


Figure 5.7: Results from simulations 10 and 11 show that the phase shift in temperature oscillations have negligible effect on model predictions.

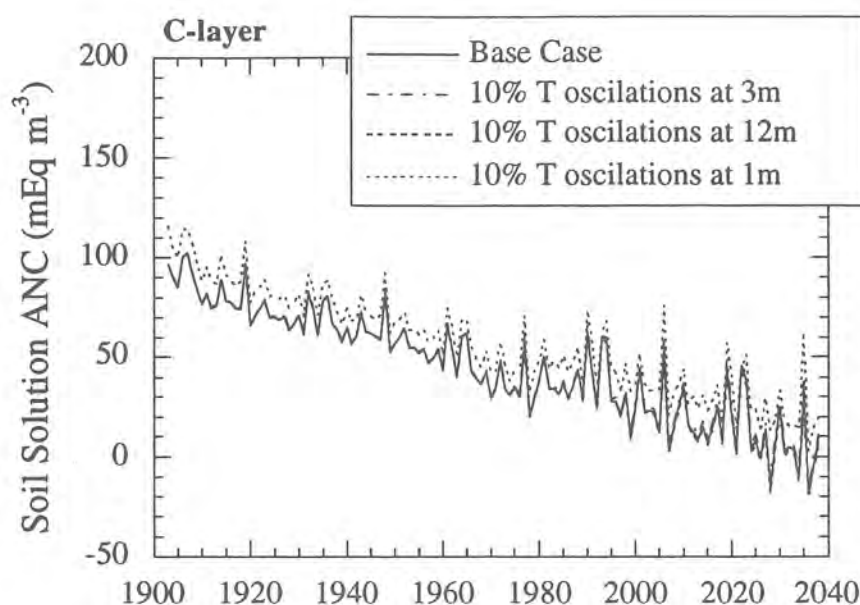


Figure 5.8: Simulations with different damping temperature oscillations show that moving the point for 95% damping to 1 m (Simulation 14) results in different predicted ANC. This is caused by the increased annual average temperature, leading to an increase in weathering rate as compared to base case simulations.

Discussion

In Figure 5.9, the results from all 14 runs within this sensitivity analysis is shown. The calculations show, that with the limited possibilities for calibrating the model's predictions of ANC and pH in the soil solution, an accurate hydrological submodel and good estimates of parameters are necessary for the credibility of the model and its output.

From the perspective of assessing environmental damage caused by acidic water, either to groundwater or surface water, there is a significant difference if the ANC in 2020 turns out to be 0 or 120 meq m⁻³.

The pattern in the changes in base saturation is quite similar. In order to give perfect justice to the differences between the different runs, and to be formally correct, the base saturation should have in fact been recalibrated to go through the value for 1987. This would have led to different starting points for the base saturation, but not affected the initial conditions in the solution. This may have led to different ANC patterns, but only slightly different from those presented here.

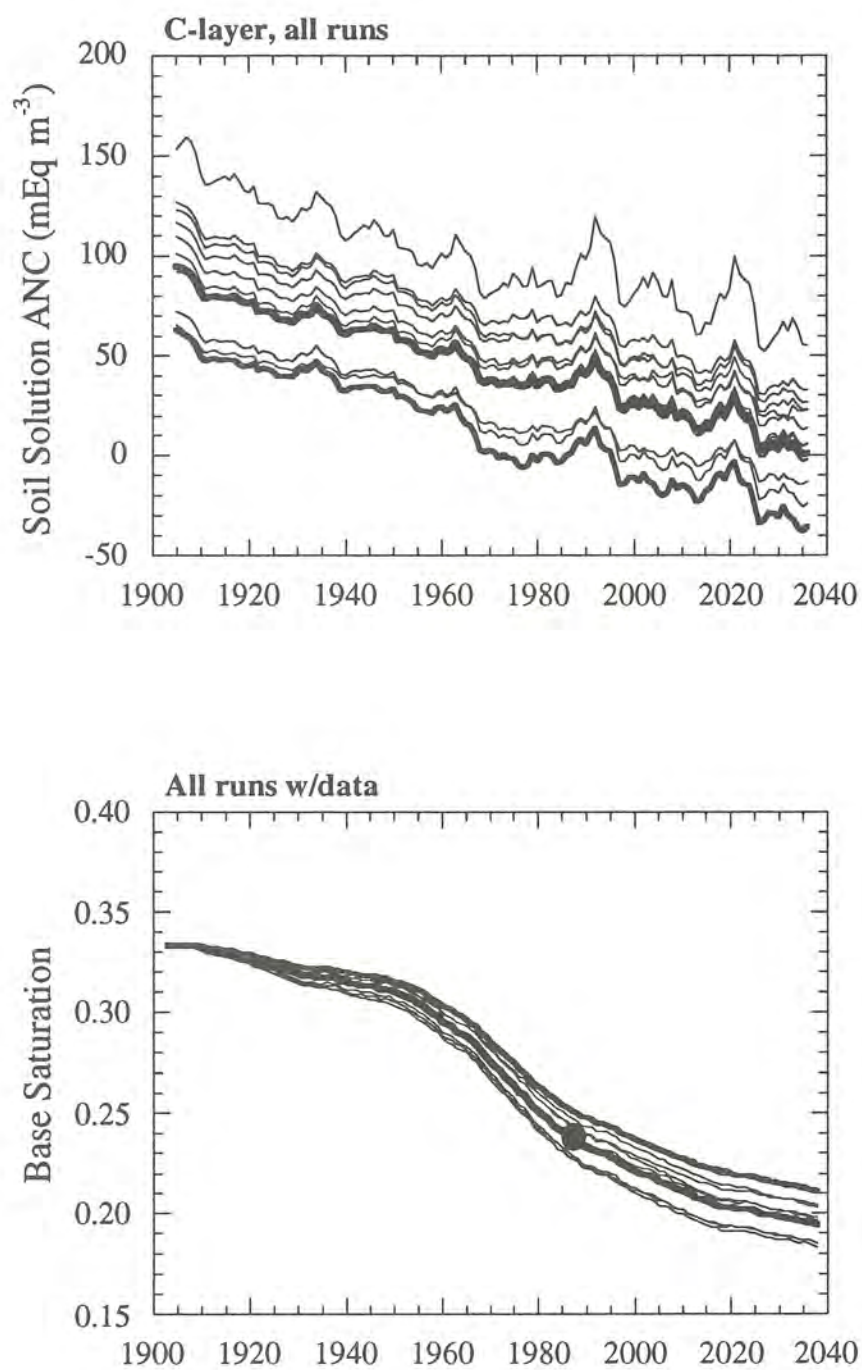


Figure 5.9: Range of predictions in groundwater ANC and total soil base saturation, including all simulations.

Although the ANC levels are rather different, the picture becomes different if the changes in ANC are considered instead. As Figure 5.10 shows, the ANC time series calculated are actually almost parallel to each other. The change in concentration is thus fairly independent of the assumptions in the hydrological model. This is analogous to the conclusions drawn by Jenne *et al.* (1989), who compared three different acidification models. In this study, ILWAS, MAGIC and ETD generated very similar changes in ANC but very different predictions of concentrations, under different deposition scenarios. Here, the differences in change in ANC are very small. When comparing pairs of runs, i.e. 2 and 3, and 4 and 5, it is also clear that the run with the highest ANC also exhibits the greatest change.

It is also interesting to study the change in fluxes, not only concentrations. Figure 5.11 shows that for the groups of runs 2–7 and 10–14, the differences in change in flux are rather small. The runs with different water flux are rather different however. A high water flux also results in a much higher leaching of ANC. This is compensated for by two processes, increased weathering, as well as less change in base saturation as compared to the base case.

Except for runs 8 and 9, the ANC level can be explained by the differences in ANC supplied to the solution from weathering (Figure 5.12). This figure also shows that in the model, the weathering rate largely depends on the soil moisture content. This is thus the key parameter that most directly links PULSE and SAFE.

Of runs 10–14, there is one point in the bottom diagram in Figure 5.12 that falls outside the cluster formed by the other 4 values. This is the value for run 14, where the annual average temperature is 1 °C above the others. This is reflected in a higher weathering rate, as formulated in the SAFE model.

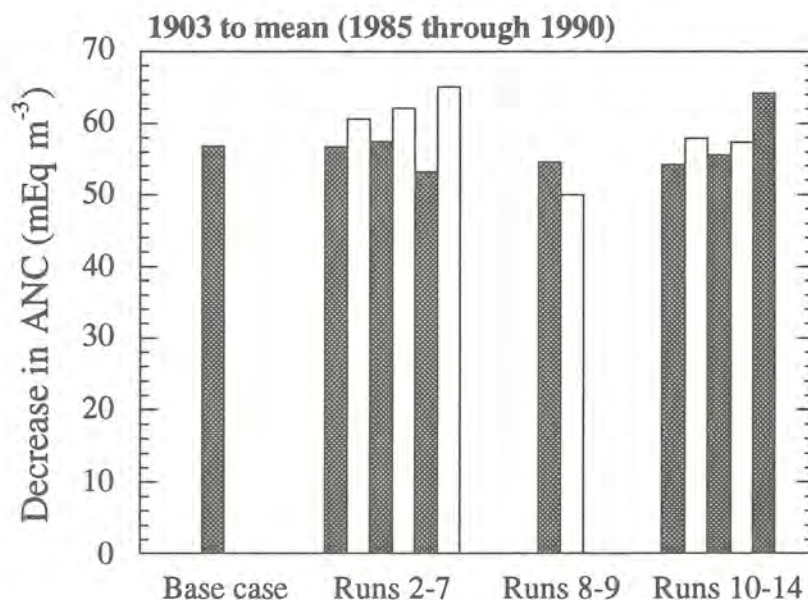


Figure 5.10: Change in ANC as predicted by simulations 1 through 14.

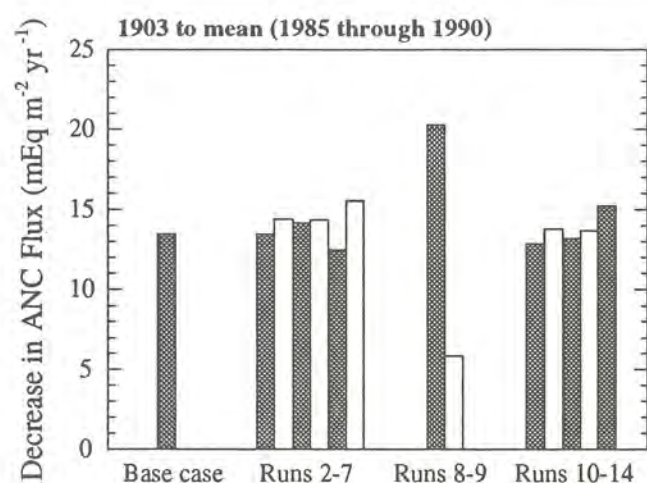


Figure 5.11: Changes in ANC flux for the 14 runs in the sensitivity analysis. The largest differences occur for changes in precipitation amount.

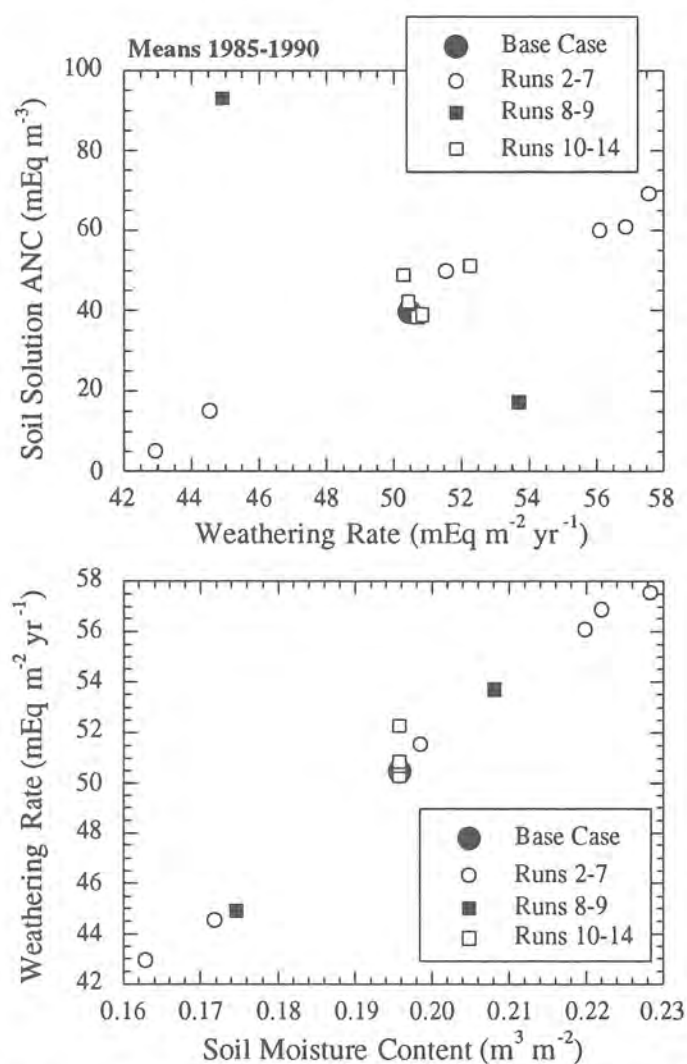


Figure 5.12: Relationship showing that for constant flow rate, the ANC is largely determined by the weathering rate (upper panel). The differences in weathering rate is mainly a function of the modeled soil moisture content (lower panel).

5.2.2 Sensivity to time resolution

There has been some debate about whether it is necessary to model soil chemistry processes on a less than annual scale, if only long term changes are considered. Looking only to the processes in the watershed, it cannot be excluded that a short time-step is necessary. For example, how will the chemistry be affected if the weathering takes place when it is hot, dry and the fluxes are high, as compared to when it is cold, dry and no renewal of the water within each layer? Clearly, these processes are highly nonlinear and these questions cannot be answered without actually performing calculations with the specific model.

Figure 5.13 shows calculations carried out with SAFE with different levels of resolution in the hydrological input data. It must be pointed out that the numerical resolution is different, and extremely high standards for accurate numerical treatment are met. The results show a significant difference in model output. The finer the resolution, the more rapid is the rate of acidification. The differences within each year are also very clear from the calculated base cation concentration, shown in Figure 5.14. While the calculations with the daily time step exhibit huge variations through the year, the run with constant, averaged values only display the slow trend. This illustrates that the fine resolution model provides an opportunity to verify the inner working of the model on experimental data.

This difference in base cation concentration also leads to dynamics in the cation exchange process, driven by the hydrological model. Figure 5.15 shows the driving force for cation exchange, expressed as potential for increased or decreased base saturation. When compared with the water flux, it is clear that hydrological processes to a large degree are responsible for the dynamics in soil chemistry. This is reflected in the differences obtained with different resolution, and justifies using a daily time step in the calculations.

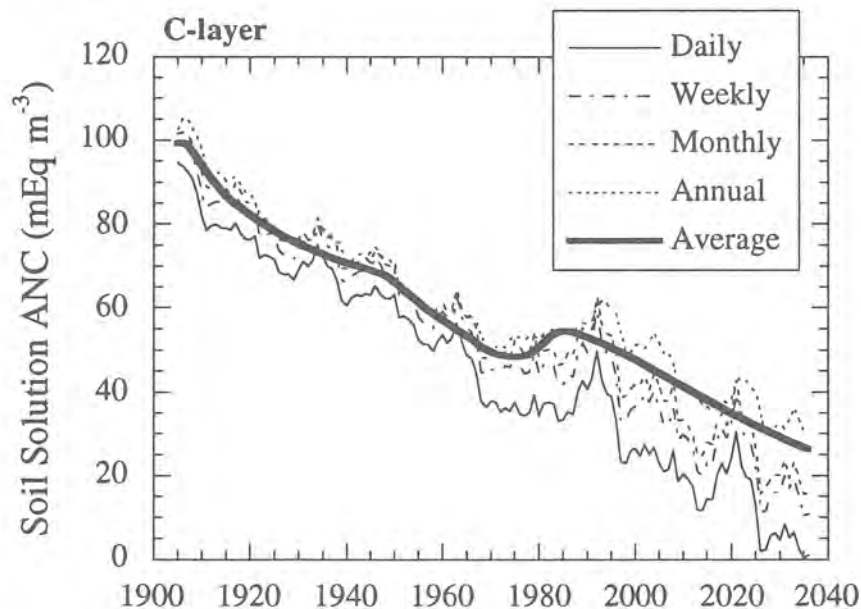


Figure 5.13: Dependence of simulated trends on the time resolution in hydrological input data.

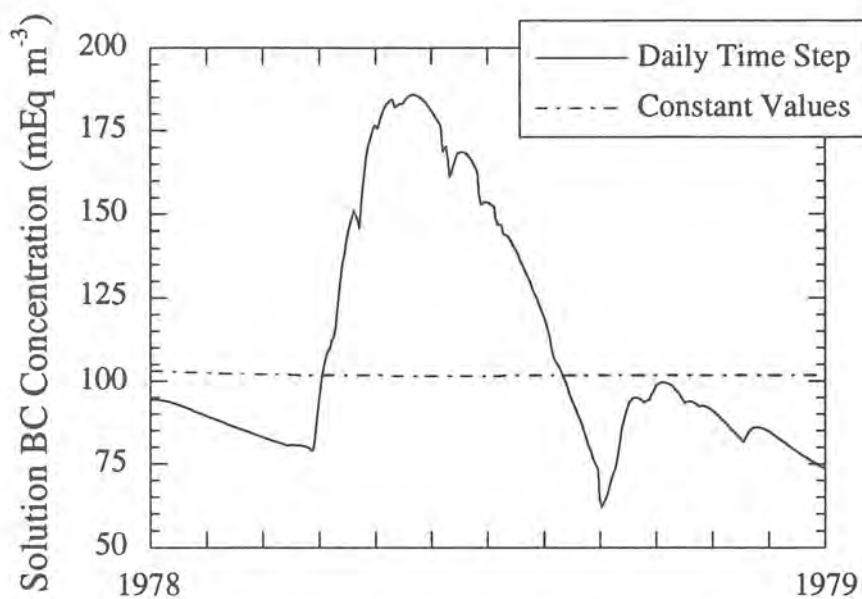


Figure 5.14: Temporal variation in soil solution BC for calculations with daily hydrological time-resolution and averaged hydrological data concentration, as modeled by SAFE.

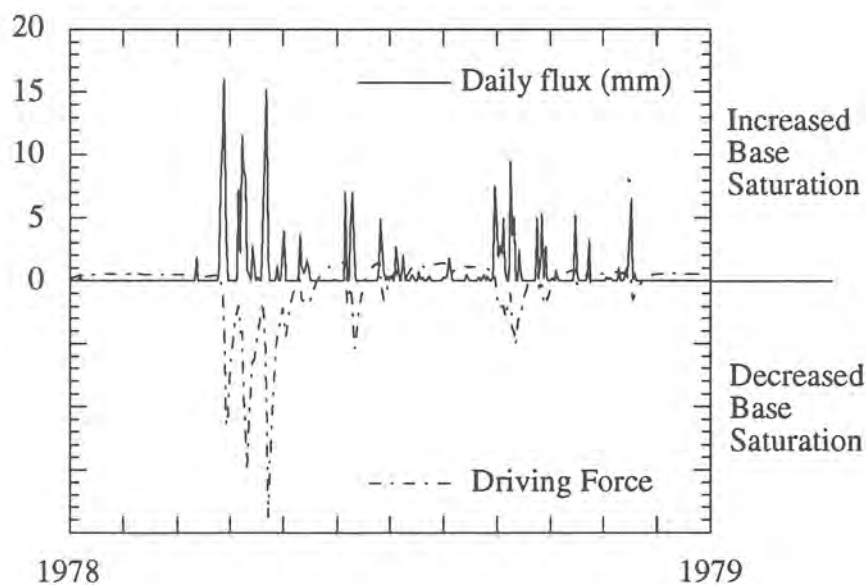


Figure 5.15: Temporal variations in driving force for cation exchange in the organic soil layer where a significant part of the cation exchange takes place. In lower soil layers the short-term variations are not as great.

5.2.3 Sensitivity to chemical model parameters

To assess the impact of different model parameters on SAFE calculations, and hence the predicting capacity, the model was run with a range of values.

Parameters were selected for the sensitivity analysis, either because they are known to have large influence on the calculations, or because they are hard to assess, either in the field or from literature data. It must already at this point be stressed that the importance of different parameters vary between sites. For instance, the acidification of peat soils should be virtually independent of all parameters dealing with silicate weathering, but largely influenced by factors determining the cation exchange capacity.

Also, this section will demonstrate some obscure effects on model calculations that can occur when only one parameter is changed at the time. This is due to the fact that changing the model parameters not only changes the trajectory in time, sometimes the initial conditions, calculated by PROFILE, are also changed. This can alter the buffering conditions, change cation exchange selectivity coefficients etc., leading to odd consequences.

The parameters selected for the sensitivity analysis, and the range of variation was:

- Mineral surface area: 50%, 80%, 125% and 200% of base case values
- Cation exchange capacity: 80% and 125% of base case values
- Cation exchange rate coefficient: 20% and 500% of base case values
- CO₂ partial pressure: 50% and 200% of base case values
- Soil density: 80% and 125% of base case values

The rational for selecting these ranges is given in the specific sections.

Mineral surface area

One key process in SAFE, and PROFILE, is weathering of silicate materials. To calculate the weathering rate from geophysical data is one of the most important element, since it is a unique feature of these models.

The weathering rate depends on input parameters such as mineral abundance, exposed surface area and CO₂ pressure, as clear from the model description (Chapter 4). In addition, the models contains a vast number of kinetic rate coefficients that have been determined by laboratory experiments. To assess the important of all these parameters could be rewarding in some contexts, but in this case, the objective should be to assess the impact of the total uncertainty in weathering rate. As shown in previous sections, the track record of the weathering rate component is very good; the model generally agrees with determinations made with other methods within 0.1 keq ha⁻¹ yr⁻¹.

The most obvious way to change the weathering rate, is to alter the exposed surface area. It is also reasonable in the sense that it is operationally determined by a rather simple algorithm from a soil texture analysis that is based on standard surface areas for the sand, silt and clay fractions, added together based on their

relative proportions. This algorithm is described in Chapter 8. Another way to manipulate the weathering rate is to vary the mineral content, but since the computer applications do not accept more than 100% mineral content, this is not possible in practice.

For this study, SAFE was run with four different values. The largest changes, corresponding to 50% and 200% of the best estimate, should be viewed as a maximum uncertainty, including uncertainties in all elements in the weathering rate equations. On the other hand, the documented performance of the weathering model indicates that this range could be vastly exaggerated. The more moderate range, 80% and 125% of the base case surface area indicates the boundaries of surface area determinations from soil texture analysis, and a more typical difference in comparison with 'true' weathering rates determined with other methods.

The output from all runs is shown in Figure 5.16. It shows that not only the slopes, but also the initial conditions is strongly affected by the weathering rate. With this range of predictions, it is of course not possible to present views of water quality at individual sites. The diagram does serve to indicate that weathering is a very important process in catchments such as Stubbetorp.

Varying only one parameter can give unexpected results. In Figure 5.17. the expected result would be that decreasing the weathering rate should lead to a more rapid acidification, and thus a faster decline in base saturation. As the results show, however, the base saturation decreases faster the higher the weathering rate is, until the area is increased by very much. This is in fact an artifact, caused by different starting points for the calculations. A low pH at the beginning of the simulations leads to a situation where the exchange complex holds on to the exchangeable bases very hard, resisting acidification better than if the pH was high at the beginning. For the largest area, this effect is, however, overshadowed by the effect of increased weathering. If the calculations were performed with the same selectivity coefficient, this effect would not have occurred.

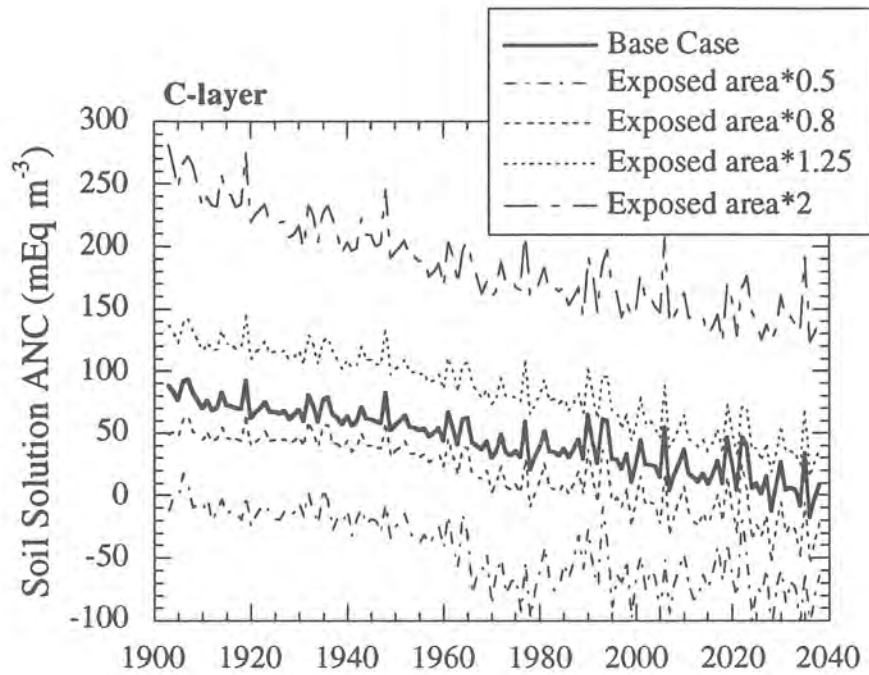


Figure 5.16: Modeled groundwater ANC as dependent on different values for the exposed surface area. Since the area affects the weathering rate, the initial conditions as well as the trajectory change.

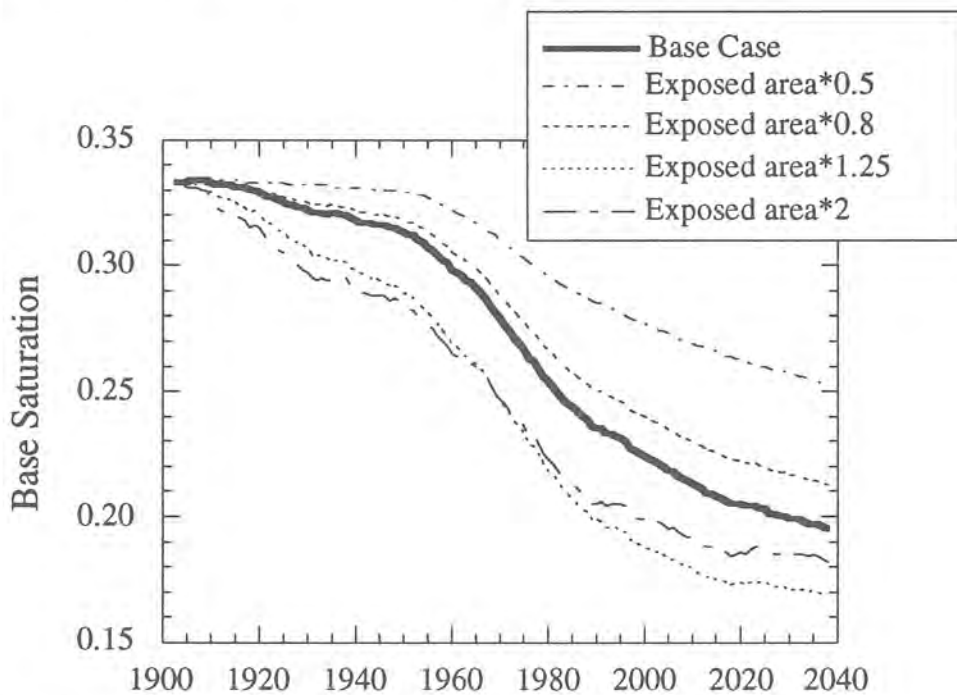


Figure 5.17: Modeled soil base saturation as dependent on different values for the exposed surface area.

Cation exchange capacity

The cation exchange capacity affects the extent of medium term buffering of input of acidity. Unfortunately, the CEC is not a constant, although it is almost always modeled that way. In the temperate climatic zone, the mineralization of organic matters slower than the litterfall, which results in a build up of an organic soil layer, and a continually increasing CEC. To model this process would, however include estimates of both the long term buildup, and also about the change in exchange properties during the humification process.

Also, the CEC changes with pH, which makes experimental determination of CEC a hazardous exercise. The CEC is always determined per unit mass, and the total exchange capacity is obtained after multiplication with the soil bulk density, another source of uncertainty.

The range selected for the sensitivity analysis only reflects the uncertainty in the experimental determination in CEC, not alternative processes. As shown in Figure 5.18, however, this uncertainty have little effect on the model's prediction.

It is clear that in the early phase of acidification, when the changes in soil solution composition is fairly slow, and the amount of exchangeable bases is close to the historical equilibrium value, the CEC has little influence on the total result of all bufferening mechanisms.

The calculated base saturation differ by no more than 2% between the two cases. This reflects the great pools of base cations that the exchange complex represents, and also that quite large changes in soil solution composition are necessary to alter the composition of the exchange complex.

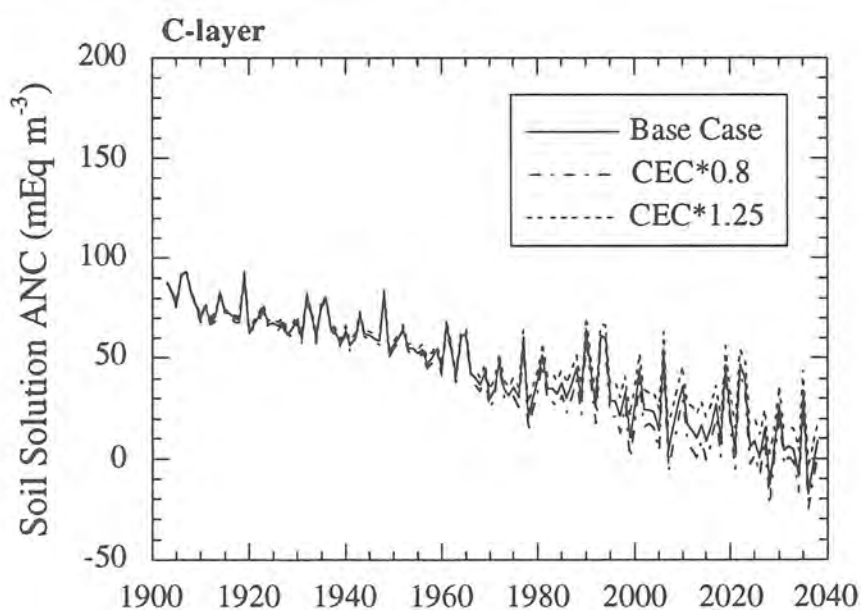


Figure 5.18: Differences in model predictions for different CEC values.

Cation exchange rate coefficient

The by far most uncertain parameter in the entire model is the cation exchange rate coefficient, k_m . It quantifies the transport of ions to and from the exchange surface, as a response to a concentration gradient between the soil solution and the exchange complex on soil particle surfaces. An earlier attempt to quantify this theoretically has not been conclusive [Warfvinge, 1988]. The value use is based on experience from modeling of soil liming, where cation exchange is very important in controlling the overall rate of changes in the system.

Thus, the value were varied within a very large range, based on the data obtained in Warfvinge and Sverdrup (1989) . As shown in Figure 5.19, this parameter has a very small influence on the long-term simulations. Short term calculations show larger differences. Therefore, a better understanding of the cation exchange dynamics, as expressed by this parameter, is necessary to model changes in soil solution in a short term scale. This calls for extensive experimental work, both in the laboratory and in the field.

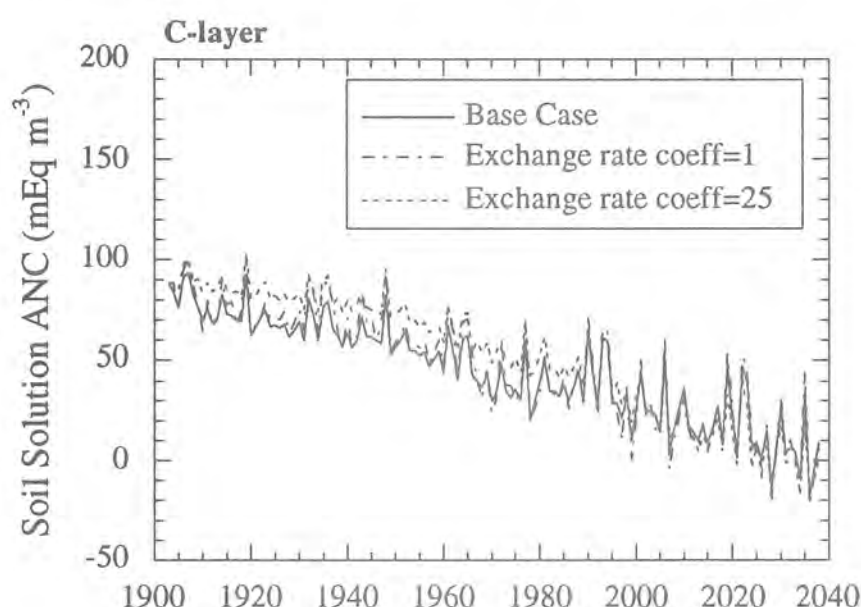


Figure 5.19: Differences in modeled ANC for different cation exchange rate coefficients. The results show that the differences are small.

5.2.4 Soil CO₂ pressure

In the hydrochemical model, the soil CO₂ has a role in two reactions systems. First, CO₂ is one reactant in weathering reactions, although it's influence is rather small. Secondly, it is the key component of one of the three buffering systems of the soil solution, the others being Al and dissolved organic carbon. The effect of CO₂ is largest at pH values above 5. Below this level, Al buffering dominates. The exception would be the deeper groundwater where the CO₂ is very high.

The CO₂ pressure is known to vary seasonally, and this automatically gives a range of plausible values when one single value should be selected to represent a complete annual cycle. The best estimates for these simulations are based on a number of studies, but uncertainties remain. The range chosen is thus very large, but most published data for comparable systems fall within this range. For instance, for Risfallet, the CO₂-pressure at 1 m depth was calculated from pH, concentration of HCO₃⁻ and temperature. These calculations show that the equilibrium concentration corresponds to a pressure of 23.4 times ambient partial pressure of CO₂.

The simulations (Figure 5.20) show that the increase in CO₂ has little effect on the acidification path, while the decrease leads to a larger difference as compared to the base case run. This is simply because the system becomes more vulnerable to changes when the total buffering intensity of the system is decreased.

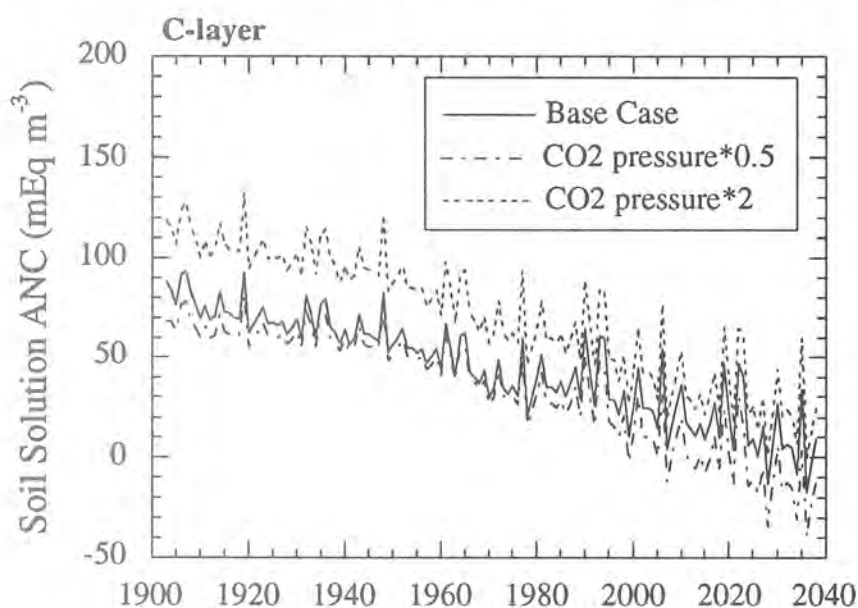


Figure 5.20: Differences in modeled ANC for different CO₂ pressures. The results show that the effect of ANC reduced pressure as compared to the base case are larger than if the CO₂-pressure is increased correspondingly.

Soil density

Besides the exposed surface area, the soil density is the parameter with most effect on model prediction, which is illustrated by the differences in modeled ANC for different soil densities (Figure 5.21). This is because it influences two systems in the model, both acting the same way. First, the soil density affects the calculated moisture saturation in a way that makes the weathering rate strongly dependent on the soil density (Figure 5.22). Secondly, it affects the exchange capacity, leading to higher buffering with increasing values. The former effect is, however, most important. The range chosen is based on the range of variability for the field sites Stubbetorp, Masbyn and Risfallet. In conclusion, these results show that the total effect of the water content and water saturation is very important when ANC is predicted in areas where the weathering is an important buffering mechanism.

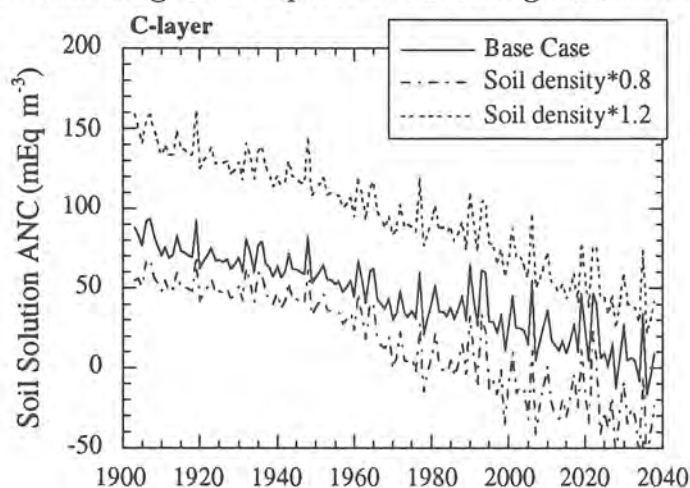


Figure 5.21: Modeled ANC for different soil densities.

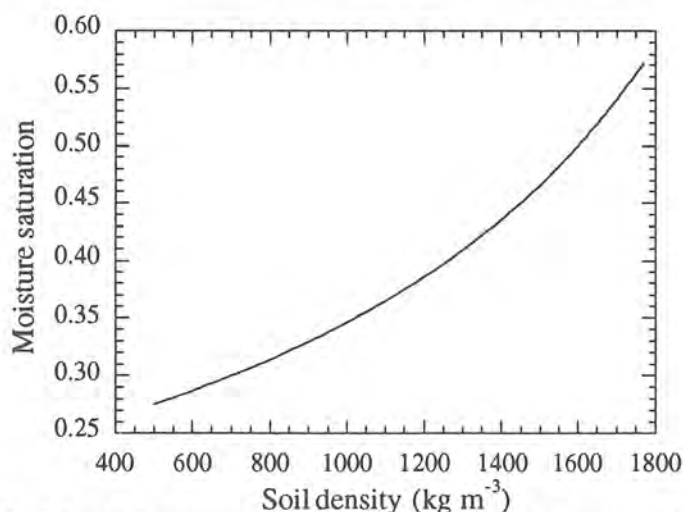


Figure 5.22: The influence on the soil moisture saturation θ of the soil density. The weathering rate is directly proportional to θ .

Discussion

The results from the runs within this sensitivity analysis shows that the model is very dynamic with respect to some input parameters. In Figure 5.23, the range of predictions of present ANC in the surficial groundwater, at the 80–100 cm level is shown. With the exception of two runs, the predictions of present ANC fall within 80 meq m^{-3} . The predictions for the end of the simulation period result in lower ANC values, that fall within 64 meq m^{-3} . There are no differences in conclusions regarding if the groundwater will acidify further at this site, but to what level.

Figures 5.24 and 5.25 show that the higher the ANC at pristine conditions, the larger is the drop due to acidification. This is largely due to the effects of starting the calculations from the same base saturation values, but different composition of the soil solution. Regarding individual runs, the sensitivity analysis show that a higher CO_2 pressure results in the calculations results in a larger ANC decrease.

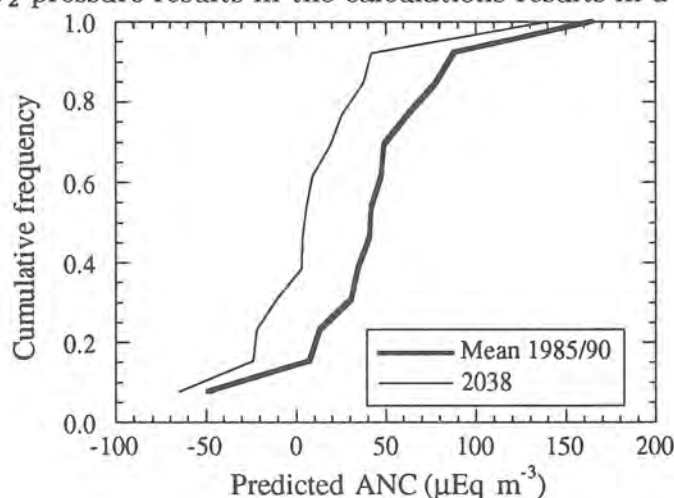


Figure 5.23: By comparing modeled ANC at 1985–1990 with predicted ANC for 2038, we can conclude that the trends in acidification are similar for all runs.

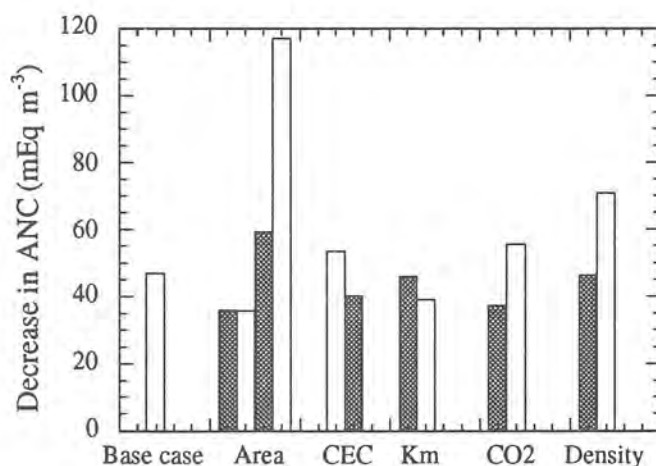


Figure 5.24: The change in ANC differs most for runs made with large variations in exposed area, soil density and CO_2 pressure.

This is because the CO_2 increases the weathering rate, and therefore a higher ANC at the start of the calculations. But the increased CO_2 also results in a lower pH, and higher base cation concentration, which decreases the buffering by cation exchange. Finally, Figure 5.26 illustrates the importance of chemical weathering in determining the prediction of ANC in groundwater. The predicted value is basically proportional to the weathering rate, while the decrease in ANC depends on other factors, such as cation exchange. As the base saturation decreases, however, the importance of chemical weathering increases. As an example, the present rate of depletion of exchangeable cations at Stubbetorp is in the range of $10 \text{ mEq m}^{-2} \text{ yr}^{-1}$, while the chemical weathering contributes 5 times that buffering capacity. This stresses the importance of accurate methods to determine weathering rate, independently of other processes in the terrestrial ecosystem. Considering the track record of the weathering submodel in SAFE and PROFILE, the dynamic shown with respect to weathering could be regarded as a strength rather than a source of uncertainty.

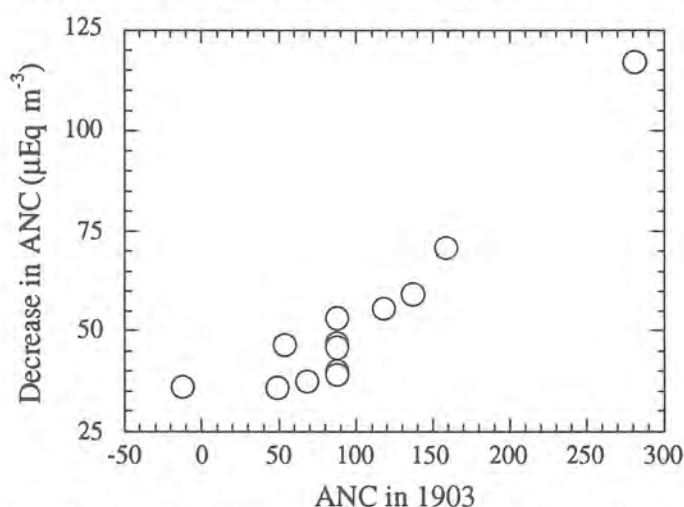


Figure 5.25: The decrease in ANC is larger the higher the initial ANC of the solution is. This is partly due to differences in cation exchange selectivity properties.

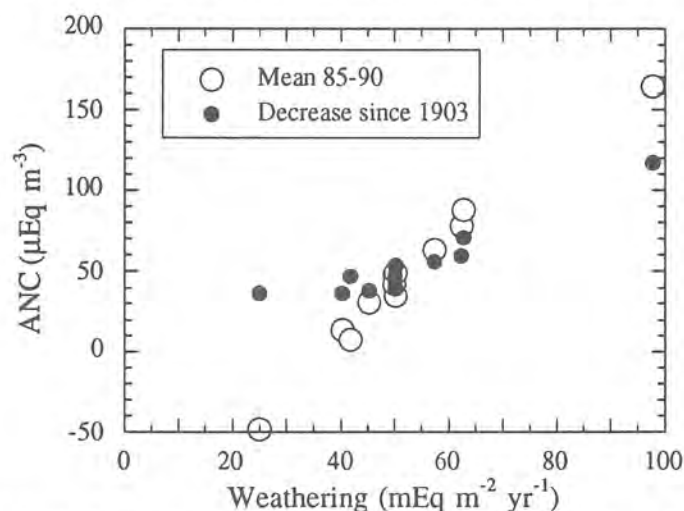


Figure 5.26: Influence of weathering rate on modeled ANC and modeled decrease in ANC, which shows a more complex behaviour than the ANC-value.

6 SCENARIOS FOR ACIDIFICATION OF GROUNDWATER

(P. Warfvinge and H. Sverdrup)

In this chapter, model predictions for the groundwater chemistry is reported. The model calculations show the response to four depositions scenarios; no reduction, reduced deposition by 30 % and 10% for sulfuric acid and total nitrogen deposition respectively, as well as a 60% and 30% and a 85% and 50% reduction scenario. The scenarios were created by applying linear reductions between 1990 and 2000, thereafter keeping the deposition above canopy constant at the 2000 level. The reductions are taken from the 1988 level of deposition. The most moderate scenario is, unfortunately, quite realistic taken as reductions to 2000. The 60/30 scenario corresponds roughly to the outcome of introduction av Best Available Technology in western Europe and Energy Efficiency optimization for eastern Europe. The calculations are limited to three field sites within the integrated ground water acidification project; Stubbetorp, Masbyn and Risfallet.

The scenarios relate to the atmospheric acid deposition of 1988. For the reductions, the deposition to the top of the canopy was reduced linearly between 1990 and 2000. To the sites where the forest stand is still young, the increased filtering of dry deposition was then superimposed on the reduction, as outlined in Chapter 2. The levels of reduction of sulfur deposition, 60% and 85%, were chosen based on the regional analysis of Critical Loads, some of which are presented in Chapter 8. These indicate that still at 60%, Critical Loads of surficial groundwater, forest soils and surface water are exceeded in many areas. Consequently, more radical reductions are necessary to avoid perpetual mitigation measures.

While the predictions based on the Critical Loads methods are sufficient to determine the long-term consequences of deposition reductions, dynamic models are necessary to predict the rate of recovery of different receptors to changes in chemical climate. Because of the complexity and nonlinearity of soil processes, a simple and reliable method to predict the rate of recovery is yet to be developed. To estimate the time scales involved is not a purely academic exercise; mitigation of the effects of acidification ties up economic resources, and new technology for mitigative actions may be called for if large scale damage is foreseen.

6.1 STUBBETORP

In Figure 6.1, the results from simulation of the response to different depositions scenarios with the SAFE model is shown. Both reduction plans result in significant improvement as compared to the no reduction scenario. With the latter, the model predicts that the rate of acidification will increase, leading to ANC-levels below 0 before 2050. The simulations indicate that with the different reductions, the ANC at 1 m depth initially increases, then appears to level off. The level that the ANC approaches, $[ANC]_{ss}$, can be calculated with a steady-state mass balance as:

$$[ANC]_{ss} = \frac{D - W + N_u - BC_u}{Q} \quad (6.1)$$

where D = Deposition of all acid precursors
W = Weathering rate
 N_u = Rate of N uptake
 BC_u = Rate of Ca+Mg+K uptake
Q = Runoff

The deposition is expressed in terms of 'potential acidity' from sea-salt corrected deposition rates. It is defined as

$$D = D_{SO_4^{2-}} + D_{NO_3^-} + D_{NH_4^+} - D_{BC} \quad (6.2)$$

The concept of 'potential acidity' is based on the assumption that there is no leaching of NH_4 from the soil column. This can be a consequence, either of complete uptake of NH_4 in the biomass, or complete nitrification in the soil. The net result of these two reaction paths are equivalent with regard to acidity produced or consumed. In the SAFE model, or any multi-compartment model, the assumption is in fact that there is no net leaching of acidity from the organic soil layer. Sea-salt corrected base cations are assumed to be deposited with alkalinity rather than Cl.

The results from the steady-state calculations are shown in Table 6.1. It is clear that the acidification at Stubbetorp will develop to quite acid conditions unless the 60/30 scenario is put into effect. At the CO_2 pressure in the deeper soil horizons, an ANC of zero corresponds to a pH below 5, suggesting enhanced corrosion if the water was used as drinking water supply. The 30/10 scenario results in a reduced rate of acidification. The N reduction has no effect on the simulations since it is assumed that all N is immobilized in the biomass under all circumstances. The 85/50 scenario is, in fact, the only scenario that leads to acceptable ANC in surficial groundwater.

Figure 6.2 shows the relative importance of weathering and cation exchange for neutralizing acid inputs. At Stubbetorp, weathering is the most important buffering mechanism. The calculations suggest that the rate of cation exchange buffering has peaked, and that accelerated acidification therefore should be expected.

Table 6.1: Steady State Mass Balance for Stubbetorp.

% Reduction		ANC Supply ($\text{meq m}^{-2} \text{ yr}^{-1}$)				$[ANC]_{ss}$
S	N	D	W	N_u	BC_u	
0	0	-118	51	68	-35	-137
30	10	-93	51	61	-35	-64
60	30	-62	51	48	-35	4
85	50	-34	51	34	-33	64

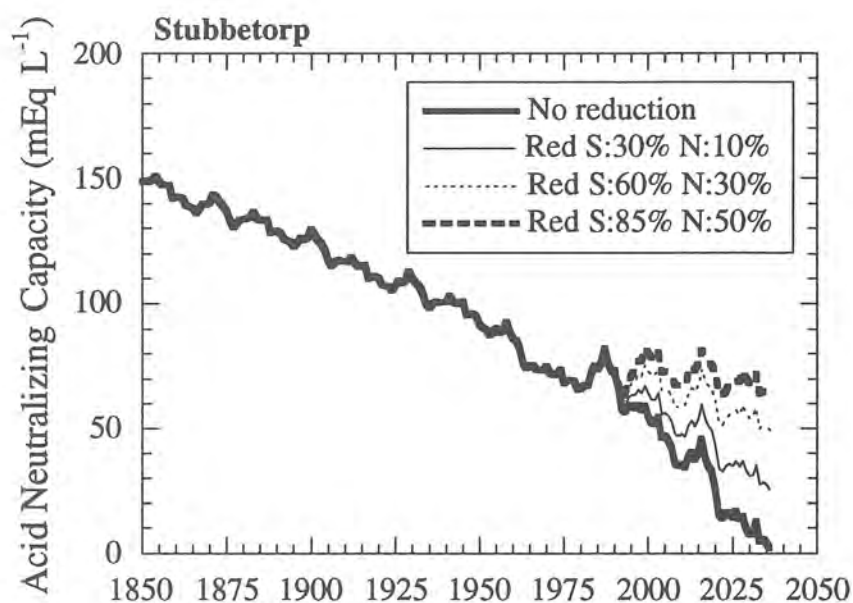


Figure 6.1: Calculated ANC at the 1 m level for different future deposition scenarios. The groundwater will not reach the steady-state condition as given in Table 6.1 until well after 2050.

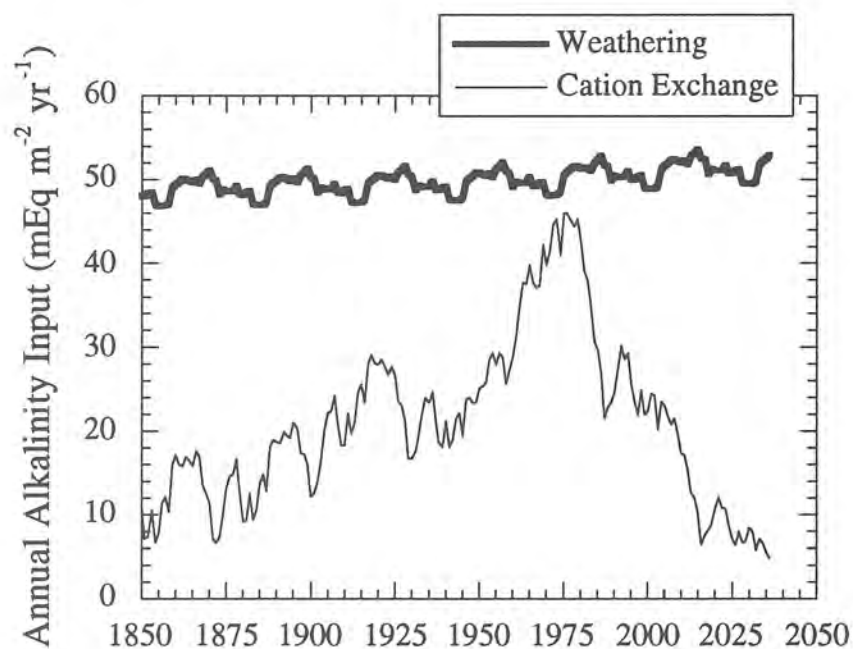


Figure 6.2: Soil buffering reactions at Stubbetorp appears to be dominated by weathering. The relative importance of cation exchange reactions is presently decreasing.

6.2 MASBYN

The Masbyn site differs from the others mainly because of the higher runoff rate. This makes all changes smoother than at Stubbetorp and Risfallet, and the dilution effects make the ANC tend to stay closer to 0.

In Table 6.2 steady-state mass balance calculations for Masbyn are shown. The modeled weathering rate is slower than the weathering rate at Stubbetorp. The N uptake is based on the net uptake in the stand, and accumulation of N in the organic layer is not considered. The calculations show that only 85/50 reductions will give a significant alkalinity in the groundwater, while no reductions will lead to a damaged groundwater resource.

In Figure 6.3 and 6.4, the results from SAFE simulations with present deposition is shown, horizon by horizon. The model is calibrated to fit the base saturation, which leaves no more degrees of freedom for the ANC of the solution. The soil solution pH is compared with pH measured in soil-water suspension. The model predictions are within 0.3 pH-units from the measured $\text{pH}_{\text{H}_2\text{O}}$. There are no lysimeter data to compare the calculated water chemistry with. The raggedness in the calculations come from the cyclic patterns of the repeated hydrological data series. The base saturation is expected to continue to decrease.

Together, Figures 6.3 and 6.5 can be used to translate the ANC to a pH. For example, an ANC of 50 meq m^{-3} corresponds to a pH of 5.5 for the lowest soil layer. Since the DOC, CO_2 pressure and gibbsite equilibrium constant is different for all layers, the pH-ANC relationships are not the same for the different horizons.

The model suggests that the groundwater chemistry is expected to respond directly to reduced deposition. For the 85/50 case, the final value of 46 meq m^{-3} will not be reached until after 2040.

Figure 6.6 shows the ANC production at Masbyn from weathering and cation exchange respectively. Here, the cation exchange is relatively more important than at Stubbetorp. The cation exchange capacity, however, is 300% higher than at Stubbetorp. This illustrates the observation in the sensitivity analysis that the CEC only has small influence on the acidification rate, while the weathering is of primary importance. The sudden increase in weathering rate, from $39 \text{ meq m}^{-1} \text{ yr}^{-1}$ to $46 \text{ meq m}^{-1} \text{ yr}^{-1}$ is caused by changes in hydrology after the clearcutting in the mid 1970's. The decrease in cation exchange buffering is due to a combination of several factors; decreased deposition, increased ANC and cation supply from weathering and reduced base cation uptake.

Table 6.2: Steady State Mass Balance for Masbyn.

% Reduction		ANC Supply ($\text{meq m}^{-2} \text{ yr}^{-1}$)				$[\text{ANC}]_{ss}$
S	N	D	W	N_u	BC_u	
0	0	-104	46	28	-27	-114
30	10	-81	46	28	-27	-68
60	30	-50	46	28	-27	7
85	50	-24	46	28	-27	46

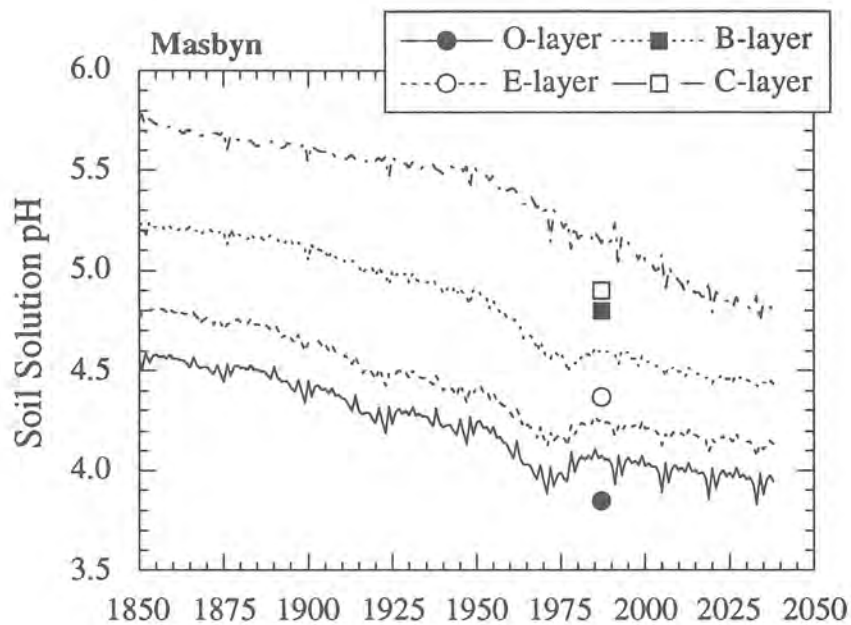


Figure 6.3: Simulated solution pH as compared to pH measured in soil-water suspension.

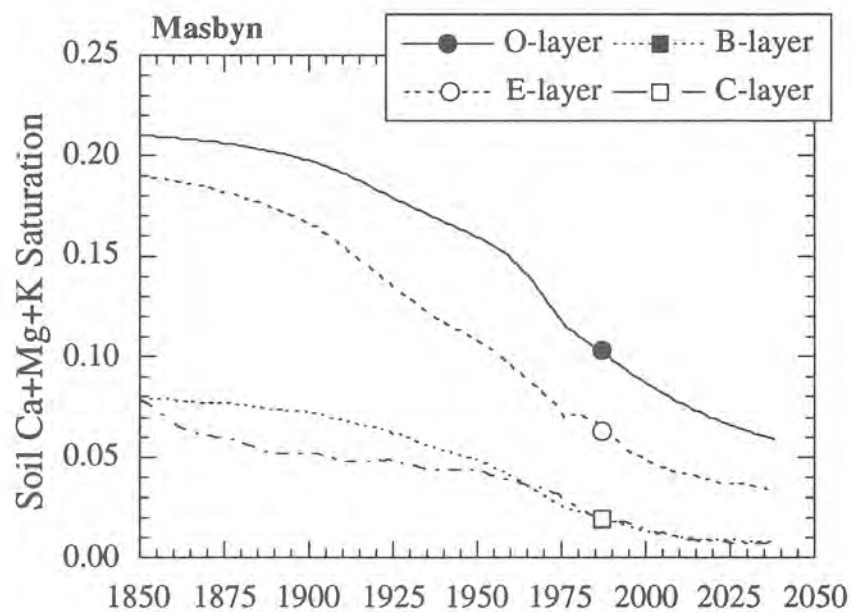


Figure 6.4: Calculated Ca+Mg+K saturation, calibrated to fit data.

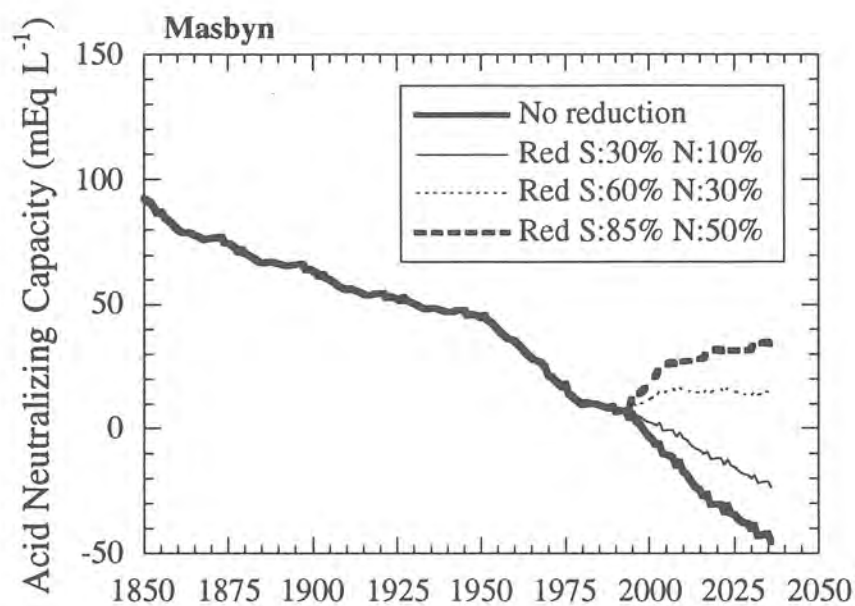


Figure 6.5: Calculated soil solution ANC.

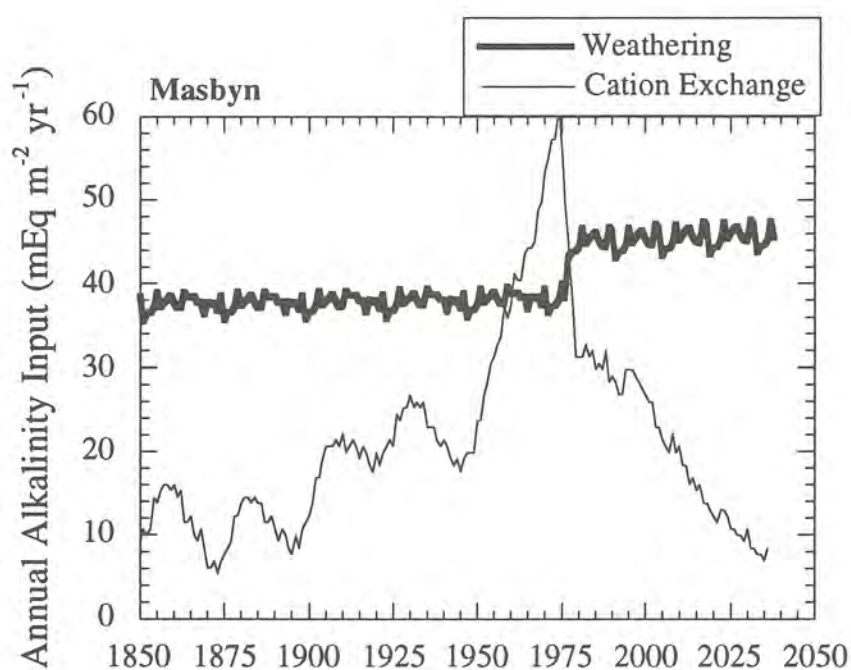


Figure 6.6: The buffering at Masbyn has been dominated by weathering, although cation exchange buffering may have been as important during the period of most intensive acidification.

6.3 RISFALLET

Risfallet is by far the poorest site in this study, the weathering amounting to only $28 \text{ meq m}^{-2} \text{ yr}^{-1}$, as determined both by SAFE and other methods. Still the acidification has not proceeded very far as compared to Masbyn. This is due to the stand characteristics. At Risfallet, a new pine generation was planted around 1970. Thereby, during the years with the highest deposition rate, the stand only received small amount of dry deposition. Also, a pine stand receive only 2/3 of the deposition of a mature spruce stand.

The simulated pH values are close to measured $\text{pH}_{\text{H}_2\text{O}}$. The exeption is the E-layer. In addition, a groundwater analysis shows that the water at 1 m holds pH 5.5, very close to the value predicted by SAFE. Following the clearcutting, the ANC in the groundwater as calculated by SAFE increases due to reduced deposition. The base saturation, however, continues to decline, indication the load during this phase exceeds the critical load of the system.

As the stand grows, the deposition will increase, as will the rate of acidification. This leads to an accelerated rate of decline in groundwater ANC and base saturation in the C-layer. The final state, however, will not be reached until well into the next century. The response to reduced deposition resembles that of Stubbetorp, a rapid improvement followed by a levelling off. The base saturation will continue to decrease even with the 85/50 scenario, however at a slower and slower rate. This is explained by comparing the modeled ANC values with the steady-state chemistry as shown in Table 6.3. The ANC is predicted to drop by an additional 13 meq m^{-3} for the 85/50 reduction scenario, and by 55 meq m^{-3} for the 60/30 scenario.

Since the weathering rate at Risfallet is low, the cation exchange reactions contribute with a large part of the soil buffering. The decrease in exchange rate is a cause of alarm, for groundwater and surface water acidification as well as for forest nutrition.

Table 6.3: Steady State Mass Balance for Risfallet.

% Reduction		ANC Supply ($\text{meq m}^{-2} \text{ yr}^{-1}$)				$[\text{ANC}]_{ss}$ (meq m^{-3})
S	N	D	W	N_u	BC_u	
0	0	-87	28	45	-35	-175
30	10	-67	28	45	-35	-103
60	30	-42	28	43	-33	-25
85	50	-20	28	23	-22	32

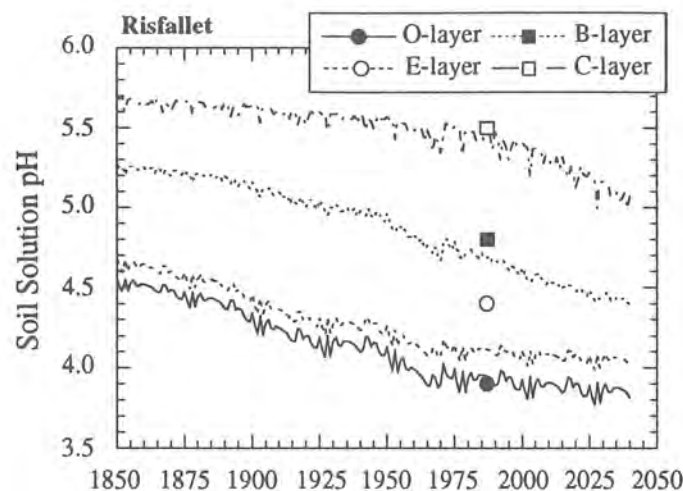


Figure 6.7: Simulated solution pH as compared to pH measured in soil-water suspension.

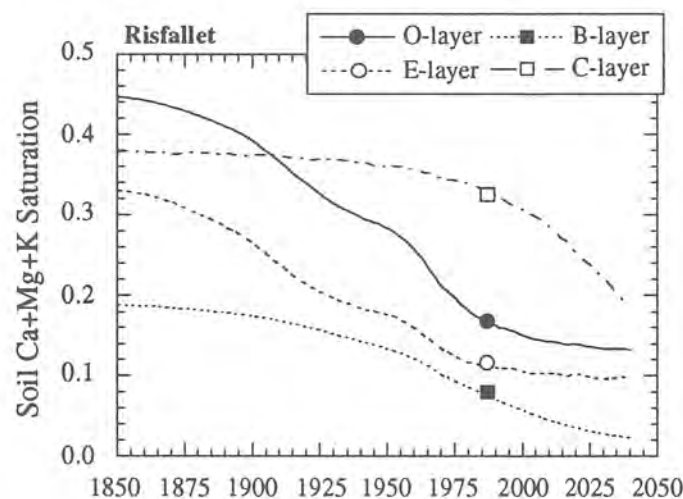


Figure 6.8: Calculated Ca+Mg+K saturation, calibrated to fit data.

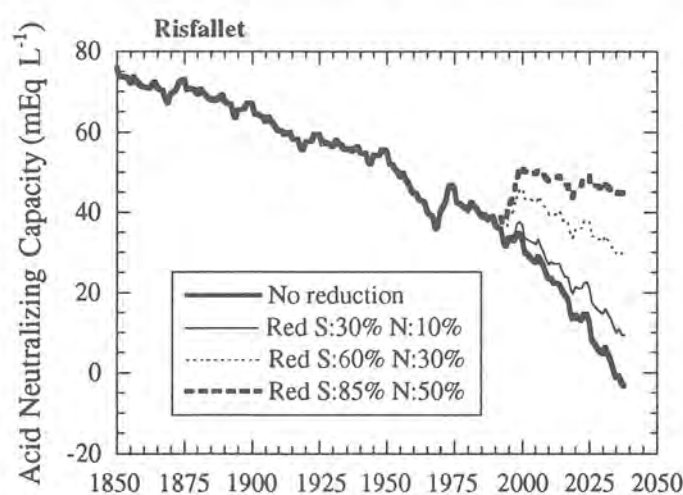


Figure 6.9: Calculated soil solution ANC.

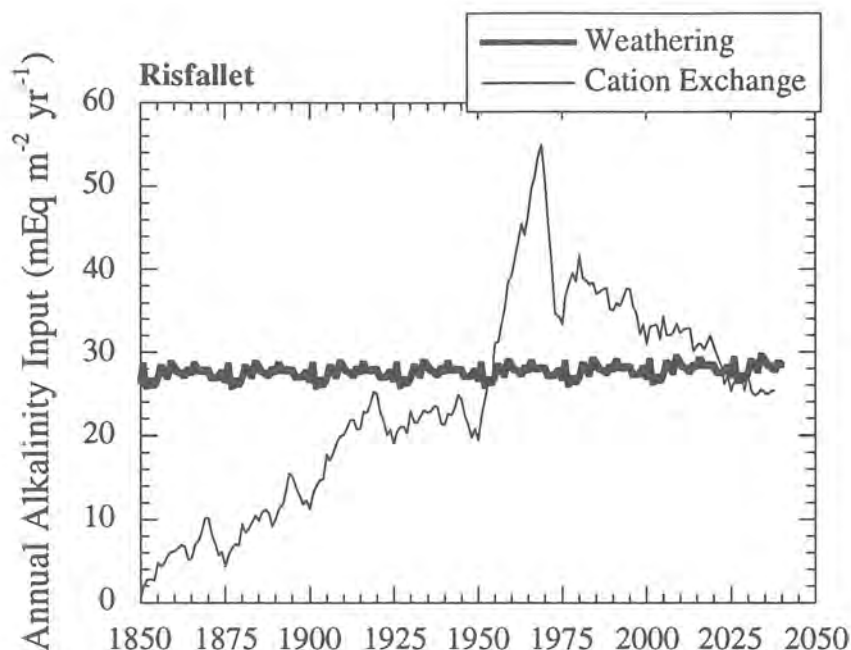


Figure 6.10: At Risfallet, weathering and cation exchange buffering appears to be equally important to neutralize the acid load.

6.3.1 CONCLUSIONS

It has often been argued that the recovery from acidification by necessity is a very slow process. If the base saturation is the sole indicator of acidification, this would certainly be true, but these calculations show that the response of the ANC itself is relatively rapid. This is supported by similar calculations with other dynamic acidification models [Wright *et al.*, 1991]. This result can be explained by the relative role of different buffering mechanisms during different phases of acidification, as shown in Figure 6.2. This figure shows that at Stubbetorp, the weathering is far more important than the cation exchange reaction, except during the period of most intense increase in acid deposition. As the soil pH and the base saturation decreases, the cation exchange buffering is reduced, opening up for a breakthrough in groundwater pH. This phenomenon can, however, only be simulated with multilayer models, where the exchangeable cations in the different soil layers are exhausted in sequence. It has also been shown that SAFE predicts a more dramatic acidification of surface waters, as compared to one box models [Wright *et al.*, 1991].

The hypothesis that weathering is the key process in determining groundwater acidification has been supported by this modeling work.

The three study sites within the project are representative of the areas where they are located. In Chapter 8, dealing with critical loads of groundwater, the steady state ANC of groundwater at 2 m depth is shown. Assuming that the weathering down to 2 m is 2.5 times the weathering down to 1 m, the steady-state chemistry for different deposition scenarios fall out as in Table 6.4. Except for Stubbetorp, the sites fall in, or near, the classes on the maps, showing mean values within each grid.

Regarding Stubbetorp, the N uptake in excess of the amount needed to balance the tree growth is a very large source of alkalinity, that has not been regarded as a possible long term source in the calculations leading to the maps. In fact, this reveals one shortcoming of todays acidification models; the lack of feed-back mechanisms to biological processes in the catchment. Future changes in N mineralisation rate and N fixation processes introduce large uncertainties in the calculations, possibly larger than the uncertainty in the model itself.

Table 6.4: Steady State Mass Balance for groundwater at 2m.

		ANC Supply ($\text{meq m}^{-2} \text{ yr}^{-1}$)				$[\text{ANC}]_{ss}$ (meq m^{-3})
		D	W	N_u	BC_u	
No reduction:	Stubbetorp	-118	127	68	-35	182
	Masbyn	-104	115	28	-27	24
	Risfallet	-87	70	45	-35	-25
30/10 reductions:	Stubbetorp	-93	127	61	-35	240
	Masbyn	-81	115	28	-27	70
	Risfallet	-67	70	45	-35	46
60/30 reductions:	Stubbetorp	-62	127	48	-35	339
	Masbyn	-50	115	28	-27	132
	Risfallet	-42	70	43	-35	128
85/50 reductions:	Stubbetorp	-34	127	34	-33	408
	Masbyn	-24	115	28	-27	184
	Risfallet	-20	70	23	-22	182

7 SCENARIO MODELLING WITH THE MAGIC MODEL

(P. Sandén, L. Maxe and R.F. Wright)

Predicting acidification in the far future is always very uncertain. Both model formulation and estimation of parameters and input data are based on a number of assumptions. It is hard to evaluate the model formulation especially considering the uncertainty in past input data. The degree of complexity needed and the alternative formulations of different processes could have a marked impact on the conclusions drawn about the acidification 50 years into the future.

In order to get some idea about the model formulations effect on the result, it was decided to use the MAGIC model (Model of Acidification of Groundwater In Catchments) on the same catchment as SAFE, and with the same input data as far as possible. MAGIC differs from SAFE in a number of important aspects. There is also extensive experience in running MAGIC for different types of catchments.

7.1 MODEL STRUCTURE

MAGIC is a process-oriented model of intermediate complexity, by which long-term trends in soil and water acidification can be reconstructed and predicted at the catchment scale (Cosby *et al.* 1985a, 1985b). MAGIC consists of: 1) soil matrix - soil solution equilibria equations, in which the chemical composition of soil solution is assumed to be governed by simultaneous reactions involving sulfate adsorption, cation exchange, dissolution and precipitation of aluminum, and dissolution of inorganic carbon; and 2) mass balance equations in which the fluxes of major ions to and from the soil and surface waters are assumed to be governed by atmospheric inputs, mineral weathering, net uptake in biomass, and loss in runoff. MAGIC produces long-term reconstructions and predictions of soil and stream water chemistry in response to given acid deposition scenarios. MAGIC uses a lumped approach in two ways: (1) all chemical and biological processes active in catchments are aggregated into a few simplified processes, and (2) the spatial heterogeneity of soil properties within the catchment is lumped in to one set of soil parameters.

The most important differences between MAGIC and SAFE is as follows:

- MAGIC allows two soil layers while SAFE can specify up to 6 soil horizons.
- MAGIC does not include any nitrogen reactions, while SAFE has a simple formulation of the nitrogen cycle.
- SAFE models cation exchange by a kinetic expression, while MAGIC uses an equilibrium formulation.
- The weathering rate is a calibration parameter in MAGIC, while SAFE uses observed mineral composition to calculate weathering.
- MAGIC uses annula or monthly average precipitation data, while SAFE can be run with daily input of hydrological data.

MAGIC has been applied to a wide variety of catchments in both Europe and North America. The model has been evaluated by comparison with independent historical data such as fisheries records and paleolimnological reconstructions based on diatom remains in lake sediments (Neal *et al.*, 1988; Jenkins *et al.*, 1990). Further the model has been applied to the catchment manipulation experiments of the Norwegian RAIN project (Wright and Cosby, 1987; Wright *et al.*, 1990a). MAGIC has been used to estimate the future effects of changes in forest cover, and the interactions of forests with acid deposition. A technique by which MAGIC can be applied to entire lake regions has also been developed and evaluated using repeated lake surveys in southernmost Norway (Cosby *et al.*, 1989; Hornberger *et al.* 1989).

7.2 PARAMETER ESTIMATION

The Stubbetorp catchment is described in Chapter 2. For a more complete description of the chemistry see Lundin *et al.* (1992). The MAGIC-model was setup as a two layer model, where the upper layer represents shallow groundwater and soil properties of the first 0.75 m. The resulting water chemistry from this layer is compared with the water from a spring (see Figure 2.2). The chemical composition of this water is close to that of groundwater tubes in the recharge area (location 2 in Figure 2.2). The lower soil layer represents groundwater below 0.75 m and is compared with water from a tube with the inlet at 2.3 m below soil surface. This tube is situated close to the stream (location 3). The simulated stream chemistry is compared with water at a weir in the stream. Table 7.1 summarize the water chemistry of these three types of water and presents estimated deposition chemistry used in the simulations.

The physical and chemical properties of the soil vary strongly with depth and shows also a large spatial variation. The chemistry of the upper soil layer (O-, E- and B-horizons) has been surveyed at about 90 points throughout the catchment, while samples of the lower soil layer at greater depths (>0.8 m) have only been taken at 4 sites. The measured soil properties for these two layers have been aggregated to mean values for the catchment (Table 7.2).

Because of the large area with little or no soil cover, the estimated mean soil depth of the catchment is only 0.8 m. The soil depth, in areas covered by soil, is known by measurement only in a few points and the uncertainty in the estimated soil depth may be large (approx. $\pm 30\%$). Due to the large interdependence of the soil parameters with depth this uncertainty will also affect the other parameters.

Beside the input data and parameters that are presented in Table 7.1 and Table 7.2 additional parameters are needed for the simulation. A summary of these parameters and their values can be found in Table 7.3. The solubility constant for $\text{Al}(\text{OH})_3$ and the CO_2 partial pressure were calculated from the observed chemistry. The fraction of runoff passing through the two soil layers were calculated from concentration data of cations and anions in springwater, deeper groundwater and streamwater.

The fluoride deposition was estimated to be $1.5 \text{ meq m}^{-2} \text{ yr}^{-1}$; the few measurements of fluoride concentration in streamwater indicate a runoff flux of this magnitude.

The deposition of base cations was assumed to be equal to present-day levels over the entire 190-year simulation period from 1848 to 2038. SO_4 deposition was assumed to be $2.3 \text{ meq m}^{-2} \text{ yr}^{-1}$ in 1848. The deposition of nitrogen components were assumed to be zero in 1848.

Table 7.1 Volume weighted concentrations of major ions in precipitation, spring-water, and streamwater (at weir), for 1988. Also shown are mean concentrations in samples of deep groundwater (n=3), and input-output fluxes for the catchment. Al: total concentration. ANC: alkalinity titrated to fixed pH 5.4 endpoint. Units: concentrations meq m⁻³; fluxes meq m⁻² yr⁻¹.

	Wet dep. ¹	Spring	Ground-water	Stream-water	Flux	
					In ¹	Out
Precip. and runoff (m)	0.68			0.28		
pH	4.4	4.9	6.6	5.9		
H ⁺	40.1	11.7	0.3	1.4		
Ca	7	97	404	143	9.1	40.0
Mg	5	66	173	76	5.5	21.2
Na	13	97	188	105	16.0	29.4
K	2	14	30	17	2.3	4.7
NH ₄	26	0	0	0	26.8	0.0
SO ₄	47	173	226	169	54.4	47.2
Cl	17	70	102	77	20.2	21.6
NO ₃	28	1	0	3	24.3	0.7
ANC		-16	478	42		
Al		24	6	21		

¹ Chemistry and dry deposition for late 80'ies, (Lövblad *et al.*, 1992).

The deposition sequence for SO₄ were taken from Granat (1990) for the period 1955-1988. For the period 1848-1955 the deposition of SO₄ was assumed to be proportional to the European emissions of S as reconstructed by Bettelheim and Littler (1979). A nitrogen deposition sequence was also taken from Granat (1990) for the period 1955-1989. The earlier period was simply found by interpolation between zero and the 1955 value (Figure 7.1).

Net uptake of NH₄ and NO₃ in the catchment was set to 99% of the deposition; this value gives reasonable streamwater for the calibration year 1988. Net uptake of base cations was set proportional to the nitrogen uptake (Table 7.4). Data on proportions between nitrogen and base cations in trees were taken from Rosén (unpublished data). Uptake of base cations at the start year was set to 10% of present uptake. The uptake sequence for base cations follows the nitrogen uptake.

The SO₄ deposition is larger than the outflow through the weir (see Table 7.1) and the deposition of SO₄ has decreased over the last decade (Figure 7.1). This suggest that part of the sulphur is lost to the atmosphere or retained within the catchment, possibly as metal sulphides. Reversible SO₄ adsorption would, with the decreasing deposition lead to higher outflow than deposition at present. This sink is treated in the simulation by uptake proportional to the deposition of SO₄. In order to get Cl concentrations to match in all three types of water (shallow groundwater, deeper groundwater and streamwater) a minor uptake was used in the upper soil layer and an addition of Cl used for the lower soil layer. A similar minor correction was used for SO₄ for the lower soil layer.

Table 7.2. Soil characteristics at Stubbetorp.

	Upper soil layer	Lower soil layer
Depth (m)	0.75	0.25
Bulk density (kg m^{-3})	1275	1425
Porosity (%)	55	45
Cation exchange capacity (meq kg^{-1}) ¹	12.4	5
Exchangeable cations (%) ¹		
E_{Ca}	28	40
E_{Mg}	5	8
E_{Na}	1	2
E_{K}	3	4
E_{H}	16	5
E_{Al}	47	41

¹Base cations measured in 1M NH_4OAc extract (pH 7); aluminum and hydrogen ions in unbuffered 1M KCl extract.

Table 7.3. Additional model parameter values.

	Upper soil layer	Lower soil layer	Stream
Solubility of solid phase aluminum ($\log_{10}$) ¹	9.47	9.47	9.47
P_{CO_2} ¹ (atm)	0.004	0.01	0.0007
Temperature ($^{\circ}\text{C}$) ²	7	7	7
Total organic carbon (mmol m^{-3}) ³	70	10	80
pK1 organics ⁴	4.5	4.5	4.5
pK2 organics ⁴	8	8	8
Fraction of runoff through layer (%) ¹	100	15	
SO_4 half-saturation capacity (meq m^{-3}) ⁴	100	100	
SO_4 adsorption capacity (meq kg^{-1}) ⁵	1	1	

¹ Calculated from measured variables.

² Average yearly air temperature from close by regular climatological station (Simonstorp).

³ Estimated from single measurement in streamwater.

⁴ Earlier used values for scandinavian catchments (Wright *et al.*, 1990b).

⁵ Data from Lindalen ($58^{\circ}36'\text{N}$, $15^{\circ}36'\text{E}$, 120 m a.s.l., Nömmik *et al.*, 1988).

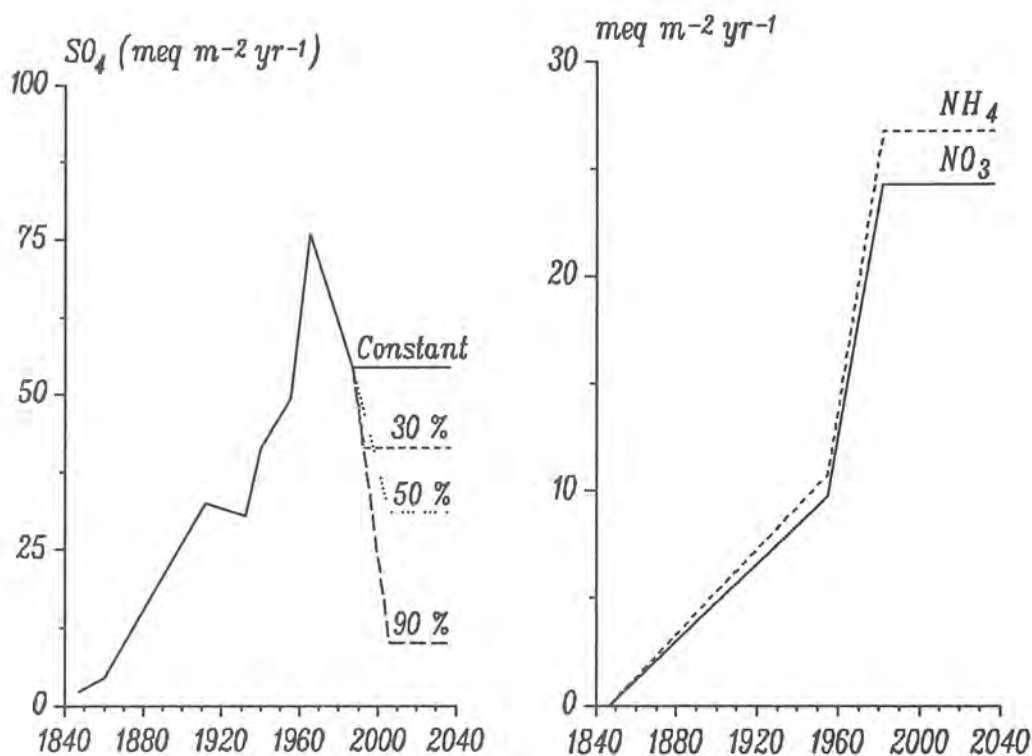


Figure 7.1. Used deposition sequences and scenarios for SO_4 , NO_3 and NH_4 . The values represent total deposition (wet and dry).

Table 7.4. Uptake and addition of cations and anions to the two soil layer in the simulation. Positive values represents uptake. All values in meq $m^{-2} yr^{-1}$.

	Upper soil layer		Lower soil layer	
	1848	1988	1848	1988
Ca	2.5	25.4	0.3	2.8
Mg	0.5	5.2	0.1	0.6
Na	0	0	0	0
K	0.5	5.2	0.1	0.6
SO_4	0	10	0	-0.5
Cl	0.4	0.4	-1.4	-1.4

We used the automatic optimization procedure of MAGIC (Jenkins and Cosby 1989) to set weathering rates and initial saturation for the base cations in order to reproduce present day chemistry. The optimization was done in two steps. First the optimization was targeted on the chemistry of the spring. The spring could be regarded as fairly shallow groundwater. This optimization was then used as an input to a two soil layer model of the watershed. The target chemistry and fixed parameters for the second soil layer were taken from deeper part of soil profiles (Table 7.3 and Table 7.5)

Table 7.5. Range used for optimization for variables and parameters.

	Upper soil layer		Lower soil layer		Stream	
	Min	Max	Min	Max	Min	Max
Solution concentration (meq m ⁻³)						
Ca	93	101	394	419	119	167
Mg	63	68	156	197	69	82
Na	87	108	178	200	92	118
K	14	14	25	36	15	19
Base saturation (%)						
E _{Ca}	18	32	6.3	32		
E _{Mg}	3	6	1.4	7.1		
E _{Na}	0.7	1.8	1.9	4.8		
E _K	2.6	4.6	2.7	7.8		
Depth (m)	0.52	0.99	0.2	0.34		
Bulk density (kg m ⁻³)	1180	1364	1400	1450		
Cation exchange capacity (meq kg ⁻¹)	10	15	1.8	10		
Aluminum solubility (log ₁₀)	9.31	9.51	9.31	9.51	9.31	9.51

The optimization procedure of the model version used does not allow different weathering rates in the two soil layers. It proved impossible to reproduce present day groundwater and streamwater chemistry with this restriction. To circumvent this problem additional uptake was used. If one of the soil layers needed a higher weathering rate, the other layer was given a corresponding uptake. This uptake is subtracted from all weathering rates and uptakes reported here.

The model allows for a multiple optimization with varying parameters and target chemistry (Jenkins and Cosby, 1989). The optimization was performed 10 times using randomly chosen values for parameters and target chemistry within the intervals specified in Table 7.5. A number of important parameters and input data of the model can unfortunately not be handled in this way as they demand recalibration of the model.

For the forecast scenarios four different deposition sequences were used (Figure 7.1). The first represents constant deposition at the 1987 level of sulphate. The second scenario represents the results that would be the effect of the ECE (United Nations Economic Commission for Europe) Convention on Long Range Transboundary Air Pollution (30 club). That is a 30 % reduction of sulphur emission (and hopefully deposition) between 1980 and 1993. The last two scenarios represent a 50 % and 90 % reduction from 1980 until 2006. The maximum reduction scenario of 90 % was carried

out to get an idea of how large the reduction would have to be in order to reverse the acidification process. In all scenarios the nitrogen deposition was held constant at the present-day level.

7.3 RESULT

In MAGIC the initial saturation, weathering rates and selectivity coefficients for the base cations are interrelated. Two of the three are specified and the third is then calculated. The optimization routine chooses initial saturation and weathering rates, calculates selectivity coefficients, runs the 140-year hindcast and compares the 1988 soil saturation and base cation concentrations in soil solution with the measured values (the targets). This procedure is repeated until the best match is obtained.

Table 7.6. Optimized weathering, base saturation and selectivity coefficients. Minimum and maximum of 10 optimization.

	Upper soil layer		Lower soil layer	
	Min	Max	Min	Max
Weathering (meq m ⁻² yr ⁻¹)				
Ca	0.52	1.47	13.60	13.93
Mg	2.56	5.50	2.14	3.17
Na	9.63	12.01	1.11	1.95
K	0.80	1.25	0.86	1.02
Initial base saturation (%)				
E _{Ca}	38.5	48.3	15.0	28.0
E _{Mg}	11.3	17.7	2.8	4.3
E _{Na}	2.5	3.4	2.8	4.2
E _K	5.4	7.9	4.3	6.9
Selectivity coefficients (log ₁₀)				
S _{AlCa}	-0.7	0.1	9.0	10.2
S _{AlMg}	1.0	1.7	9.2	10.9
S _{AlNa}	-1.2	-0.4	1.5	2.7
S _{AlK}	-5.0	-4.4	-1.0	0.1

The optimized initial base saturation of Ca and Mg obtained by this procedure is higher in the upper soil layer compared to the lower soil layer (Table 7.6). The weathering rates for Ca and Mg in the upper soil layer are very low, while the Na weathering rate is high. The other weathering rates are given reasonable values. The selectivity

coefficients are highly different between the two soil layers. The coefficients for the lower layer seem to be very high.

The calibrated base saturation is well within the range observed for present-day chemistry (Figure 7.2). The same is true for ANC in soil solution in the upper soil layer and for the stream (Figure 7.3). The lower soil layer has a higher observed ANC than simulated. The pH is lower than observed for the upper soil layer and higher for the lower layer, while pH in stream water is simulated within the observed range (Figure 7.4)

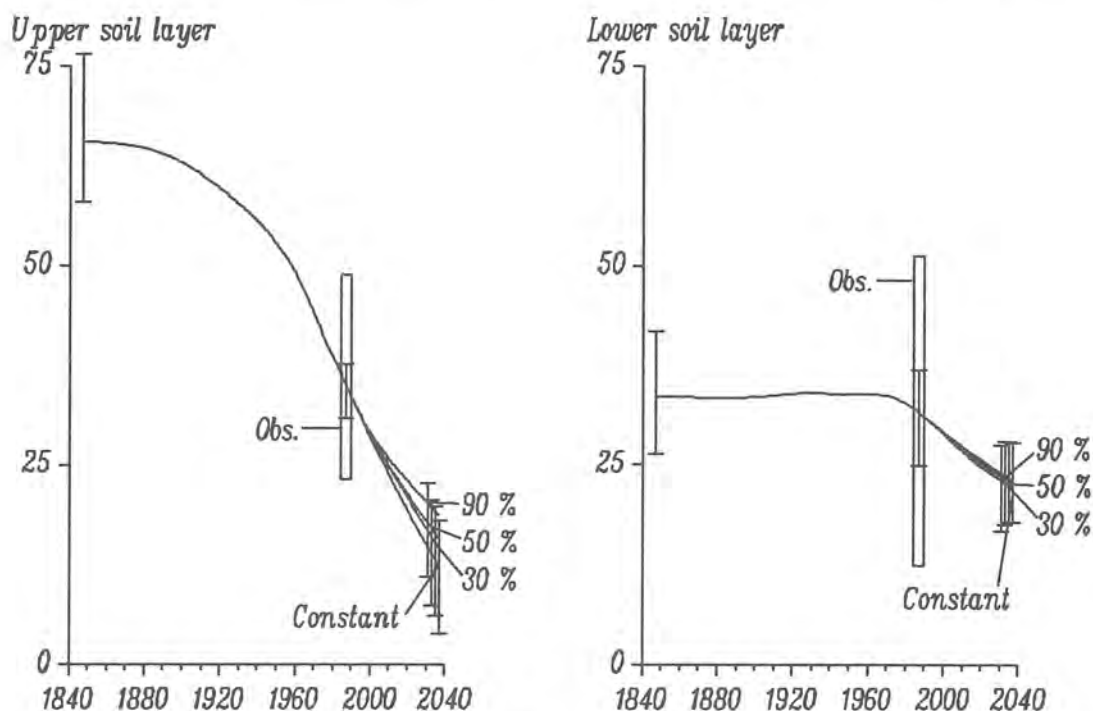


Figure 7.2. Simulated and observed base saturation (%) over the period 1848-2038 for the two soil layers at Stubbetorp (see Figure 7.3 for details).

The calibrated model successfully reproduced measured concentrations of base cations and anions in the three water types within the ranges for present-day.

The MAGIC calibration indicates significant acidification of streamwater and soil at Stubbetorp over the past 140 years. ANC (Figure 7.3) and pH (Figure 7.4) decline gradually at first and more rapidly during the past 30 years, in part as a consequence of the depletion of soil base saturation (Figure 7.2). The rate of change during the last 10-years is again slower.

The forecast scenarios suggest that 30 or 50 % reduction in deposition would not halt the acidification. Even a 90% reduction can not stop a continuing depletion of the base cation storage in the upper soil layer (Figure 7.2).

The multiple optimization routine produces estimates of uncertainties (presented by the bars in the figures). Although these uncertainties are in some case quite substantial, the overall trends are readily apparent. The uncertainties are, in part, due to the uncertainty in model parameters, but also to uncertainty in the measurements and aggregation estimates of soil and stream characteristics used to calibrate and run the model. The bars

overlap each other for all cases in the lower soil layer. The upper soil layer and the stream also show a large degree of overlap in the bars.

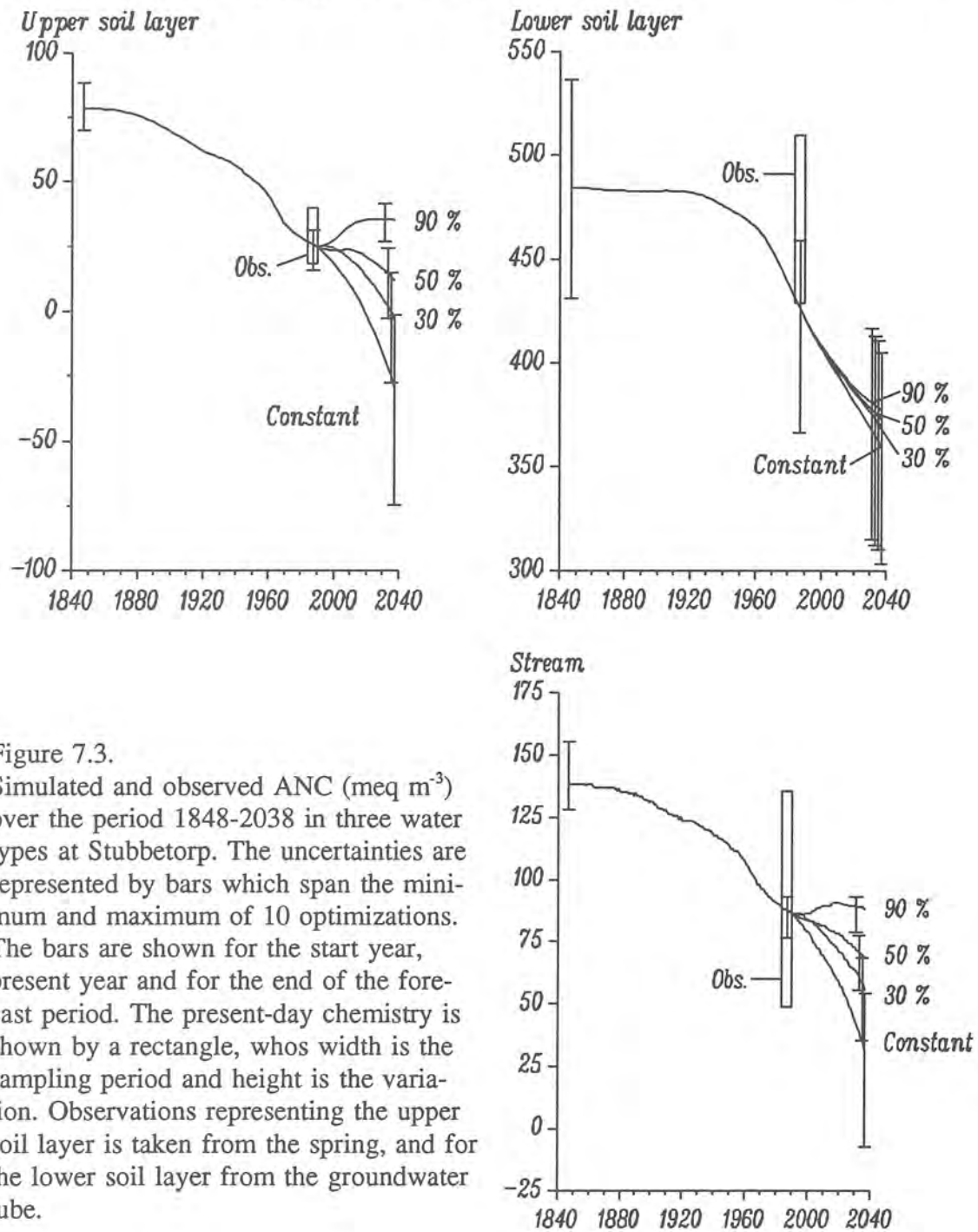


Figure 7.3.
Simulated and observed ANC (meq m⁻³) over the period 1848-2038 in three water types at Stubbetorp. The uncertainties are represented by bars which span the minimum and maximum of 10 optimizations. The bars are shown for the start year, present year and for the end of the forecast period. The present-day chemistry is shown by a rectangle, whose width is the sampling period and height is the variation. Observations representing the upper soil layer is taken from the spring, and for the lower soil layer from the groundwater tube.

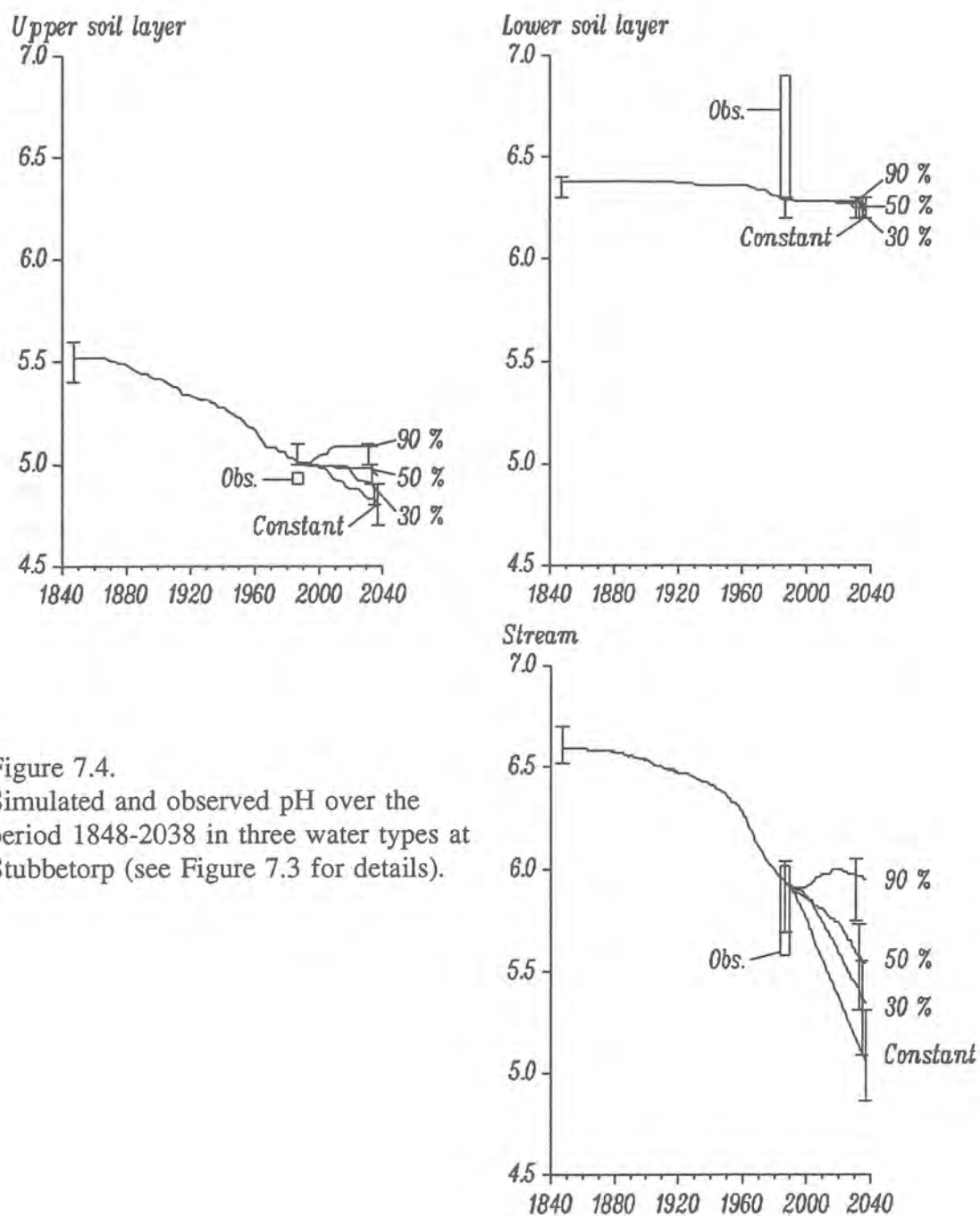


Figure 7.4.
Simulated and observed pH over the
period 1848-2038 in three water types at
Stubbetorp (see Figure 7.3 for details).

7.4 DISCUSSION AND CONCLUSIONS

The low base saturation used for the lower soil layer in 1988, result in low initial base saturation and high selectivity coefficients. As the input of base cations is large to this soil layer, the change over time in base saturation is small in the lower soil layer. The initial base saturation will therefore be close to the present. The intervals specified for the lower soil layer, based on measurements, have a lower minimum than the upper layer, and about the same maximum. With this low base saturation and the high base cation concentration in the solution the selectivity coefficients must be high. The present day base saturation for the lower soil layer might be a good areal representation for the 1 m deep in the soil. At the depth of the groundwater tube (2.3 m), used for the lower soil layer solution chemistry, the base saturation is probably much larger (not measured). A larger base saturation would give lower selectivity coefficients. The results are not, however, in any important way affected by this discrepancy.

The low weathering rates for Ca and Mg is coupled to the relatively high deposition used for these elements in 1848. If the true deposition, at that time, was close to the seasalt composition the weathering of Ca would be about $6 \text{ meq m}^{-2} \text{ yr}^{-1}$ in the upper soil layer.

The total weathering rate of $30\text{-}40 \text{ meq m}^{-2} \text{ yr}^{-1}$ estimated by the model is low but reasonable for these highly siliceous soils. The soils are shallow, coarse and dominated by slow weathering feldspars. The calibrated weathering rate used by MAGIC is somewhat lower than obtained by the steady-state PROFILE model (see Chapter 5), about $50 \text{ meq m}^{-2} \text{ yr}^{-1}$. In PROFILE the weathering rate is estimated from soil texture and mineralogy in the soil profile down to 1 m and therefore not calibrated. The difference in estimates might be due to inadequacies of the model structures, uncertainty in the estimates of soil parameters, or estimates of base cation uptake by the forests.

The departure of the simulation from observations for pH and Acid Neutralizing Capacity (ANC) is of minor importance. The difference between observed and simulated pH of the water in the two soil layers is only 0.1 unit, and could be caused by a minor difference between calculated and true P_{CO_2} . The same explanation can be used for ANC in the lower soil horizon.

A model is always a simplification of the real processes. Uncertainties in the data and parameters result in a substantial uncertainty in the model results. Large overlaps between different scenarios are obvious in the figures. The uncertainty portrayed by the used sensitivity analysis are, however, to the major extent a question of level. None of the tested parameters gives any notable change in the pattern.

Parameters and data that could give another pattern are more difficult to study as they demand recalibration of the model. The anion deposition sequence, the base cation uptake and sequence, the base cation deposition and sequence are for the past situation (at least before 1970) mostly set as a result of a qualified guess.

The anion deposition sequence can be estimated with some certainty based on the usage of fossil fuel and other material that could emit acidifying substances to the atmosphere. There is, however, considerable difficulties regarding the long-range transport. The importance of chimney height for instance is hard to evaluate. During the 1960's industries in many European countries increased the chimney heights to carry pollutants further away from heavily-polluted areas. The connection between emission and deposition is therefore not straightforward.

The model results, especially the scenarios, suggest that a major part of the acidification is due to base cation uptake by the forest, and removal of base cations with the timber. Even the 90% reduction scenario seems to give only temporary improvement of ANC and pH in the shallow groundwater and the stream and no improvement for the deeper groundwater. The base cation uptake value is, however, difficult to estimate and is probably the most uncertain value used in the model. It is based on the assumption that all deposited nitrogen, minus runoff nitrogen, are taken up by the trees in a long-term perspective, where storage in soil and annual vegetation can be neglected. The base cations are then assumed to be taken up in proportion to nitrogen according to their ratios in tree stem, branches and roots, taken from literature. This neglects possible denitrification and accumulation of persistent organic nitrogen in soil, mire and streams. In estimating the base cation uptake sequence, possible changes in denitrification and accumulation are also neglected. Taking these assumptions into account it is likely that the base cation uptake is overrated, and so is the importance of forestry on the acidification of this catchment.

The base cation deposition data before 1970 are not available and there is little information on their variation and possible trends. It is plausible that there has been an increasing emission of base cations as a result of increasing industrial production and road transport.

The model results suggest that small positive effects such as increased pH and ANC can be expected if a sulphur reduction above 50% can be attained. A reduction of 90% would bring about a considerable improvement of the pH of the streamwater, and in the ANC of the shallow groundwater. It can be seen that in the shallow groundwater the standards determined by the Swedish Environmental Protection Agency (ANC > 140 meq m⁻³, pH > 6, HCO₃:SO₄ > 1 at 1 m depth) will not be met. (Sverdrup *et al.*, 1990)

The very shallow groundwater represented by the spring is not often used for drinking water purposes. The deeper groundwater in the model, however, represents a type often found in dug wells. The change in this water is slow.

The conclusion of this chapter is that the MAGIC calibration to soil, streamwater and groundwater data from Stubbetorp indicate that the soils and waters have undergone significant acidification during the past 140 years. Although groundwater and streamwater at Stubbetorp still have positive ANC and pH above 6, they are threatened by the combination of acid deposition and soil acidification caused by forestry practices.

The simulations suggest that reductions in acid deposition of >50 % are required to halt and reverse the ongoing acidification at Stubbetorp. To halt the acidification of the shallow groundwater a more drastic reduction in acidic deposition is needed. This might not, however, be enough. Forest management practices might also have to be changed.

The deeper groundwater is in no immediate danger, and this water would probably sustain the present acidification.

The uncertainties in these model results are due to inadequacies and simplifications in the model itself, difficulties in estimating catchment-scale aggregated values for key input parameters, and uncertainty in the measured soil and water chemistry data to which the model is calibrated.

Of these uncertainties, one of the larger in this type of simulation is the input data for the past. This data controls much of the output, both in terms of level and pattern. Especially important and uncertain are the base cation deposition and uptake.

The MAGIC and SAFE simulation both lead to the same overall conclusion. That is that a drastic reduction in acidifying substances must be obtained if the groundwater at

Stubbetorp should be protected against acidification. A qualitative comparison of the models is difficult as key process are handled in different ways. The physical representation of the two models in this report is also different. SAFE is used for a single soil profile, while MAGIC was run for the whole basin.

8 CRITICAL LOADS FOR GROUNDWATER

(H. Sverdrup and P. Warfvinge)

The objective of this chapter is to demonstrate how critical loads for groundwater and areas where they have been exceeded can be calculated using the modelling tools developed in the project. Critical loads were calculated based on data from the Swedish forest survey programme, and the maps apply to wells outside urban areas and agricultural areas.

The critical load of acid deposition was defined at the International Workshop on Critical Loads held at Skokloster as [Nilsson and Grennfelt, 1988]:

The maximum amount of sulphur and nitrogen deposition that will not cause long term damage to ecosystem structure and function.

The calculation of the critical load is an important tool for assessing the acceptable levels of acid deposition throughout the different parts of a region. 19 European countries have agreed to map critical loads for their respective territories, and use this information as a basis for negotiating the new protocols on sulphur and nitrogen emissions. It is also an important instrument in balancing the acidification stress imposed on catchments by the forest practices against acid deposition.

Maps over critical loads are among the most important results of the work carried out in the Integrated Groundwater Project. It has not been the stated objective of the project from the beginning to produce such maps, but they represent a clear way to present the groundwater acidification sensitivity of shallow groundwater in Sweden once the ability to produce such maps is available. It must also be remembered that without the results from the Swedish Integrated Groundwater Acidification Project in the form of different general soil chemistry models, mapping of critical loads for forests and groundwater in Sweden would not have been possible at the present level of ambition. The maps for critical loads will be used by the Swedish government in the international efforts to get emission reductions in acidifying compound sufficient to protect our nations natural resources.

When critical loads are mapped, the first element is to define the receptor considered. Examples of receptors include groundwater resources, forest soils and surface waters. Secondly, a biological indicator is selected. For groundwater, humans drinking water from shallow wells have been selected for the Swedish critical loads programme. In this context, the definition of critical loads is the maximum acidic deposition that will not cause the water infiltrating to aquifers at 2 m to induce health problems, either directly or indirectly through corrosion or mobilization of heavy metals. This criteria has been translated into chemical criteria that should prevent damage to the groundwater resource. Several such chemical limits have that would be proposed, and the criteria applied here is:

- The acidity of the water should stay above pH 6 equivalent to an air-equilibrated pH of approximately pH 6.5 and alkalinity above 100 meq m⁻³ at 2.0 meter depth.

Corrosion of water accelerates when the water is acidified to below pH 6, high alkalinity and hardness tend to decrease the rate of corrosion. Further considerations

take into account that if the groundwater is buffered to at least 100 meq m^{-3} at the 2 meter level, then the deeper parts of the aquifer will be well buffered enough to prevent corrosion. This implies that we require a small net alkalinity contribution from the top 2 meter of soil to the groundwater aquifer. At pH below 6 aluminium concentrations will rise in the water, and at lower pH values small amounts of heavy metals can sometimes be mobilized. Naturally occurring heavy metals do not regularly constitute any problem in Sweden, but still it will be desirable not to have any future increase in the heavy metal concentration in groundwater used for drinking.

Different chemical criteria can be applied in different areas if different receptors are considered. For instance, the chemical criteria may vary between specific locations where the water installations are important, or where heavy metals are known to occur in amounts that could cause trouble if released. It was considered to apply the critical loads calculations to different soil depths than 2 meter, but it was felt that by applying the limit at the 2 meter level, the deeper parts of aquifers would be protected sufficiently. It has been considered if an ANC limit of 150 meq m^{-3} could be applied at the 1 m level. This is, however, very close to, or in certain instances above, the natural pre-historic background ANC for many soils. It was therefore felt that this would not be a realistic approach.

The calculations have been limited to moraines only. Calcareous soils may be leached in the upper soil layers, while the carbonate content, and hence the weathering rate, may be high further down in the soil profile. The necessary extrapolation of soil properties down to 2 m depth could not be done based on available soil data.

In this section, maps of critical loads for groundwater are shown. The maps were produced from critical loads calculated in 1395 different points, unevenly spaced over the country to minimize covariance between samples. The results are presented as shaded grids, 50 km by 50 km, and each grid may hold up to 30 calculating points. Since each calculation point has a unique critical load, the data can be presented in many ways. Here, it was decided to let the shading in a grid be based on the median value of all critical loads data within the grid. This is also expressed as the 50%-tile value. This means that 50% percent of the groundwater resources within the grid will not be protected if the load corresponding to the shading is applied. The 50%-tile was selected since there could be flexibility when selecting source of drinking water.

For groundwater, the chemical weathering in the unsaturated zone is a most important long term buffering process. Therefore, separate maps showing the magnitude and regional distribution of weathering has been included.

8.1 METHODS

8.1.1 Principles of calculation

Calculating loads for groundwater is basically to make a balance of acidity and alkalinity for the soil column down to the specified depth. Within this volume, only sinks and sources of acidity that are effective over a long time period should be included. This excludes processes where the pool is exhaustible, such as cation exchange and anion adsorption.

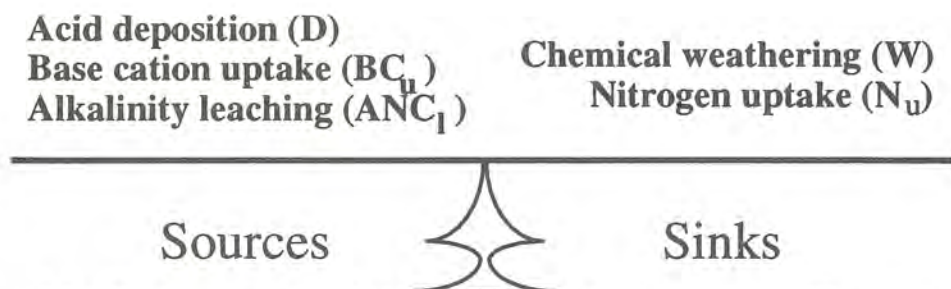


Figure 8.1: Basic principle of the critical loads estimation. The essence of the calculation is to define the alkalinity leaching for the receptor considered, to quantify uptake and weathering, and thereafter adjust the deposition to achieve a balance.

Figure 8.1 illustrates the balance used for calculating critical loads of groundwater. The critical load is by definition the acid load (D) that brings the sinks and sources to balance. Of the remaining terms in the balance, the ANC leaching (ANC_l) is defined by the chemical criteria. To quantify the remaining terms, different approaches can be taken. In this study, the uptake of N (N_u) and base cations (BC_u) was input data, while the weathering rate (W) was calculated from geophysical data using the PROFILE model, described in Chapter 4.

8.1.2 Calculation procedure

The critical loads have been calculated in each of the 1395 points, as shown in Figure 8.2. Thereafter, the results have been aggregated into maps and cumulative distributions. Due to the complex interactions between processes that must be taken into account in the calculations, it was not considered appropriate to take the approach to calculate regional critical loads from aggregated data.

In order to calculate critical loads of groundwater with the PROFILE model, a considerable amount of data was collected. All data in this regional critical load assessment is based on information collected within the framework of the Swedish National Forest Survey (Rikskogstaxeringen/Ståndortsskarteringen). Within this programme soil and stand data has been collected from 27,000 stations. For this study, a subsample of 1395 sites were selected to utilize the soil samples that were available down to the C-layer at approximately 60 cm soil depth. These samples were used to obtain the mineralogy data for the PROFILE model, either directly or by the method to reconstruct mineralogy from total digestion analysis.

As shown in Figure 8.3, a number of different models and correlations was used. The correlations indicated in the diagram will be discussed in detail below. In addition to those correlations, deposition data were produced by interpolation between monitoring stations, and forest uptake rates were determined from regional estimates of the element contents in the biomass.



Figure 8.2: Map of the 1395 sites used for the calculations.

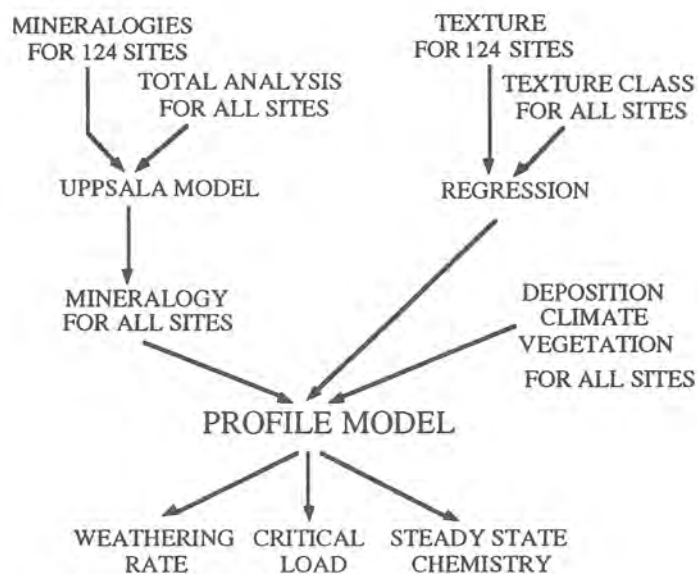


Figure 8.3: The calculation procedure used in the determination of critical loads using the PROFILE model.

8.1.3 Minerology

Regional determination of weathering rates has not previously been pursued. In addition to making critical loads assessments possible, application of models such as UPPSALA, PROFILE and SAFE on a finer regional scale in Sweden have opened up possibilities for forest resource management, renewal of forest management procedures, groundwater resource planning and management and more. Much of this depends on the ability to obtain mineralogy data for soils on a regional scale.

The soil mineralogy was derived for a subset of 124 sites by measurement at the Swedish Geological Survey (SGU) at Uppsala. The mineralogy analysis scheme required each soil sample to be divided into 4 parts, based on density and particle size. The fast weatherable minerals will tend to concentrate in the heavier fraction, and the analysis can then be carried out on the enriched fraction, despite that they may be present in very small amounts in the whole soil sample. Separation of the mineral sample in a liquid with density in the range 2.680 g/cm^3 , will generally concentrate easily weathered minerals 30-70 times. The mineralogy determination is generally carried out on the silt and clay fraction of the soil, since all particles larger than $50 \mu\text{m}$ dissolve too slowly to be significant for the weathering rate. Each fraction is analysed with XRF and XRD for identification of the minerals present and semi-quantitative analysis. The methodology is outlined in Table 8.1. Total elemental content of the soil after complete dissolution was determined for all samples and sub-samples. In a total analysis, the minerals in a soil sample are totally dissolved in hot hydrofluoric acid or a lithiumborate-alkali melt, diluted in water and analysed. These were analysed using standard wet chemistry methods for Ca, Mg, Na, K, Al, Si, Fe, Ti and trace metals. These data are used to assemble the mineralogy of the whole soil sample.

Table 8.1: The mineralogy analysis scheme in which each soil sample is divided into 4 parts, based on density and particle size to enrich different minerals. Each fraction is analysed with XRF and XRD for identification of the minerals present and semi-quantitative analysis, and wet methods for total elemental content.

	Light fraction < 2700 kg/m^3	Heavy fraction > 2700 kg/m^3
Sand-silt > $2 \mu\text{m}$	Feldspars Quartz Muscovite Biotite	Pyroxene Amphiboles Epidote Biotite Nesosilicates
Clay < $2 \mu\text{m}$	Vermiculite Montmorillonite Quartz	Chlorite

Table 8.2: The equations used in the UPPSALA model for calculation. The units are % weight. The calculation is checked by calculating the amount quartz in the sample, and all samples where the total mineral amount does not add up to within the range from 95 to 105% are rejected from the set. Any value less than 0 should be put to 0.

K-feldspar:	KF	=	$5.88 \cdot K_2O - 0.588 \cdot Na_2O$
Oligoclase:	OL	=	$11.1 \cdot Na_2O - 0.22 \cdot KF$
Apatite:	AP	=	$2.24 \cdot P_2O_5$
Hornblende:	HO	=	$6.67 \cdot CaO - 3.67 \cdot AP - 0.2 \cdot OL$
Muscovite:	MU	=	$2.08 \cdot K_2O - 0.208 \cdot Na_2O$
Chlorite:	CL	=	$3.85 \cdot MgO - 0.39 \cdot HO - 0.39 \cdot MU$
Epidote:	EP	=	$0.1 \cdot HO + 0.03 \cdot OL - 0.3$

The UPPSALA-model is a normative back-calculation model for reconstructing the mineralogy from the total digestion analysis. It can be used to provide input to models like PROFILE from data collected in regional survey programmes. The UPPSALA model was developed within the framework of the critical loads projects, and has been described in Sverdrup *et al.* (1992). In this project, the soil mineralogy was calculated using the total analysis for all samples, backchecked against the 124 accurate mineralogy determinations.

The model is based on assumption of the stoichiometric composition of the minerals of the particular soil. The minerals have been grouped into assemblies of minerals with similar composition and dissolution rate. Accordingly for soils of granitic origin or soils derived from rock of secondary granitic origin (sandstones) as well as originating from different types of schists and shales, it is assumed that the following mineralogical groupings are valid; Muscovite is assumed to comprise muscovite, secondary di-octahedral illite, di-octahedral chlorite and vermiculite of secondary weathered type. Chlorite comprise tri-octahedral chlorite, primary illite and tri-octahedral vermiculite of primary type as well as biotite and phlogopite and glauconite. Hornblende imply all amphiboles, such as hornblende, riebeckite, arfvedsonite, glauconphane and tremolite. Epidote comprise all epidotes, zoisites and pyroxenes. Plagioclase has for Sweden been assumed to be oligoclase with 80% albite feldspar component. K-feldspar is assumed to be relatively pure with a 10% albite feldspar component. All phosphorous has been attributed to apatite.

The weak point in the UPPSALA model is the expression for epidote. Epidote occur in small amounts only, in most soils of granitic origin. Soils with minerals derived from volcanic rocks rich in heavy minerals, must be treated somewhat differently. In such soils other minerals dominate. Volcanic soils are often rich in epidote, amphiboles, pyroxenes, feldspars, muscovite and biotite, whereas there will be little of vermiculite and chlorite. The coefficients in the model are based on a limited range of Swedish mineralogies, and the model applies only to Swedish granitic and glaciated soils. Originally, the intention was to calibrate the model for different

regions in Sweden.

8.1.4 Additional input data

The basic soil parameters for this study were analysed on soil samples. Several other parameters such as CO₂ pressure, soil solution dissolved organic carbon, distribution of uptake and evapotranspiration and gibbsite coefficients have less influence and are entered as standard values taken from the literature.

The soils and vegetation data was taken from the data base of the Swedish National Forest Survey. For each site the net long term uptake is specified, based on the measurements in the survey of base cation and nitrogen contents of stem and branch, combined with site specific estimates of net long term forest growth. Each tree species is considered separately, and the total uptake weighted together for each calculation point.

The soil profile is divided into 4 layers, using input data for the thickness of each soil layer (O, A/E, B, C). The soil database included field determination of the thicknesses of the different layer.

The texture of the soil is an important factor in the weathering rate calculations. Texture was measured by granulometry and BET/adsorption analysis on the 124 mineralogy analysis samples, and correlated against field texture classification. The texture for the remaining sites were read from the correlation using the field classification. The simplest way to calculate the soil texture is from a particle size distribution. The conversion from a standard sieve curve to surface area was carried out using:

$$A_{tot} = (x_{clay} \cdot 8.0 + x_{silt} \cdot 2.2 + x_{sand} \cdot 0.3) \cdot \frac{\rho_{soil}}{1000} \quad (8.1)$$

where A has the dimension 10⁶m³/m³ soil, and where we have the condition:

$$x_{clay} + x_{silt} + x_{sand} + x_{coarse} = 1 \quad (8.2)$$

and x_{clay} is the fraction of soil particles less than 2μm, x_{silt} the fraction of 2-60μm, x_{sand} the fraction of 60-200μm, and x_{coarse} the fraction of soil matrix coarser than 200μm. ρ_{soil} is the bulk density of the soil in kg/m³. For this study, the granulometric approach was used, due to difficulties of interference from secondary precipitates and organic matter with the BET measurements. BET measurement is good for soil samples not affected by these factors. The distribution of soil texture in the B/C-layer boundary is shown in Figure 8.2. Other input data to the present calculations were derived strictly in accordance with the "Mapping critical loads" [Sverdrup *et al.*, 1990].

8.2 RESULTS

8.2.1 Mineralogy and weathering

The results of the mineralogical survey indicate that epidote occur in amounts significant for the weathering rate. Figure 8.4 show the occurrence of feldspars and dark minerals of importance for the weathering rate in Swedish soils. It can be seen that K-feldspar is fairly evenly distributed over the country. Plagioclase shows more variation, which is also seen in the soil weathering rate. The area in western central Sweden with very low soil content of plagioclase coincides with an area of low weathering rate, the same pattern is repeated for epidote and hornblende. Both epidote and hornblende increase towards the north, perhaps a function of the fact that the ice retreated from south to north after the last ice age. The ice disappeared approximately 11.000-12.000 years ago in the south, but only 7.000-8.000 years ago in the far north. The areas of low weathering in central Sweden, have also very low soil contents of epidote and hornblende. It appears, unexpectedly, that apatite is also present in many soils in amounts of relevance for the weathering rate, whereas primary tri-ochtahedral chlorite and biotite are not significant. There is a tendency of higher soil contents of apatite in the north with more recently exposed soils and colder conditions. The soil texture is uncorrelated to the content of chlorite and vermiculite or any other mineral, i. e. there is no texture-bearing mineral.

The map in Figure 8.5 show the average weathering down to a soil depth of 2.0 meter, relevant to water infiltrating to the groundwater aquifers. Very low weathering rates are calculated for central Sweden. This is a function of a very low content of minerals important for the weathering rate. There is a general decrease in the weathering rate from south to north, mostly due to a decline in temperature.

The weathering rate in nature is determined by the abundance of weatherable minerals and their texture in the soil. Accordingly, an understanding of the soil mineralogy and texture distribution on a regional scale is essential for understanding the conditions for the weathering prevailing in a region. Three minerals in the soil are of major controlling importance for the weathering rate in the field:

- Epidote
- Hornblende
- Feldspars

Biotite and chlorite seem to occur in amounts not significant for weathering in most parts of the country. The base cation release in the soil profile vary from soil layer to soil layer, and is generally very low in the O-, A- and E-layers of forest soils. For the organic layer, is primarily due to the low exposed mineral surface area. In the E-layer, the content of easily weathered minerals is often low as compared to the C-layer mineral composition. This is natural, considering that the leached layer has been formed by depletion of weatherable minerals.

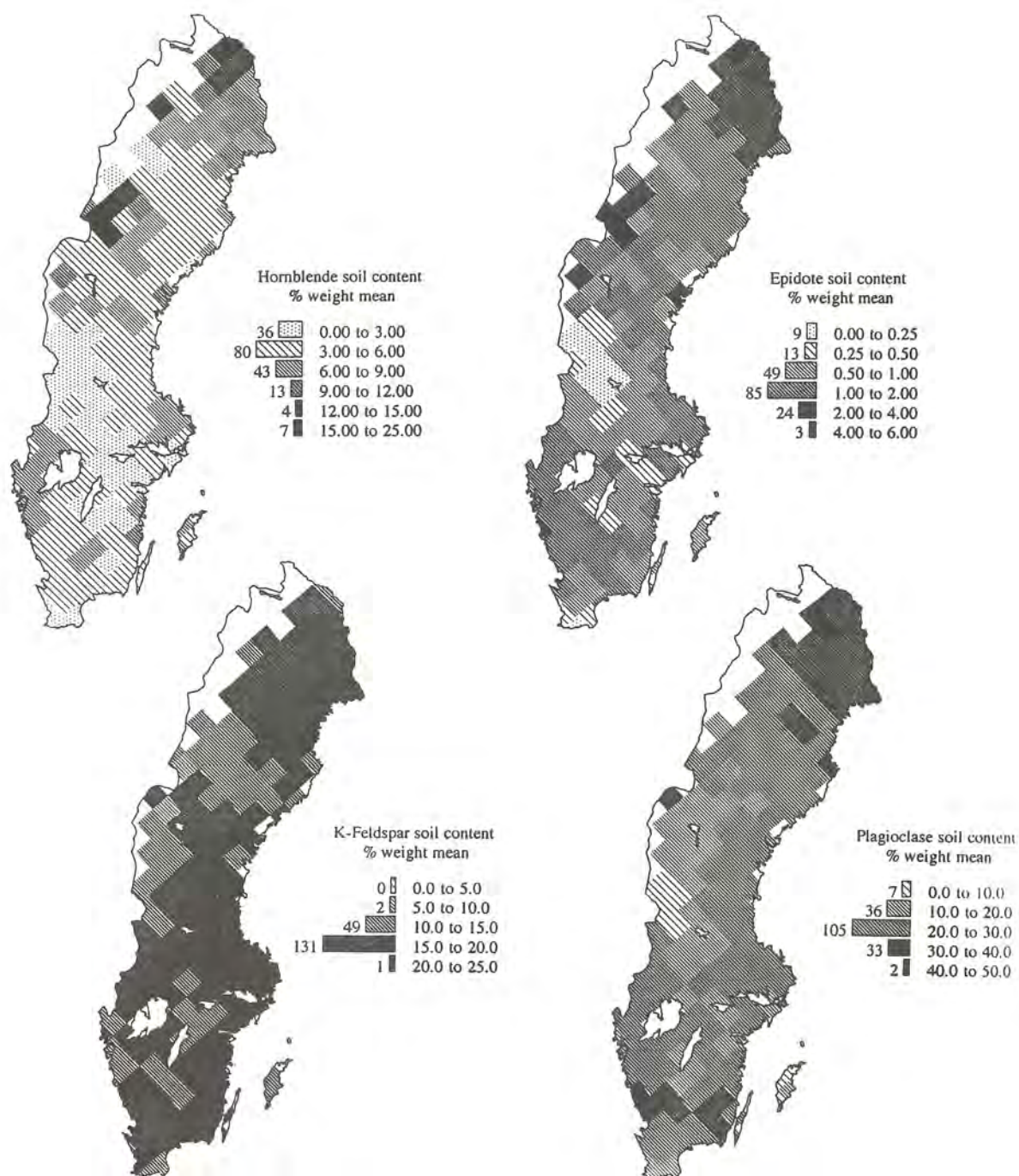


Figure 8.4. Key forest soil mineralogy at the 50 cm level in Swedish soils. Plagioclase feldspars, hornblende and epidote are the most important minerals for soil weathering in Sweden. In the calculations, the mineralogy is assumed to stay constant below the 0.5 meter level.

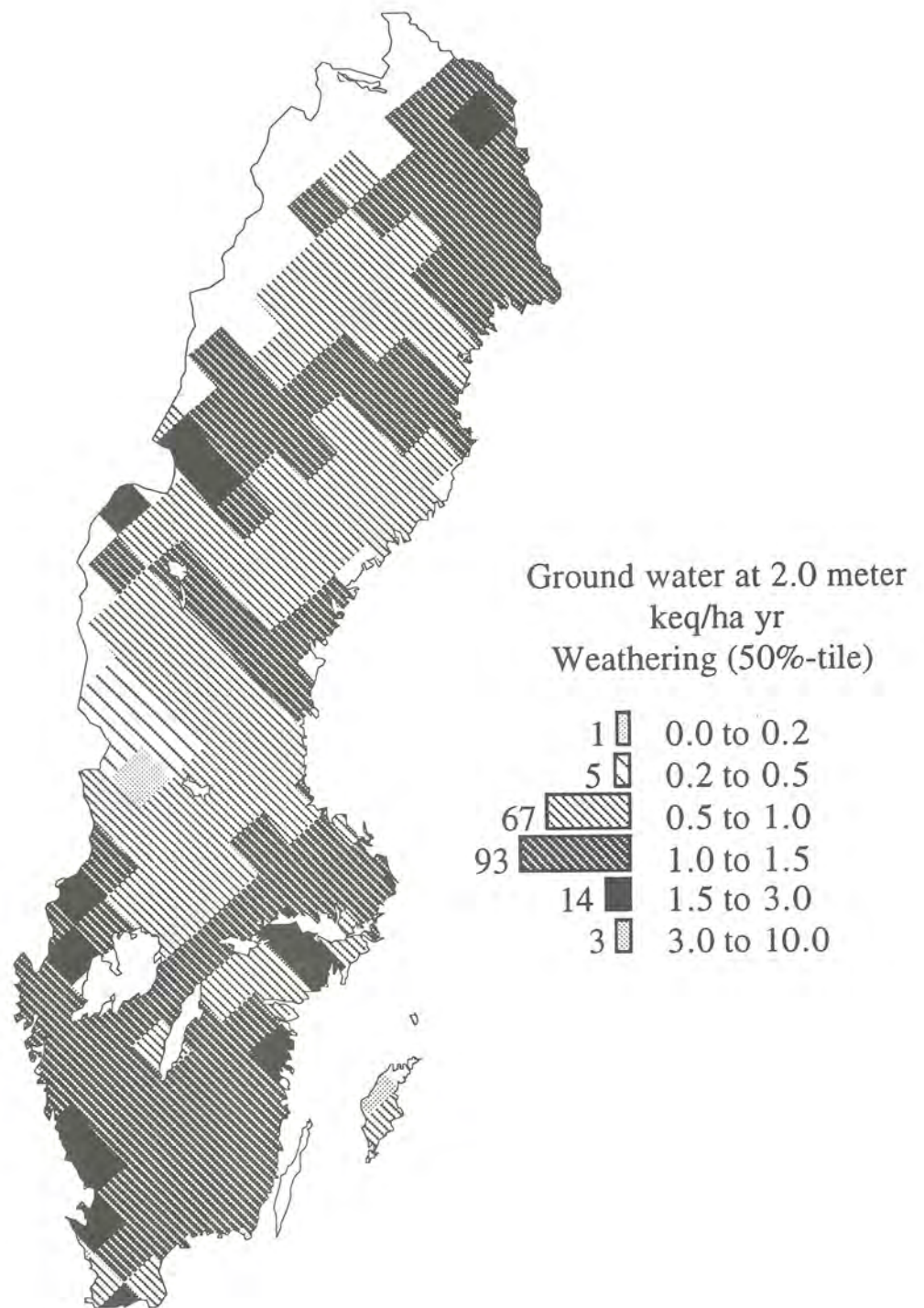


Figure 8.5: Forest soil weathering down to the 2 m level.

8.2.2 Critical load maps

Critical loads for groundwater were calculated applying the critical limit of 100 meq l^{-1} at 2 meter depth, and areas where these critical loads have been exceeded at the present deposition level has been calculated. The result of the critical loads calculation is shown in Figure 8.6. It can be seen from the map that groundwater is very sensitive to acidification in certain areas of Sweden. The location of these areas are closely connected to the weathering rate, as it is by far the dominating source of alkalinity. Especially sensitive is a large area in middle Sweden in the province of Härjedalen. This coincides with the poorest mineralogy in Sweden, and the lowest weathering rates. There are also areas of sensitive groundwaters in Lappland and around to the north of the city of Sundsvall. The eastern part of Scania also show a small area of very sensitive groundwater, corresponding to the area with quartzites occurring locally. On the average, the critical load for the groundwater is approximately $0.7 \text{ keq ha}^{-1} \text{ yr}^{-1}$ of acidity, if all expressed as sulphur, $11 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ or $1.1 \text{ g S m}^{-2} \text{ yr}^{-1}$.

Exceedence maps are made to illustrate where the critical loads are exceeded, and by how much. On the average, critical loads from groundwater has been exceeded in 68% of the land area of Sweden. This implies that 32% of the aquifers are at present not being negatively affected by acidification. This can be seen from the righthand map in Figure 8.6. A major part of the protected area is located in northern Sweden. In central Sweden, in the province of Härjedalen and all of southern Sweden, the present deposition largely exceeds the critical load, despite southern Sweden having the highest weathering rates. In southern Sweden, the exceedance is approximately $1.5\text{--}2.5 \text{ keq ha}^{-1} \text{ yr}^{-1}$ of acidity, or indicating that the excess acidity over the critical load of acidity is $24\text{--}40 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ if all acidity is converted to corresponding sulphur equivalents. However, approximately 30-40% of this acidity in reality originates from nitrogen deposition effects, illustrating the necessity of obtaining both sulphur and nitrogen deposition reductions. This illustrate the substantial reductions in total acidity deposition are required for southern Sweden to protect the groundwater from acidification.

Preliminary calculations for the 4 m level show no exceedence of critical loads outside the province of Härjedalen.

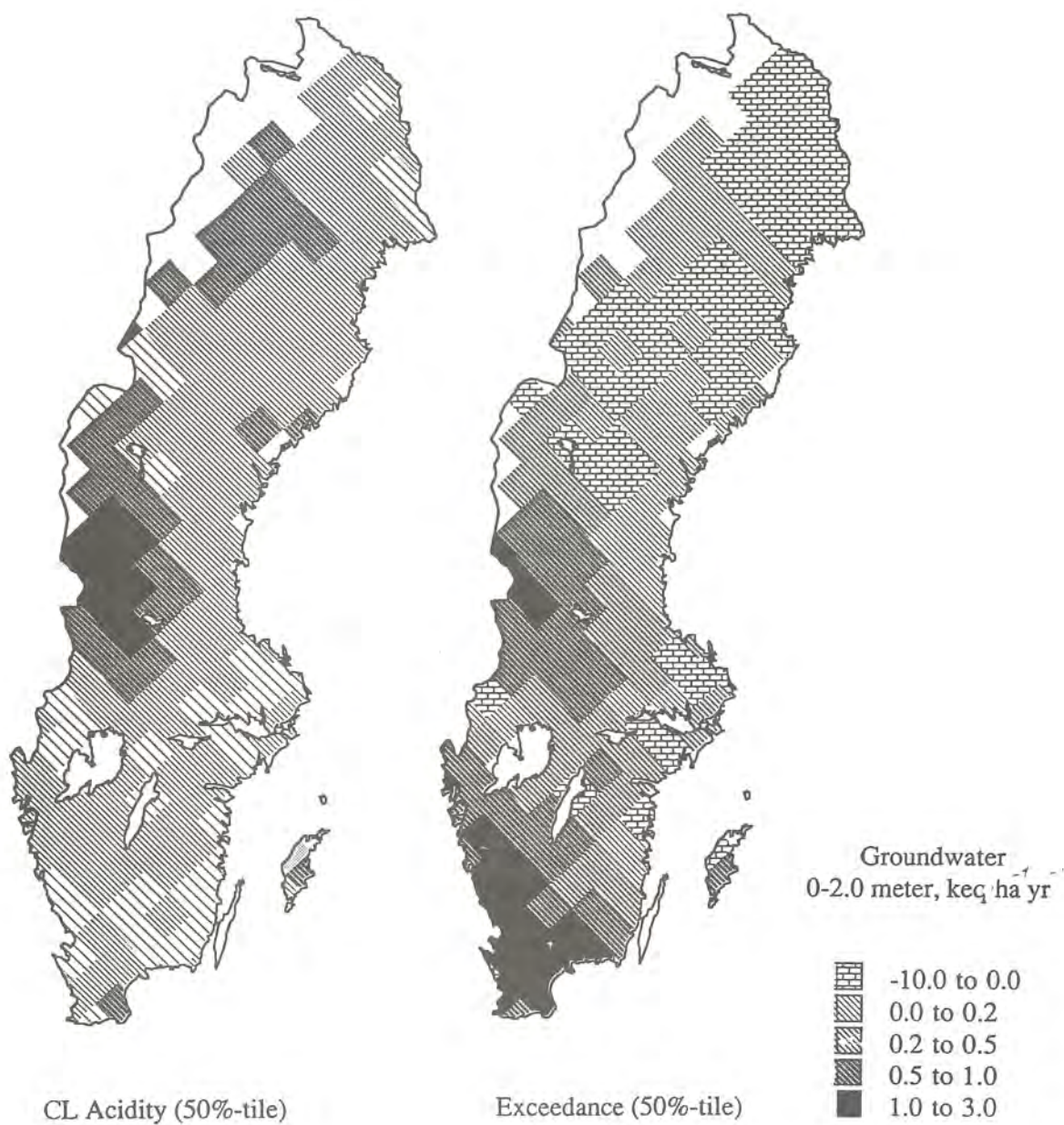


Figure 8.6. Maps showing the critical load (CL) for groundwater and present exceedance. The critical limit was applied at 2 meter depth. The maps illustrate the median value (50%-tile) of the sites within each grid.

Table 8.3: The different deposition scenarios considered in the steady state calculation.

Scenario	SO ₂	NO _x	NH _y
1990 AD level	no change	no change	no change
Planned reduction	-30%	-10%	-10%
Future option	-60%	-30%	-30%
Future option	-85%	-50%	-50%
Pre-industrial level	-95%	-95%	-85%

8.2.3 Steady state chemistry maps

The PROFILE model may also be used to calculate the steady state chemistry in response to a certain deposition input. Thereby, the long-term consequences of different deposition scenarios can be assessed. The same sites were used for the steady-state calculations as for the critical loads study. The methodology used to calculate the steady-state chemistry has been described in Chapter 6. The key element in the procedure is to determine the weathering rate down to a certain depth, and the remaining input data are the stand uptake data and the deposition.

The steady-state chemistry for groundwater at 2 m depth has been calculated regionally for 4 different scenarios, listed in Table 8.3. Pre-industrial deposition was assumed to be to 5%/5%/15% of present deposition respectively for sulphur, nitrate and ammonium. The net forest uptake of base cations and N was set at 40% of 1990 level. The state of the groundwater in the past, the natural alkalinity, was calculated in order to establish a point of reference. Of the future scenarios, the 60%S/30%N scenario is a possible scenario to be implemented in countries with a high level of ambition. The 85%S/50%N reduction scenario corresponds to required reductions in deposition in order to protect 95% of the forest area. The reductions assumed were flat reductions in deposition over Sweden, and not related to any particular emission reduction scheme. For proper evaluation, the required deposition reductions should be converted to emission reductions using long range transport models.

The steady state chemistry corresponding to present deposition and the three reduction scenarios are shown in Figure 8.8. Figure 8.7 shows the cumulative distributions based on all calculation points, including the preindustrial-deposition. The data points have been weighted by the area they represent.

According to the calculations, there are hardly any naturally acid groundwater. There is simply too little of naturally acid generating processes in relation to the sources of alkalinity, for natural acidification to occur. In the Härjedalen district, the groundwater was very weakly buffered. These points appear in the lower tail of the cumulative distribution, where the ANC values range down to 10 meq m⁻³. At such low ANC-value, the pH can still be < 5 at elevated CO₂-pressures, potentially causing corrosion. In relation to the chemical criteria of an ANC of 100 meq m⁻³, this value was not reached at some 7% of all aquifers. In Figure 8.7 shows that 70% of Sweden will be threatened if the deposition continues at the 1990 level, and the water infiltrating at 2 m may have negative ANC at 50%. With the 60/30

reduction scenario, 10% will have negative ANC, while 30% of the sites show ANC values less than 100 meq m^{-3} . The 85/50 scenario will yield a result similar to the pre-industrial level, with a general shift in ANC of approximately 50 meq m^{-3} . This agrees with the calculations with the dynamic model (Chapter 6).

According to the model calculations presented in Chapter 6, acidification down to the 1 m level will have reached steady-state conditions well into the next century. At the 2 m level, the same time scale is involved since the medium-term buffering mechanisms, such as cation exchange and anion adsorption is of minor importance in the non-weathered mineral soil. For the reduction scenarios, the water-quality will reach steady-state conditions faster than with a continued level of deposition.

The steady state maps show the same regional patterns as the exceedance map shown earlier. It can be seen from the map shown in Figure 8.8, that the acidity will drop to very low levels in southern Sweden and the Dalarna/Härjedalen district, but that acidification will be less pronounced in Lappland in the far north. In southern Sweden the alkalinity will drop below -100 meq m^{-3} , in southernmost Sweden even below -250 meq m^{-3} , taken as a median for all sites. The water will be corrosive to any type of normal metal or concrete water supply system. A large area will have negative ANC under the 30/10 reduction scenario, while more significant improvement will follow a 60% S and 30% N reduction. A small area in Dalarna/Härjedalen and southern Sweden will still be acidified under the 60% S/30% N reductions, and very drastical reductions in deposition levels are required if these areas are to be protected. 85% S/ 30% N reductions would lead to a steady state map as shown in Figure 8.8. This can be compared to the calculated steady state chemistry corresponding to pre-industrial deposition. As for the preindustrial situation, no grids will be characterized by negative ANC.

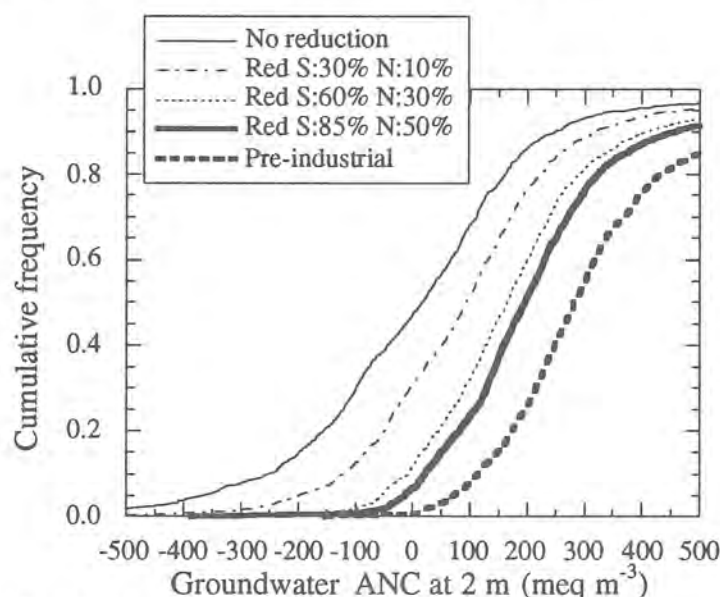


Figure 8.7: The cumulative distribution of ANC in the groundwater at 2.0 meter depth under different deposition scenarios as listed in 8.3.

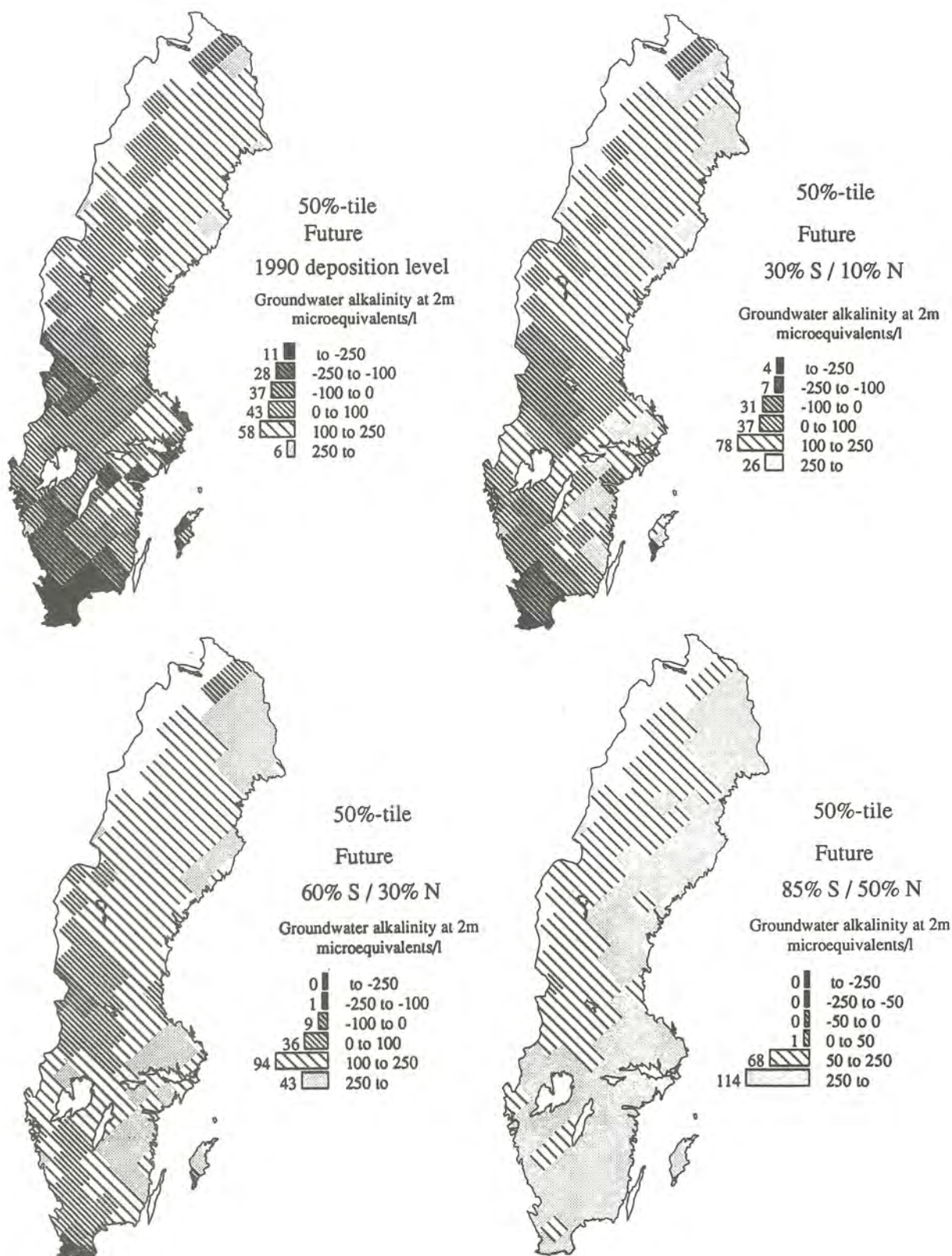


Figure 8.8. Steady state future ANC in groundwater at 2.0 meter calculated with the PROFILE model for different deposition scenarios.

8.3 CONCLUSIONS

Groundwater down to 2.0 meter depth is very sensitive to acid deposition. Deposition reductions in the same order of magnitude as required for streams, lakes and forest soils are also required for groundwater resources. These reductions go beyond the 30% S from the 1980 level already agreed on. If such deposition reductions cannot be obtained, a drastic increase in acid groundwater will follow in the next 20–70 years. If no nitrogen deposition reductions can be achieved over Sweden, then significantly higher deposition reductions for sulphur are required. With unchanged nitrogen deposition from 1990 level, a 90–95% S reduction only would be required to achieve what a 60% S / 30% N reduction would do.

The groundwater at 4.0 meter depth is much less sensitive, and at the 8.0 meter and 16.0 meter level, very small areas have exceedance of the critical load at present deposition, mainly the Dalarna/Härjedalen district and southernmost Sweden. Important conclusions are also that the steady state model PROFILE is sufficient for determining the sensitivity of groundwater to acidification. The dynamic models have not been necessary for determining the sensitivity of groundwater to acidification, and when used will estimate the sensitivity with significantly poorer accuracy than the PROFILE model. Soil and groundwater acidification can be accounted for by acidic deposition, and landuse and forestry effects are invoked only to contribute a minor contribution.

9 CONCLUSIONS

The conclusions from the present development and application of the models can be divided into three groups. The first concerns the models and how they operate, the second concerns the acidification processes within the soil. Conclusions can also be drawn about the acidification of groundwater in Sweden.

Hydrological and hydrochemical models

The models developed are generally applicable for the simulation of groundwater sensitivity to acidification. The requirements for climatological and geological data can be met from existing data bases. The chemical and hydrological soil properties can be obtained from field measurements and soil analysis.

The weathering rates can be calculated from soil mineralogy, as was initially hypothesized. This is an important strength of the hydrochemical model, which makes it possible to calculate critical loads from measured properties.

The models need limited calibration. The steady state model PROFILE is run solely on input data and is therefore calibration-free. The dynamic model, SAFE, need calibration of the initial base saturation to reproduce present values. The overall water balance of the PULSE model must be calibrated against runoff, which is done by adjustment of parameters in the precipitation and snow accumulation routines. The many applications of this model within Sweden, however, makes it possible to run the model confidently even without calibration.

The models were controlled against extensive field data. The different components of the PULSE model were tested against data from snow surveys, soil moisture, transit times using ^{18}O and groundwater levels. For all these data the model produced good or fair simulations. The PROFILE model was tested against soil chemistry in a profile on the Swedish west coast, with fair results. The weathering rate submodel was tested in a number of areas in northern and central Europe and USA. At these sites weathering rate estimates from different direct and indirect methods could be obtained. The results showed a good agreement between estimated and simulated weathering rates. The dynamic hydrochemical model, SAFE, was tested against soil chemistry at three sites in southern Sweden, where data is available both from 1949 and 1984, with fair results.

The soil moisture routine of the PULSE model was also compared to soil moisture simulations from the physically based SOIL model. This test showed that the level of sophistication of PULSE is sufficient. An application of an existing acidification model, MAGIC, at one of the field basins gave results similar to those obtained with SAFE. The overall conclusions from both models, about long term acidification were essentially similar.

The ^{18}O study showed that complete mixing within horizons is the best description of water movement in the first 40 cm of the soil and that piston flow is better for the lower

soil layers. The differences were small though, which is why complete mixing was used in the integrated modelling.

The highly different chemical properties of the soil horizons makes it necessary to use a vertically distributed formulation of the model. The pH might, for instance, range from about 4 in the surface horizon to almost 7 in deep horizons.

An important tool for the model development has been sensitivity analysis. Both the hydrological and the dynamic hydrochemical models have been tested for sensitivity to input data and parameter values. Both models show considerable sensitivity to changes in parameter values. This indicates that the modelled processes are significant and that it is important to correctly specify the parameters for any application of the models. The uncertainty that can result from spatial heterogeneity of soil characteristics or uncertain estimates of parameter values must be considered in the interpretation of the long term simulations.

The sensitivity of the hydrochemical model to the time step of hydrological input data was considerable. This supports the hypothesis that short term variations in hydrological variables have an important effect on acidification, even in the long term perspective.

The model testing did reveal some points that should be considered in future development. The hydrological model is somewhat hampered by the fixed groundwater table. A dynamic formulation of the groundwater table coupled to the soil moisture routine might help to reproduce the high water content observed during some circumstances in the surface horizon. A dynamic groundwater table can also have an important effect on the hydrochemistry, since the vertical movement of water in the unsaturated zone is shifts to horizontal flow at saturation.

Gibbsite equilibrium is a poor representation of the aluminum chemistry in the soil. One proof of this is that different soil horizons demand different equilibrium constants. An alternative formulation of the aluminum chemistry involving the formulation of precipitates and complexes with organic acids has been initiated within the project. This should be considered for future versions of the model.

The ion exchange model needs further testing. So far no ion exchange model has been tested on natural soil for the wide pH range across which they are assumed to apply (4 - 7). In SAFE the ion exchange is modelled as a kinetic process that converges upon an equilibrium, in contrast to other models which usually use a pure equilibrium formulation.

The interactions with vegetation, mineralization and the nitrogen cycle need to be considered in a stricter way. The nitrogen accumulation in excess of base cation uptake at Stubbetorp, implies an alkalinity flux of more than 50% of the weathering rate.

Acidification processes

The steady state model, PROFILE, is sufficient for a general assessment of groundwater sensitivity to acid deposition. It is, however, necessary to use the dynamic model SAFE if the time aspect of the acidifying process is of interest. The dynamic approach is important both for analysis of the present acidification and for evaluation of the recovery which can result from management activities.

The most important acidifying process is the deposition of acid compounds. The imbalance between forest uptake of nitrogen and base cations also makes a significant contribution to groundwater acidification.

The buffering mechanism in the field sites is ion exchange during the period from 1950 to 2010. Before and after this period, the buffering is controlled by weathering.

Groundwater acidification

The scenario simulations for the field sites indicate that groundwater ANC at 1 m depth will stay below the critical load limit of 100 meq m^{-3} at all sites and scenarios. With the present deposition, a steady state will not be reached until long after 2050. A reduction of S by 85% and N by 50% would bring the ANC at 1 m to about 50 meq m^{-3} at steady state. The system will take several decades to reach this steady state, which emphasizes the need for immediate action. The observed differences between the basins are due to different weathering rates and forest growth history. These general conclusions from SAFE and PROFILE are supported by the MAGIC scenario simulations.

On the regional scale, the critical load calculations suggests that the groundwater at 2 m depth is very sensitive to acid deposition. The reductions currently agreed upon (30% S and 10% N) would leave 53 % of the groundwater resources located in moraine with an ANC below 100 meq m^{-3} at steady state. A 60% reduction of S and 30% of N would result in 32% of groundwater with an ANC below the specified limit. The extreme reduction scenario (85% S and 50% N) would still leave 22% of the groundwater at an ANC below 100 meq m^{-3} . The groundwater insensitive to acidification is generally located in areas dominated by soils with very fine texture, carbonate soils or other soil types with very rich mineralogy.

The overall conclusion is that we have a set of modeling tools which are generally applicable. They demand limited calibration, if any, and the requirements for input data and parameter values can usually be met. This makes it possible to use them for assessment of groundwater acidification. The initial objectives of the project have, therefore, been met. The spatial and climatic variability, however, is large. The uncertainties introduced by this variability must be considered when the results are used for decision making.

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