WORKING PAPER

Comparison of RAINS Lake Module with MAGIC-model simulations and paleolimnological records

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Preface

The IIASA Acid Rain Project started in 1983 in order to provide European decision makers with a tool which can be used to evaluate policies for controlling acid rain. Emphasis of the IIASA RAINS model is on the transboundary aspects of the acidification problem. The model consists of three major compartments: Pollution Generation, Atmospheric Processes and Environmental Impacts. Each of these compartments can be filled by differents substitutable submodels. Linked submodels are currently available for SO_2 and NO_x emissions, cost of SO_2 control strategies, atmospheric transport of sulfur and nitrogen, forest soil acidity, the direct impact of SO_2 on forests, and lake acidification.

Model testing and sensitivity analyses have been an important part of the work of the Acid Rain Project. The following paper describes the application of the RAINS Lake Module (RLM) to four Finnish lake catchments from which paleolimnological pH-reconstructions are available. The simulation results of RLM are also compared with the results from a more complex acidification model, MAGIC.

The author of this paper, Martin Forsius, was a participant of the YSS-Program at IIASA in 1987. He is from the Water and Environment Research Institute, PB 250, Helsinki, Finland.

Bo R. Döös	Roderick W. Shaw
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Abstract

The International Institute for Applied Systems Analysis is developing a simulation model (RAINS) which can be used by decision makers to evaluate policies for emission control in Europe. As part of this task a simple dynamic model has been developed for describing the processes leading to acidification of surface waters.

In this paper some aspects of the uncertainty incorporated in the RAINS Lake Module (RLM) are evaluated. Simulation results of this lake model are compared with results from a more complicated acidification model (MAGIC), using data from four Finnish forest lake catchments. A Monte Carlo parameter estimation procedure is used in both models to evaluate the uncertainty of the model predictions. The simulation results are also compared with historical pH and alkalinity values reconstructed from diatom remains in the lake sediments.

RLM applied to the independent lake data yielded pH and alkalinity reconstructions that are probably within the range of uncertainties inherent in both this model and the diatom method. The models generally predicted similar changes in lake acidity, when MAGIC was run with initially calibrated input values from RLM. Some problems, however, occurred in the MAGIC applications using these RLM input values.

The use of the Monte Carlo testing procedure on both models showed that large differences in the simulated acidification path of the lakes were obtained when sensitive model parameters were randomly changed. A fairly large number of allowable outcome were still reproduced in both RLM and MAGIC applications.

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1. INTRODUCTION

Lakes and streams in large areas of Europe and eastern North-America have acidified during the past decades (e.g. Wright, 1983; Brakke *et al.*, 1988). The causal relationships leading to freshwater acidification are, however, complicated and difficult to quantify. Nevertheless, the estimates of potential future impacts of acidic deposition requires understanding of the key processes. Hydrochemical simulation models can be used for making scenarios of future water chemistry of sensitive areas. The structure and complexity of such models will be determined by the degree of temporal and spatial resolution desired.

The International Institute for Applied Systems Analysis (IIASA) is developing a simulation model (RAINS) which can be used by decision makers to evaluate policies for emission control in Europe (Alcamo *et al.*, 1987). As part of this task a simple dynamic model, RAINS Lake Module, has been developed for describing the processes leading to acidification of surface waters. The modeling philosophy of the IIASA research team has been to use a simplified approach which is warranted for a broad geographical scope. The objective has been to retain the simplicity of the model, but still have few physically realistic processes incorporated in its structure, in order to allow a theoretical basis for establishing confidence in the scenarios (Kämäri *et al.*, 1985; Kämäri and Posch, 1987).

Simulation models of environmental systems necessarily include uncertainty concerning model structure, model inputs, as well as parameter values. In case the processes under study are very slow, it is impossible to establish the validity of the predictions by comparing the outcome with measurements. Long time series of, for example lake acidity, rarely exist. The credibility of a given model must therefore be built up by means of (1) historical reconstructions and comparison with independent historical or paleolimnological data and (2) prediction and comparison with data from large-scale ecosystem manipulations (Wright *et al.*, 1986; Wright and Cosby, 1988).

In the following paper some aspects of the uncertainty incorporated in the RAINS Lake Module (RLM) are evaluated. Simulation results of this lake model are compared with results from a more complex acidification model (MAGIC), using data from some Finnish forest lake catchments. A Monte Carlo parameter estimation procedure is used in both models to evaluate the uncertainty of the model predictions. The simulation results are also compared with historical pH and alkalinity values reconstructed from diatom remains in the lake sediments.

2. MODEL STRUCTURES

2.1. RAINS Lake Module

RLM (RAINS Lake Module) is a simple process oriented model for lake acidification (Kämäri *et al.*, 1985; Kämäri and Posch 1987). The model separates the catchment into three distinct water reservoirs (two soil layers and the lake), between which it computes the fluxes of major ions contributing to acidity or alkalinity of surface waters. The mass flow is influenced by the forcing functions as well as by the internal processes taking place in the reservoirs. Those processes are considered that have an effect on the long-term development of lake acidity (Table 1).

Table 1: Processes considered in the RAINS lake acidification model affecting the year-to-year development of lake acidification.

Process	**Reference**
Forest filtering effect	Mayer and Ulrich, 1974
Lateral flow	Chen *et al.*, 1983
Weathering of base cations	Ulrich, 1983
Cation exchange	Ulrich, 1983
Dissolution of minerals	Christophersen *et al.*, 1982
In-lake sulfate retention	Baker *et al.*, 1986
Dissolution of CO_2 in lake water	Stumm and Morgan, 1981

The principal driving variable of the lake acidification model is the total deposition of sulfur, d_{tot}. The throughfall deposition generally exceeds the deposition to open land. The mean deposition to an area is therefore allocated to forests and to open land by assigning the deposition on forested land to exceed that on open land by a factor of φ ($\varphi \geq 1$). The acid load on forest soils of one grid, d_{SO_4}, is then given by

$$d_{SO_4} = d_{tot}\varphi/(1 + (\varphi - 1)f) \tag{1}$$

where f is the fraction of forested land in that grid.

The basic assumption concerning the soil hydraulics is that all of the precipitation surplus, *i.e.* the annual runoff, Q_{tot} (precipitation, P, minus evapotranspiration, E), infiltrates the A-reservoir. Evapotranspiration is set proportional to the mean temperature, T, above $O^0\ C$, using an evapotranspiration rate coefficient ϵ (c.f. Christophersen *et al.*, 1984), *i.e.* $E = \epsilon \cdot T$.

The water leaves the A-layer as quickflow, Q_a, which is given by

$$Q_a = Q_{tot} - Q_b \tag{2}$$

where Q_b is the base flow leaving the B-layer, which is given by

$$Q_b = \frac{\kappa_s S\, W Z_b}{A_c} \tag{3}$$

where κ_s is the hydraulic conductivity at saturation, S is the surface slope, W the catchment width, Z_b the thickness of the B-layer, and A_c the terrestrial catchment area.

As to the soil chemistry it is assumed that few equilibrium reactions between soil and soil solution address the water quality of runoff water at a particular time. A nonlinear relationship is assumed between the base saturation, Ex, and the soil pH in the pH range 4.0 to 5.6. The equation is based on the results of an equilibrium model by Reuss (1983).

$$-\log_{10}[H^+] = 4.0 + 1.6 \cdot Ex^{0.75} \tag{4}$$

where the base saturation is given by

$$Ex = BC/CEC \tag{5}$$

where CEC_{tot} is the total cation exchange capacity of the soil. If the cation exchange system does not play any role in buffering the inputs to the soil solution, i.e. BC is in practice zero, it is assumed that the dissolution of minerals controls soil buffering. Aluminum is dissolved or precipitated until the gibbsite equilibrium is reached,

$$[Al^{3+}] = K_{so}\,[H^+]^3 \tag{6}$$

where K_{so} is the gibbsite solubility constant.

Over the long term, the flux of acids and bases into and out of the soil change the above chemical state of the soil thus affecting the soil/soil solution equilibria. In noncalcareous soils the weathering rate of base cations, wr, largely determines the long-term response of the catchments. As long as the input of base cations from weathering, wr, and from base cation deposition, d_{BC}, is larger than the acid load, there will be no change in the H$^+$-concentration in the soil. If, however, the acid load exceeds the base cation input, the capacity of the cation exchange buffer system is depleted by the rate,

$$\frac{dBC}{dt} = d_{BC} - d_{SO_4} + wr \tag{7}$$

To calculate lake water pH and alkalinity the following ion fluxes into the lake are considered. The flux of protons, F_H, is the sum of the convective flow of ions from the two soil reservoirs and the direct input from the atmosphere to the lake

$$F_H = Q_a\,[H^+]_a + Q_b\,[H^+] + d_{SO_4}A_l \tag{8}$$

where A_l is the lake surface area. The fluxes of bicarbonates contributing to the alkalinity of the lake originate both from the terrestrial catchment, $F^{(1)}_{HCO_3}$ and from the in-lake (internal) alkalinity generation, $F^{(2)}_{HCO_3}$, (c.f. Baker *et al.*, 1986)

$$F^{(1)}_{HCO_3} = (wr - d_{SO_4} + d_{BC})A_c \tag{9}$$

and

$$F^{(2)}_{HCO_3} = \frac{k_{SO_4} d_{tot}}{Q_{tot}/A_l + k_{SO_4}} \tag{10}$$

where k_{SO_4} is the sulfate retention rate coefficient. The above ion fluxes mix with the lake water and cause a change in the bicarbonate and hydrogen ion concentrations until an equilibrium is reached,

$$[HCO_3^-] = \frac{K_1 K_H p_{CO_2}}{[H^+]} \tag{11}$$

where K_1 is the first dissociation constant, K_H the Henry's law constant and p_{CO_2} the partial CO_2 pressure in water.

The risk for aquatic impacts can be estimated on the basis of simple threshold pH and/or alkalinity values. These characteristics are most likely to indicate damage to fish populations and other aquatic organisms.

2.2. MAGIC

MAGIC (Model of Acidification of Groundwater In Catchments) is an intermediate complexity process oriented model for soil and water acidification (Cosby *et al.*, 1985a; 1985b). MAGIC consists of (1) a soil-soil solution chemical equilibria section in which the concentrations of major ions are assumed governed by simultaneous reactions involving sulfate adsorption, cation exchange, dissolution and precipitation of Al, and dissolution of inorganic C, and (2) a mass-balance section in which the flux of major ions to and from the soil is assumed governed by atmospheric inputs, chemical weathering inputs, net uptake in biomass and loss to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time due to changes in acid deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The equations are solved separately for two soil layers.

A total of 24 equations describe the reactions that determine the chemical composition of soil water in the model. These equations contain 33 variables and 21 parameters; 16 of the parameters are thermodynamic constants.

Only Al^{3+} and the four base cations are assumed to be involved in the cation exchange reactions. The cation exchange reactions incorporated in the model are of the type:

$$2Al^{3+} + 3CaX_2 = 3Ca^{2+} + 2AlX_3 \tag{12}$$

$$Ca^{2+} + 2NaX = 2Na^+ + CaX_2 \tag{13}$$

where AlX_3, CaX_2, and NaX represent cations adsorbed in the soil matrix. The inorganic aluminum reactions considered in the model consist of one reaction involving a solid phase of aluminum and 12 reactions involving aqueous complexation of Al.

Equilibrium expressions for each cation are constructed using a Gaines-Thomas expression, e.g.

$$\frac{[Ca^{2+}]^3 \; E_{Al}^2}{[Al^{3+}]^2 \; E_{Ca}^3} = S_{AlCa} \tag{14}$$

In these equations E's denote the equivalent fraction of the exchangeable ion, the brackets indicate aqueous cations and S's are selectivity coefficients.

The values of the variables that must be known to solve the equilibrium equations can be obtained by considering the input-output chemical mass balance of the catchment as a whole. The mass balance is applied to the total amounts of base cations and strong acid anions in the catchment. For each of the base cations and strong acid anions in the model a dynamic mass balance equation can be written in the form:

$$dX_T/dt = F_x + W_x - Q\,[X]\,n \tag{15}$$

where X_T is the amount of ion X per unit area of the catchment ($eq\,m^{-2}$); F_x is the atmospheric flux of that ion into the watershed ($eq\,m^{-2}time^{-1}$); W_x is the net uptake-release flux of the ion ($eq\,m^{-2}time^{-1}$); $[X]$ is the total molar concentration of the ion in stream or lake water; n is the charge of the ion; and Q the volume of flow.

The routing of flow in the catchment is divided into three compartments: (1) runoff bypassing soil (overland flow), (2) soil flow bypassing soil horizon 1 (macropore flow), and (3) horizon 1 drainage entering surface waters.

In order to get the simulation results of MAGIC and RLM comparable with each other, some minor changes had to be made in the structure of MAGIC concerning the routing of internal flows. The same simple two layer structure as in RLM was adopted. Precipitation was routed into quickflow and baseflow, and no overland flow was simulated.

The Monte Carlo parameter estimation procedure in RLM was also incorporated in the structure of MAGIC (see also chapter 5.2).

3. DATA SOURCES AND PROCESSING

All lakes in this study are included in the acidification research program of the Finnish National Board of Waters and Environment. Therefore, rather extensive chemical and biological data is available from these forest lake catchments (see Kenttämies *et al.*, 1985; Kämäri, 1985).

3.1. Precipitation chemistry data

In regional applications RLM uses total sulfur deposition values calculated by the EMEP sulfur transport model as the driving force (chapter 2.1). In this study more accurate deposition values calculated by the EMEP-model in combination with a domestic sulfur transport model (Sulfur Commission of Finland, 1986) were used in the individual RLM applications.

In addition to sulfur values MAGIC requires yearly average concentrations for all the major base cations and anions in precipitation as input values. Such precipitation chemistry data is available from the monitoring stations of the National Board of Waters and Environment (Järvinen, 1986). The yearly average values were calculated from mean monthly bulk deposition values from the years 1979-81 from nearby monitoring stations.

Mean precipitation volume and air temperature calculated by RLM were used in both models. These values were derived from climatic data of European monitoring stations (Müller, 1982), stored in the data files of the RAINS-model.

The values for sulfur deposition presented by Järvinen (op. cit.) are, however, some 40–100% lower than those estimated by model calculations. The main reason is probably, that routine measurements of bulk deposition result in severe underestimation of dry deposition (e.g. Miller and Miller, 1980). Therefore, a dry deposition factor calculated from the difference between modeling and measured values, was used to correct the sulfur concentration values in the MAGIC-model.

A historical sequence of precipitation chemistry for the simulated period was required by the models. The historical deposition pattern, used to drive the models, was constructed by assuming deposition strictly proportional to European total sulfur emissions given by Fjeld (1976). The deposition was scaled such that the present day deposition agreed with measured values at each site.

3.2. Lake and soil data

All soil data has been collected by the Geological Survey of Finland in cooperation with the Department of Quarternary Geology of the University of Turku (e.g. Nuotio *et al.*, 1985). Lake water chemistry data was obtained from the water quality data bank of the National Board of Waters and Environment.

Lake alkalinity was estimated from the pH-values reconstructed by the diatom analyses. Alkalinity was defined as (Wright and Henriksen, 1983):

$$Alk = [HCO_3^-] - [H^+] - [Al^{3+}] \tag{16}$$

where the bicarbonate concentration, $[HCO_3^-]$ ($\mu eq/l$) and the sum of positively charged Al species ($\mu eq/l$) was obtained from the relationships (cf. Wright and Henriksen, 1983):

$$\log[HCO_3^-] = -5.93 + 1.22\,pH \tag{17}$$

$$\log[Al^{3+}] = 12.7 - 2.56\,pH \tag{18}$$

4. STUDY SITES AND MODEL PARAMETERS

The location of the study sites is shown in Fig. 1, and and the catchment characteristics are gathered in Table 2. The input values used for the model reconstructions are gathered in Tables 3 and 4. Measured values have been used when available. The remainder of the necessary model input data was estimated from ranges reported from other catchments or they are simply "best guesses".

4.1. Hauklampi and Orajärvi

Hauklampi and Orajärvi are small clearwater, oligotrophic, acidified lakes situated in a sparsely populated forest area about 25 km NW of the city of Helsinki. This region receives the highest load of acid deposition in Finland. Lake Orajärvi is larger, but has a relatively smaller drainage area.

The bedrock in this region is composed of Precambrian granites, with a large portion of exposed rock. The soil layer is very thin, and the prevailing soil type is gravelly moraine. The lake catchments also contain some peatland (Nuotio *et al.*, 1985). There are no roads or human settlements. The Norwegian spruce (Picea abies) is the dominant tree species at lake Hauklampi. Lake Orajärvi is mainly surrounded by Scots pine (Pinus sylvestris) forests. In both lakes Sphagnum carpets, typical of acid waters, cover large areas of the bottom.

In MAGIC simulations for lake Hauklampi and Orajärvi, somewhat larger values for baseflow had to be used than those calculated by RLM, in order not to get totally unreasonable values for the selectivity coefficients.

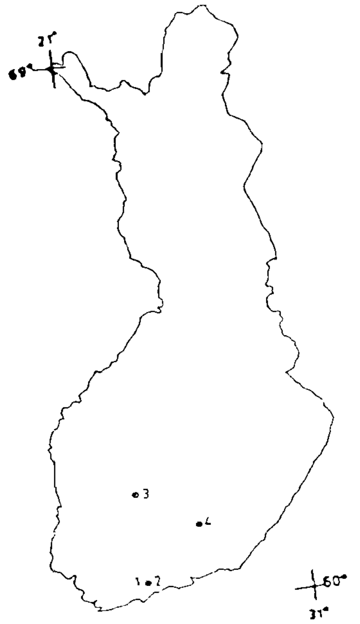

Figure 1. Location of the study sites, 1=Hauklampi; 2=Orajärvi; 3=Siikajärvi; 4=Sonnanen.

4.2. Siikajärvi

Siikajärvi is a moderate size ($0.90 km^2$) clearwater, oligotrophic, fairly acid lake in the southern part of the country. It is the largest single acidified lake so far detected by paleolimnological research in Finland (Simola, 1985). This part of the country still receives fairly high levels of acid deposition.

Coarse moraine forms a major part of the catchment, with a rather high percentage of exposed bedrock or very thin soils. The drainage area also contains some peatland. The catchment is undisturbed except a modest forest clearcutting at one side of the lake. The prevailing tree species are Norwegian spruce and Scots pine.

4.3. Sonnanen

Lake Sonnanen is the only neutral and also the largest ($1.75 km^2$) lake in this study. As the other lakes in this study, it is situated in the southern part of the country. The lake water has a low content of organic matter and a moderate buffering capacity. Large areas of glaciofluvial deposits are present in the catchment, and the prevailing soil type is moraine. There are many holiday houses along the shore of the lake, but no major source of pollution is present. The drainage area contains a small portion of arable land.

Table 2 . Characteristics of the lake catchments

Variable	Lake Hauklampi	Lake Orajärvi	Lake Siikajärvi	Lake Sonnanen
Catchment characteristics				
Total sulfur deposition ($meqm^{-2}yr^{-1}$)	115	115	80	90
Lake area (km^2)	0.03	0.22	0.90	1.75
Maximum lake depth (m)	4.4	5.9	23.0	14
Catchment area (km^2)	0.21	0.76	3.00	4.50
Soil types (%)				
bare rock or very thin soils	100	32	19	24
till	0	59	70	47
sand and gravel	0	0	0	29
peat	0	8	11	0
Lake water quality				
pH	4.8-4.9	4.7-4.8	5.0-5.5	6.3-7.0
alkalinity ($meq\,l^{-1}$)	<0	<0	<0	0.04-0.07
color (Pt $mg\,l^{-1}$)	5-10	5-10	20-25	5
COD ($mg\ O_2\,l^{-1}$)	1.0-3.0	1.4-1.8	4.7-5.2	1.4-1.6
Ca ($mg\,l^{-1}$)	1.9-2.3	1.6-2.0	1.3-2.5	3.0-3.2
Mg ($mg\,l^{-1}$)	0.7-0.8	0.5-0.6	0.5-0.6	0.5
Na ($mg\,l^{-1}$)	1.1-1.4	1.2-1.5	1.0-1.2	1.3-1.6
K ($mg\,l^{-1}$)	0.35	0.3-0.5	0.3-0.4	0.6-0.7
Cl ($mg\,l^{-1}$)	2.2-2.3	1.5-2.1	0.9-1.0	2.1-2.6
SO_4 ($mg\,l^{-1}$)	7.7-11.2	6.1-9.2	6.5-7.2	5.0-6.3

5. STRATEGY FOR MODEL APPLICATION

5.1. Initial model calibration

The aim of this study was to investigate whether the RAINS Lake Module can be verified with comparisons to indirect evidence on long term surface water responses. Therefore MAGIC was not independently calibrated to measured or estimated catchment soil and lake data. Instead a set of input values was chosen for RLM by using a trial and adjustment procedure, so that model predictions for lake and soil chemistry agreed with measured present day values, and with the pH-values from the diatom reconstructions. These input values were then used to run MAGIC in order to see if comparable simulation results were obtained. The selected period for the model reconstructions was 1850-1980.

The weathering rates for the four base cations, and the selectivity coefficients determining the cation exchange reactions in the MAGIC-model were adjusted so that the best possible fit with measured values was obtained. The total weathering rate was still kept equal to the calibrated values of the RLM applications. The parameter values determining the sulfate adsorption and nitrogen uptake rates were similarly adjusted.

5.2. The Monte Carlo parameter estimation procedure

The Monte Carlo method is a trial and error procedure for estimating poorly known input values from the required output. The basic steps of this estimation procedure are as follows (Fedra, 1983):

Table 3 . Parameter values used for RLM reconstructions. Data are either measured or estimated (see text for data sources)

Variable	**Lake Hauklampi**	**Lake Orajärvi**	**Lake Siikajärvi**	**Lake Sonnanen**
Catchment characteristics				
Precipitation ($m\,yr^{-1}$)	0.58	0.58	0.57	0.57
Runoff ($m\,yr^{-1}$)	0.31	0.31	0.31	0.32
Quickflow (%)	96.5	100	94	69
Baseflow (%)	3.5	0	6	31
Mean temperature (^{o}C)	5	5	5	5
Mean catchment surface slope ($m\,m^{-1}$)	0.06	0.06	0.01	0.01
Forest coverage (fraction)	0.4	0.4	0.4	0.25
Soil characteristics				
Mean depth (m)	0.8	0.8	0.9	4.3
Total CEC ($eq\,m^{-3}$)	100	300	36	46
Total weathering rate($eq\,m^{-3}yr^{-1}$)	0.040	0.035	0.032	0.022
Base saturation in 1850				
layer 1	0.3	0.5	0.45	0.8
layer 2	0.4	0.5	0.3	0.8
Lake characteristics				
Sulfate retention factor	0.30	0.22	0.37	0.25

(1) For the structure of the simulation model, performance criteria are formulated describing the expected satisfactory behavior of the model, based on available data.

(2) To estimate all unknown input values, allowable ranges or probability functions are defined for them.

(3) The Monte Carlo program then randomly samples the parameter vectors from the allowable ranges, runs the simulation model through a selected period and finally tests for violations of constraint conditions after simulation.

(4) This procedure is repeated for a large number of trials.

In an ideal case there should be *a priori* information on the shape of all parameters, initial conditions and catchment characteristics. In reality this is not the case and most inputs have to be selected from uniform distributions.

In this study the Monte Carlo approach was used to estimate input values for those three variables that were used by both models in a similar way: total weathering rate, total cation exchange capacity (CEC) and lake retention time (or maximum lake depth in RLM). A range of 30% was chosen for all three selected, initially calibrated parameters, and 100 Monte Carlo simulations were carried out for each catchment by randomly selecting a set of input values from within these designated ranges. The equations were then solved using these particular sets of input values.

After the simulations the model output was constrained by using measured values for lake pH in 1979–80. Only model runs for which simulated lake pH deviated at the most 0.2 pH-units from measured mean values were accepted.

Table 4. Parameter values used for MAGIC reconstructions. Data are either measured or estimated (see text for data sources)

Variable	Lake Hauklampi	Lake Orajärvi	Lake Siikajärvi	Lake Sonnanen
Catchment characteristics				
Precipitation $(m\,yr^{-1})$	0.58	0.58	0.57	0.57
Runoff $(m\,yr^{-1})$	0.31	0.31	0.31	0.32
Quickflow (%)	95	95	94	69
Baseflow (%)	5	5	6	31
Mean temperature (^{o}C)	5	5	5	5
Soil characteristics				
Mean depth (m)	0.8	0.8	0.9	4.3
Porosity (fraction)				
layer 1	0.6	0.6	0.6	0.6
layer 2	0.4	0.4	0.4	0.4
Density $(kg\,m^{-3})$				
layer 1	1000	1000	1000	1000
layer 2	1500	1500	1500	1500
CEC $(eq\,m^{-3})$	100	300	36	46
Total weathering rate $(eq\,m^{-3}yr^{-1})$	0.0400	0.0350	0.0320	0.0220
Ca $(eq\,m^{-3}yr^{-1})$	0.0160	0.0180	0.0110	0.0115
Mg $(eq\,m^{-3}yr^{-1})$	0.0130	0.0100	0.0100	0.0050
Na $(eq\,m^{-3}yr^{-1})$	0.0075	0.0035	0.0075	0.0045
K $(eq\,m^{-3}yr^{-1})$	0.0035	0.0035	0.0035	0.0010
Sulfate adsorption				
half-saturation $(meq\,m^{-3})$	150	170	150	150
maximum capacity $(meq\,kg^{-1})$	6	9	6	5
Selectivity coefficients				
layer 1: log S (AlCa)	0.4	0.3	0.0	-2.5
log S (AlMg)	1.8	2.0	1.7	-1.0
log S (AlNa)	-0.8	-1.0	-1.5	-3.9
log S (AlK)	-3.0	-3.7	-3.5	-6.2
aluminum solubility	8.2	8.1	8.0	7.9
layer 2: log S (AlCa)	5.9	5.7	5.9	6.7
log S (AlMg)	7.1	6.8	6.9	7.3
log S (AlNa)	2.3	1.9	1.9	1.6
log S (AlK)	-0.1	0.3	-0.3	-1.0
aluminum solubility	10.7	10.8	10.8	10.6
Uptake rates				
$NH_4\,(meq\,m^{-2}yr^{-1})$	96	103	92	97
$NO_3\,(meq\,m^{-2}yr^{-1})$	95	95	84	89
$pCO_2\,(atm)$				
layer 1	0.1	0.1	0.1	0.1
layer 2	0.02	0.02	0.02	0.02
Lake characteristics				
Uptake rates				
$NH_4\,(meq\,m^{-2}yr^{-1})$	96	96	86	91
$NO_3\,(meq\,m^{-2}yr^{-1})$	75	87	70	75
$pCO_2\,(atm)$	0.0006	0.0006	0.0006	0.0006

6. RESULTS

6.1. Hauklampi

The pH-reconstructions obtained from the diatom stratigraphy at lake Hauklampi (Tolonen and Jaakkola, 1983) suggests that the "pre-acidification" pH was about 6.0, compared with measured values of 4.8–4.9 in 1979–80 (Fig. 2). A slight increase in reconstructed pH can be seen in the late 1930's and early 1940's. One explanation for this increase could be a clearcut of the conifer forest on the shores of the lake that is known to have taken place some 50 years ago. According to Tolonen and Jaakkola (op. cit.) this clearcut seems to have doubled the rate of dry mass sedimentation in the lake during that time. The increase in pH is followed by a sharp break to pH 4.6–4.8 after 1962–64. A pH-value of 5.6 was measured in this lake in September 1965 (Pätilä, 1982).

RLM and MAGIC reconstructions indicate a higher initial pH and alkalinity. The simulation results of RLM point out to a more gradual decline of these values with time. MAGIC predicts the timing of maximum rate of decrease better than RLM, especially after 1930.

6.2. Orajärvi

At lake Orajärvi the diatom stratigraphy points to a somewhat slower decline of lake pH and alkalinity than in the nearby lake Hauklampi (Fig. 3). The reconstructed original lake pH is about 6.3 (Tolonen and Jaakkola, 1983), compared with measured values of 4.7-4.8 in 1979–81.

The model simulations again indicate higher initial pH- and alkalinity values. However, a better agreement over time is obtained between diatom and model reconstructions in this lake than in the case with lake Hauklampi.

6.3. Siikajärvi

The diatom curve for Siikajärvi (Simola, 1985) suggests that the lake originally had a pH of 5.8–5.9, and that acidification to present day values of 5.0–5.1 started around 1945 (Fig. 4). However, there is some indication of mixing of the uppermost 5 cm. of the sediment layer, which makes the timing of the pH-decline rather uncertain. Measured pH was 5.2–5.3 during autumn overturn of the period 1979–81. Alkalinity has been below detection limit (20 $\mu eq/l$).

The model reconstructions indicate much higher "pre-acidification" pH and alkalinity values than has been estimated from diatoms. MAGIC simulations indicate a very sharp drop in pH around 1950. MAGIC predicts the change with time, but not the absolute values, better than RLM.

6.4. Sonnanen

At lake Sonnanen the diatom stratigraphy points to very stable, slightly increasing pH. The reconstructed pH in 1850 is around 6.4 increasing to 6.6 in recent years (Simola, 1985). Measured pH during autumn overturn 1979–81 has been 6.3–6.7, and measured alkalinity 40–70 $\mu eq/l$.

In contradiction to diatom reconstructions all model simulations indicate decreasing trends of pH and alkalinity (Fig. 5). MAGIC especially indicates a rather sharp drop in pH after 1970. The simulated original level was, however, also high.

7. DISCUSSION

It is difficult to assess the uncertainties inherent in the model reconstructions despite the fact that neither model is very complicated. Both models are constructed using an "average" or lumped representation of the spatially distributed catchment processes. There are two important aspects of modeling large-scale heterogeneous catchments that must be considered when assessing the adequacy of the lumped approach (Cosby *et al.*, 1985a): The first aspect concerns the process aggregation, i.e. the degree to which a large number of the different processes which occur in a catchment can be represented by simpler conceptualizations of those processes. The second aspect concerns the scales of spatial heterogeneity in a catchment and the extent to which this heterogeneity can be neglected (spatial aggregation).

The models used in this study are examples of both types of aggregation, and therefore the processes that are included are obviously only generalizations of as yet poorly known phenomena. The dynamic nonlinear interactions between the numerous mathematical descriptions included in the models make it difficult to relate the overall performance of the models to the individual equations. Several of the input parameters are also interrelated such that an acceptable range for one parameter acts to restrict the possible range for other parameters (Cosby *et al.*, 1985a; Kämäri *et al.*, 1985). In addition the uncertainty in the deposition sequence is difficult to estimate. However, the problems of uncertainties are not solved by turning to more complicated models, because data on a catchment scale for many key parameters simply do not exist.

The diatom method naturally also includes sources of uncertainty. According to Renberg and Hellberg (1982), the ancient pH of a lake can be inferred with a mean accuracy of ±0.3 pH-units by using their pH-index. However, several factors, including changes in land use and special hydrological conditions can cause major errors in the pH-reconstructions (e.g. Batterbee and Flower, 1984). The dating of the sediment samples by lead-210 isotopes has been found to be strongly dependent on the sedimentation conditions in the lake (Appleby and Oldfield, 1978). It has also been suggested, that the adsorption affinity of Pb into sediment particles might decrease at low pH, which will cause errors in the sediment dating in acidified waters (Simola and Liehu, 1985)

Because of the great uncertainty inherent in historical reconstructions of lake acidity by paleolimnological methods, no attempt was made in this study to quantify the differences between results from diatom reconstructions and model simulations. The diatom reconstructions have been used only as an independent method to indicate the general time development of lake acidity. How well these different approaches represent reality remains still highly uncertain.

It has earlier been shown, that previous versions of the RAINS Lake Module could distinguish between acidified lakes and lakes where no indication of acidification has been observed, when driven by an assumed historical deposition pattern (Kämäri *et al.*, 1985). The applications in this study point to the same conclusion. In the RLM applications of the three acidified lakes the model could be calibrated to yield pH and alkalinity reconstructions that indicated similar changes as the results obtained by the diatom method. The parameter values used to drive the model were reasonable for lake areas in Scandinavia (e.g. Ulrich, 1983; Wright *et al.*, 1986). However, clear differences in the "pre-acidification" levels of acidity in the lakes and in the rate of acidification could still be observed between diatom and model reconstructions. RLM reconstructions generally indicated higher initial pH and alkalinity, and a more gradual decline of these values with time than the diatom results. The agreement between these methods was better for more

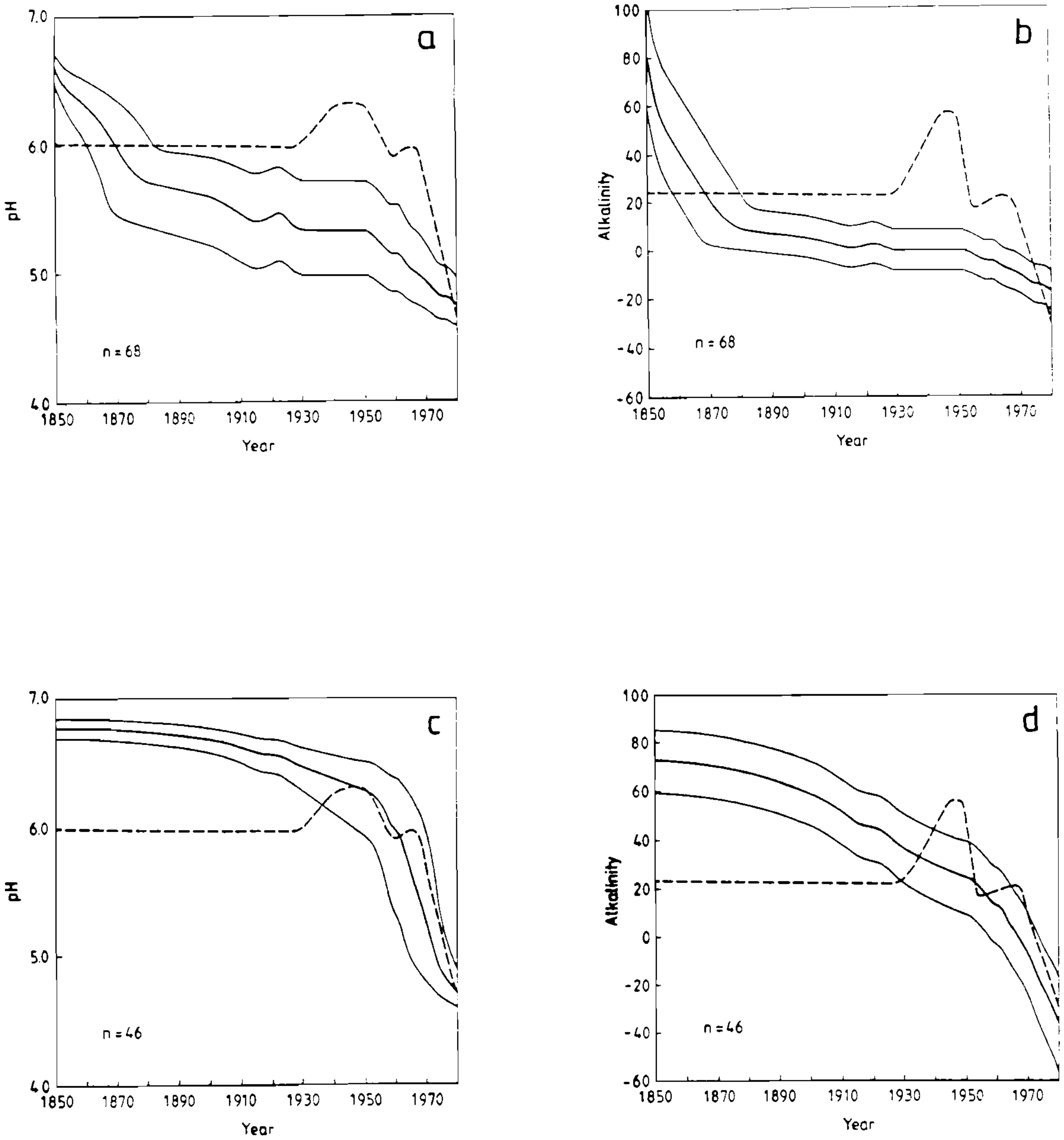

Figure 2. Reconstructed pH and alkalinity ($\mu eq/l$) for lake Hauklampi from the diatom stratigraphy (dotted line) and from RLM (a, b) and MAGIC (c, d) model applications. The mean and the minimum-maximum envelope of the accepted model runs is displayed.

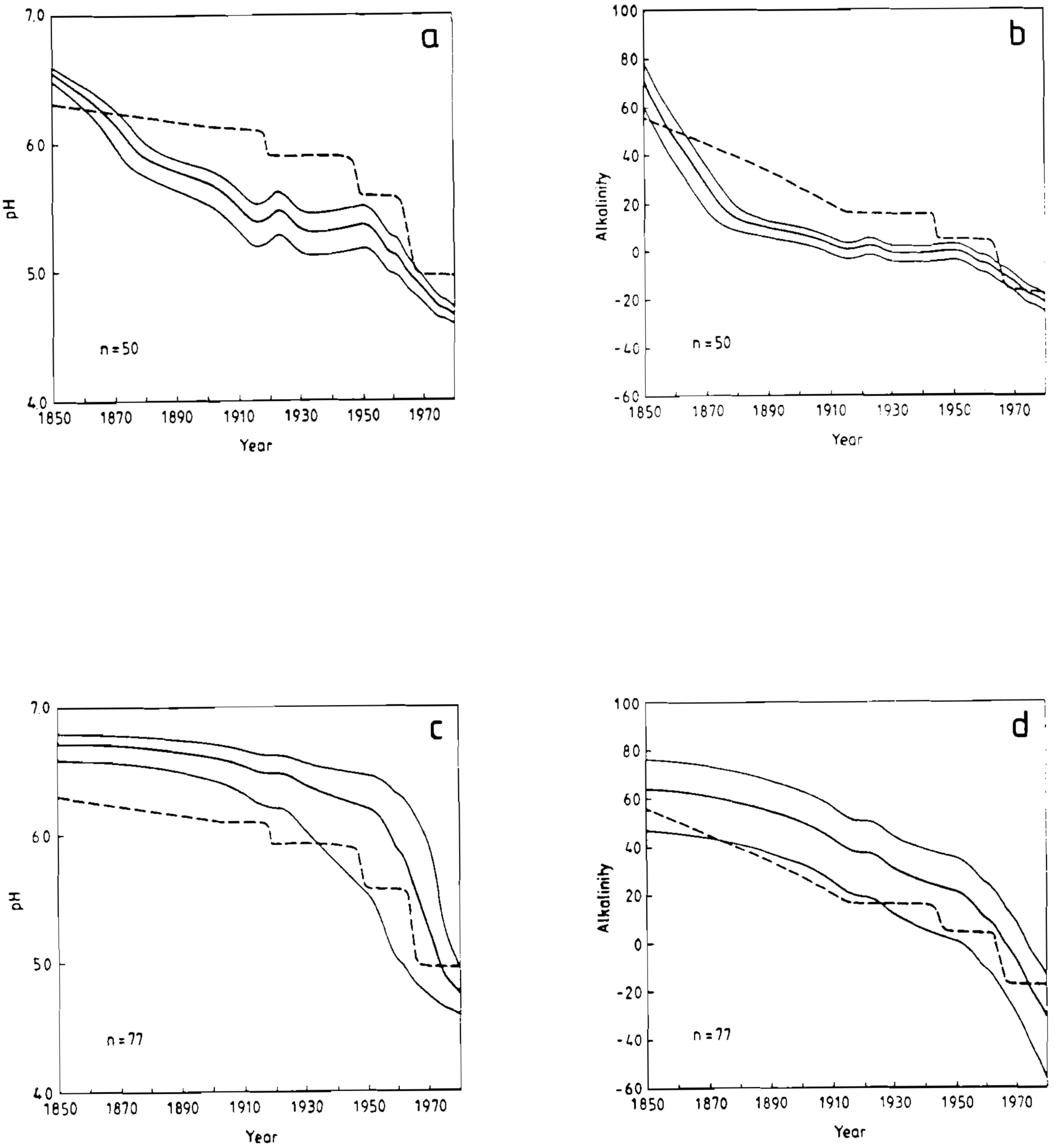

Figure 3. Reconstructed pH and alkalinity ($\mu eq/l$) for lake Orajärvi from the diatom stratigraphy (dotted line) and from RLM (a, b) and MAGIC (c, d) model applications. The mean and the minimum-maximum envelope of the accepted model runs is displayed.

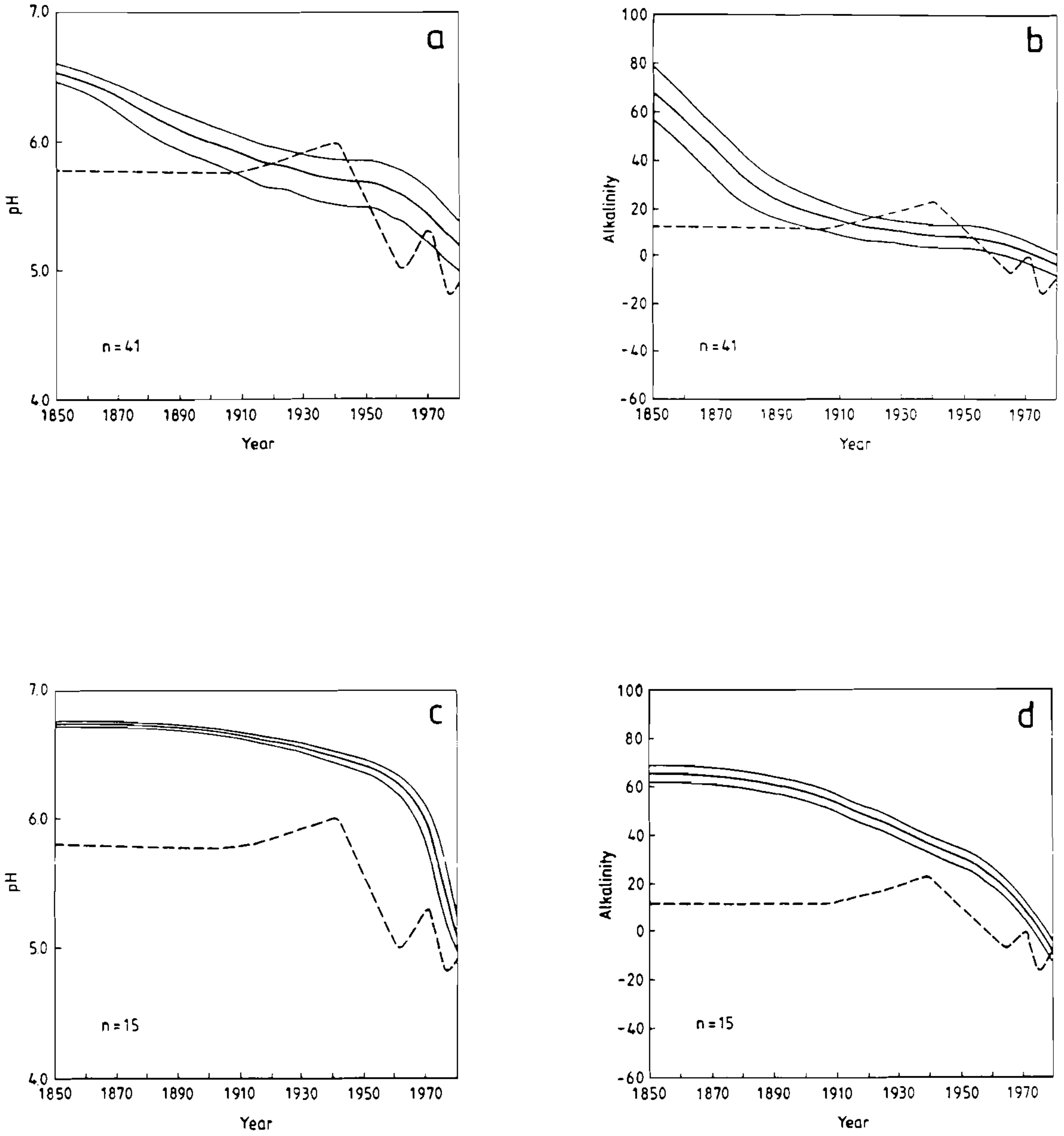

Figure 4. Reconstructed pH and alkalinity ($\mu eq/l$) for lake Siikajärvi from the diatom stratigraphy (dotted line) and from RLM (a, b) and MAGIC (c, d) model applications. The mean and the minimum-maximum envelope of the accepted model runs is displayed.

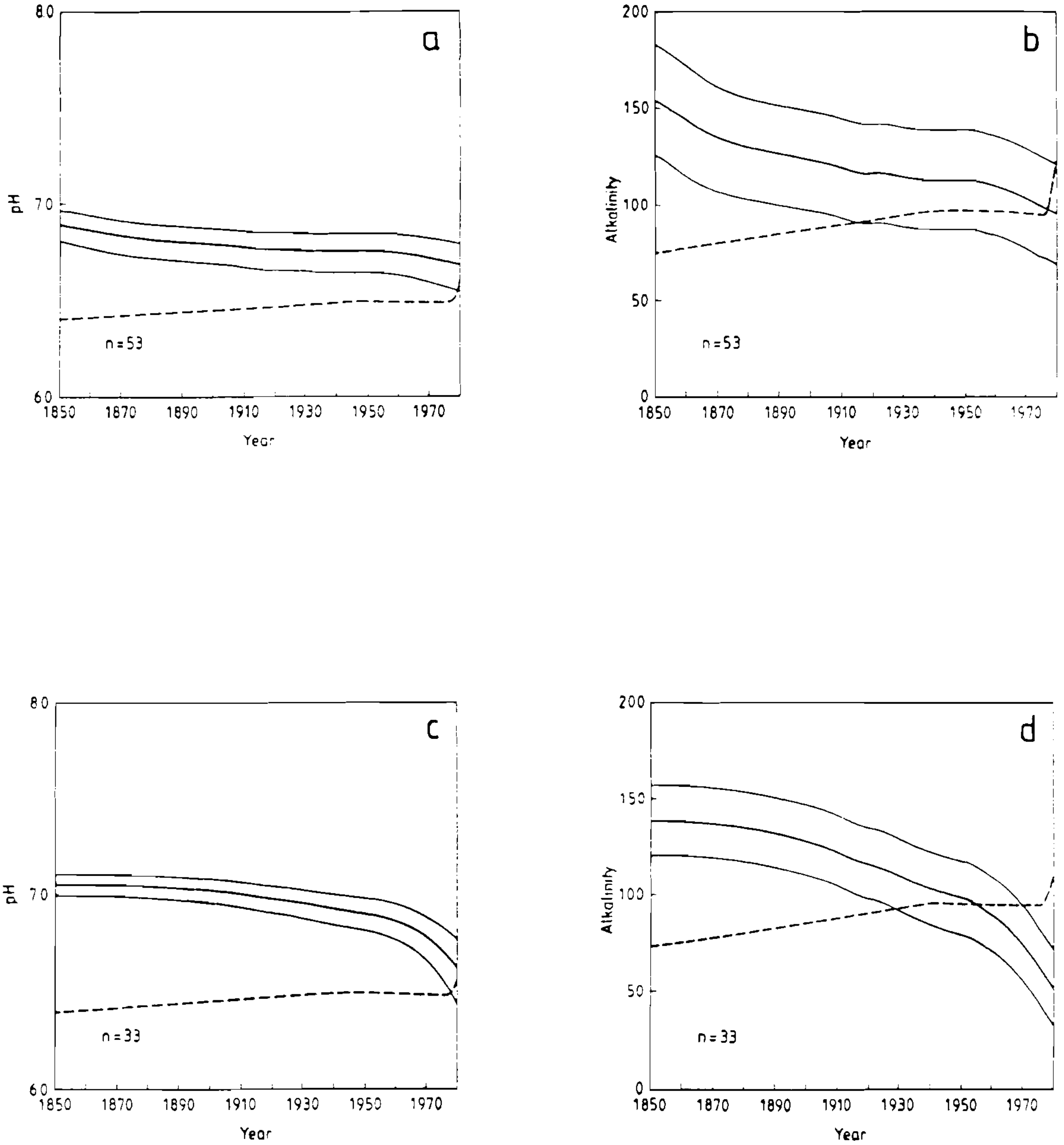

Figure 5. Reconstructed pH and alkalinity (*μeq/l*) for lake Sonnanen from the diatom stratigraphy (dotted line) and from RLM (a, b) and MAGIC (c, d) model applications. The mean and the minimum-maximum envelope of the accepted model runs is displayed.

recent times.

The difference between the pH history at lake Sonnanen and the three acidified lakes can be explained by the very different catchment characteristics. The catchment of lake Sonnanen has thick soils and large areas with glacio-fluvial deposits. A high proportion of the flow is probably groundwater.

The increasing trend in pH of lake Sonnanen indicated by the diatom reconstructions is, however, difficult to explain. One reason could be leaching of alkaline earth material and fertilizers from the small agricultural area in the catchment. This kind of external loading has not been taken into account in the model calibrations. It has, furthermore, been shown that acid deposition can make aquatic ecosystems more alkaline in nonsensitive areas (Kilham, 1982). This change is caused by an increased weathering rate in combination with biologically mediated processes of nitrate uptake and sulfate reduction. The increased alkalinity production can completely neutralize the acid input to the system and even increase the neutralizing capacity of the water. It is likely that some of these processes have been underestimated in the model applications of the fairly well buffered system of lake Sonnanen, because all model reconstructions showed decreasing trends of pH and alkalinity.

Large differences in the model reconstructions were obtained with the Monte Carlo testing procedure. This is rather obvious, because the RAINS soil acidification model has shown high sensitivity to variations in the silicate weathering rate and initial base saturation of the soil. The difference of acid load and the weathering rate of base cations determines whether the soil alkalinizes or acidifies in the model reconstructions. Especially in Scandinavia, where the acid load and the weathering rate are about equal, these parameters should be estimated with special care (Posch *et al.*, 1985). Unfortunately, no measurements of weathering rate has been made in the catchments in this study. Reliable calculations of this rate are, of course, also very difficult to make on a catchment scale.

It can be observed, that allowable outcomes were reproduced in a rather high percentage of the reconstructions for the sets of ranges of initial conditions and parameters used. Including more input values in the Monte Carlo framework, and thus increasing the amount of change in the driving variables, naturally increases the uncertainty of the predictions (see Kämäri *et al.*, 1985).

Because the calibrated input values from the RLM applications were used to run the MAGIC-model, the results of MAGIC obtained are therefore not necessarily the best possible. The simulation results of this model should for this reason be regarded rather as a test of the hypothesis incorporated in RLM, than as independent model applications.

Clear differences between the simulation results of the two models are evident, especially in the beginning of the simulation period. MAGIC reconstructions tend to have higher initial pH and alkalinity values, and sharper decline of these values with time. It must be recognized, that a more comprehensive calibration procedure of this model would have brought the simulation results closer to the values from the diatom reconstructions. For example increasing of the CO_2 partial pressure in the lake would have decreased the initial simulated pH. No measurements of CO_2 values were, however, available from the sites in this study and therefore values from the MAGIC application to Woods Lake (see e.g. Cosby *et al.* 1987) were used instead. The same decreasing effect on pH would have appeared by introducing variables for organic acids in the model, assuming that the lakes would have become clearer. This kind of clarification process in acidified lakes has been documented in e.g. Lake Hovvatn (Davis *et al.*, 1985).

The sharp increase in acidity in the MAGIC simulations of the three acidified lakes shows a rather good accordance with the diatom reconstructions after the year of 1930. RLM reconstructions show a more gradual pH decline. The delayed response of the lakes to acid deposition in MAGIC reconstructions is probably due to the more complicated buffer reactions incorporated in this model (e.g. sulfate adsorption), compared with the more straightforward approach of RLM.

Large differences in the reconstructions were obtained also in the applications of the MAGIC-model when using the Monte Carlo method. According to Cosby *et al.*, (1985a) the model has proven to be very sensitive to weathering fluxes, and currently observed water quality of the White Oak Run catchment could be reproduced only by using fluxes from a narrow range of values. In this study allowable outcomes were still commonly reproduced for the catchments, with the exception of lake Siikajärvi.

However, some major difficulties occurred when the MAGIC-model was run with the calibrated input values from the RLM applications. For the Hauklampi and Orajärvi catchments low values for baseflow were predicted by RLM. However, larger baseflow values had to be used in MAGIC because of the functioning of this model. High values for the selectivity coefficients (log$S$), and for the coefficient determining the aluminum solubility had also to be used for the B-horizon of the soils of all catchments, in order to get successful computations. These values were larger than those reported from other MAGIC applications (e.g. Cosby *et al.*, 1985a; 1985b; Cosby *et al.*, 1986; Wright *et al.*, 1986). On the contrary, the current observations of base saturation of the A-horizon of the soil at lake Sonnanen could be reproduced only when very small values for the selectivity coefficients were used.

There is very little information available on appropriate values of the Gaines-Thomas selectivity coefficients for soils likely to be impacted by acid deposition (Reuss and Johnson, 1985), which makes the evaluation of the above results very difficult. According to Reuss and Johnson (1985) the base saturation, the selectivity coefficients (log$S$) , and the solubility of the mineral phase of controlling Al in solution (logK_{Al}) interact in a complex manner. In general terms increasing values of K_{Al} predict increased soluble Al in the system and an increase in the pH at which the mineral phase dissolution buffers the system. The increase in solution Al tends to decrease alkalinity, while higher pH tends to increase alkalinity, resulting in a complex total effect. However, increasing K_{Al} seems to decrease the sensitivity to acid loading. Furthermore, increasing base saturation tends to decrease the sensitivity to water acidification, and increasing values for the selectivity coefficients would have the same effect as decreasing base saturation.

The reason why large values for the selectivity coefficients had to be used in the applications is probably, that the fairly high weathering fluxes in combination with the low values for base flow resulted in high saturation of the exchange complexes in the B-horizon of the soil. Increasing the values of the selectivity coefficients therefore had the effect of decreasing the base cation saturation. By contrast, very low values for the selectivity coefficients of the soil surface layer had to be used for lake Sonnanen. This can be explained by recognizing that the catchment had received a fairly high load of acid deposition for a long time, and a great affinity for base cations of the soil exchange complexes had to be simulated in order to match the reconstructed and the high observed base saturation values. This also explains the rather sharp increase in acidity in this lake that occurred in the model reconstructions. As described earlier it is evident that some of the buffering processes occurring in the catchment have been underestimated in the model applications of this nonsensitive site. Apparently the use of e.g. higher weathering rate values would have resulted in more realistic selectivity coefficient values and a more stable simulated lake acidity at this site.

Sulfate retention in the soils can be an important factor delaying the catchment response to acid deposition. However, young, podsolic soils developed in post-glacial times on granitic bedrock have typically little ability to adsorb sulfate, and the choice of parameter values for the sulfate adsorption characteristics has not been of critical importance in earlier MAGIC applications in Scandinavian regions (e.g. Wright *et al.*, 1986). For this reason it is interesting, that rather high parameter values for sulfate adsorption had to be used in the MAGIC applications at the catchments in this study, in order to match simulated and observed lake water sulfate values. This fact could obviously have several different explanations, including an overestimation of sulfate deposition, or errors in water quality analyses. However, peatlands have a large capacity for sulfate reduction, and sulfate reduction becomes an increasingly important source of alkalinity as rates of sulfate deposition increase. From 60–93% of annual sulfate loadings are retained as reduced sulfur in bogs across eastern North America (Urban *et al.*, 1986). Considerable sulfate retention has been reported also from Finnish catchments having a moderate to high percentage of peatland (Kallio and Kauppi, 1987). Thus, the high sulfate retention of the Hauklampi, Orajärvi and Siikajärvi lake catchments could at least partly be explained by occurrence of peatland and Sphagnum carpets. At lake Sonnanen also the thick soil deposits and the large percentage of groundwater flow could possibly increase the retention coefficient.

The sulfate retention processes are not currently incorporated in RLM. This is because these processes have not earlier been considered as quantitatively important in Scandinavian lake regions, for which this model originally has been developed. However, e.g. the budget studies described above (cf. Urban *et al.*, 1986; Kallio and Kauppi, 1987), and also the results from the MAGIC applications in this study indicate, that sulfate retention can be at least locally important. There are good reasons to believe that modeling of sulfur dynamics might be important also on a regional scale. For example in Finland and Sweden there are large areas with high percentage of peatland and humic lakes.

8. CONCLUSIONS

1. The pH inferred from the diatom stratigraphy of the lake sediments includes major sources of uncertainty. The pH index itself as well as the dating of the sediment core, are both rather uncertain analyses. In addition, there is uncertainty in determining what in fact the inferred pH represents, the minimum, annual mean or the autumn pH. For this reason, the diatom reconstructions have in this study been used only as an indicative method for estimating the general time development of lake acidity, and no attempt has been made to quantify the differences between results from diatom and model reconstructions.
2. RLM could well, considering the uncertainties above, be calibrated to yield pH and alkalinity reconstructions that indicated similar changes as the results obtained by the diatom method, using independent data from the three acidified lakes. Clear differences in the "pre-acidification" levels of acidity in the lakes and in the rate of acidification could, however, be observed between diatom and model reconstructions. RLM reconstructions generally indicated higher initial pH and alkalinity, and a more gradual decline of these values with time than the diatom results. The agreement between these methods was better for more recent times. The reconstructions were still within the range of uncertainties inherent in the model inputs and in the diatom method.
3. It is likely that some of the buffering processes occurring in the catchment of lake Sonnanen have been neglected or underestimated in the model applications of this nonsensitive system, because all model reconstructions (both RLM and MAGIC) showed decreasing trends of pH and alkalinity in contradiction to the results indicated by the diatom method.
4. The MAGIC applications in this study cannot be regarded as independent model applications because MAGIC was run with calibrated input values from RLM. The results of MAGIC obtained are not necessarily the best possible. It is therefore not surprising, that major difficulties occurred in the calibration procedure of this model. Especially calibration of the selectivity coefficients and the coefficient determining the aluminum solubility proved to be difficult. The values that had to be used were in many cases different from values used in other MAGIC applications from similar lake regions, and they might not be very realistic. There is, however, very little information available on appropriate values of the selectivity coefficients for soils likely

to be impacted by acid deposition which makes the evaluation of the results difficult.

5. The fact that high values for the coefficients determining aluminum solubility and cation exchange had to be used for the B-horizon of the soil in the MAGIC applications indicate, that the low values for baseflow calculated by RLM might be underestimations. Another explanation would be, that the weathering rate was estimated too high compared with the low baseflow values. A more comprehensive study would, however, be needed to draw any definite conclusions.
6. Both models generally predicted similar changes in lake acidity. There were, however, some obvious differences. MAGIC reconstructions usually had higher "pre-acidification" values of pH and alkalinity. Furthermore, the sharp increase in acidity indicated by diatom reconstructions, in particular for lake Hauklampi, was more closely described by MAGIC reconstructions. This is probably due to a more detailed description of the buffer processes of the catchment soil incorporated in this model (e.g. sulfate adsorption) compared with a more straightforward approach in RLM . However, the computer time needed for the individual MAGIC applications is very much longer, which makes this model less suitable for extensive regional applications.
7. The use of the Monte Carlo testing procedure showed that large differences in the simulated acidification path of the lakes can be obtained when sensitive model parameters are randomly varied. A fairly large number of allowable outcomes were still reproduced in both RLM and MAGIC applications.
8. Modeling of sulfur dynamics in the soil may be important for making reliable long-term predictions in many catchments. These processes are not currently incorporated in the RAINS-model. Also in MAGIC the adsorption/desorption isoterms for sulfur dynamics have been criticized for being too simple (see Reuss *et al.*, 1986). In addition, the question of sulfate retention by Finnish forest soils definitely deserves closer attention.

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