A MODEL FOR ANALYZING LAKE WATER ACIDIFICATION ON A LARGE REGIONAL SCALE

PART 1: MODEL STRUCTURE

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PREFACE

The IIASA "Acid Rain" Project started in 1983 in order to provide the European decision makers with a tool which can be used to evaluate policies for controlling acid rain. This modeling effort is part of the official cooperation between IIASA and the UN Economic Commission of Europe (ECE).

The IIASA model currently contains three linked compartments: Pollution Generation, Atmospheric Processes and Environmental Impacts. Each of these compartments can be filled by different substitutable submodels. The submodels currently available are Energy Pathways and Sulfur Emissions, the EMEP Long Range Transport Model, Forest Soil pH and Lake Acidity. In addition, two submodels are under development: the NO_x Emissions submodel and the Direct Forest Impacts submodel. The first version of the Lake Acidity submodel was presented in September 1984 in a UNESCO-IHP Workshop in Uppsala, Sweden. Since then several changes have been implemented following the advice of experts. This paper describes the Lake Acidity model structure as it stands in December 1985.

Leen Hordijk

Acid Rain Project Leader

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ABSTRACT

The International Institute for Applied Systems Analysis is developing a computer model which can be used by decision makers to evaluate policies for controlling the impact of acid rain in Europe. As part of this task, a simple dynamic model has been developed for describing the processes leading to acidification of surface waters. The simulation model is constructed of several modules, each of them providing an overview of a particular aspect of lake acidification. The meteorologic module calculates the amount of water and deposition entering the soil or the lake directly each month. The IIASA soil acidity submodel accounts for the soil solution chemistry. A simple hydrologic method is applied for simulating the routing of internal flows so that the convective flow of ions can be estimated. The lake response is calculated according to the equilibrium reactions of inorganic carbon species. These modules are described in this paper. In part 2 the application of the model on a large regional scale will be described. Monte Carlo techniques will be used to determine those ranges and combinations of input values that produce an acceptable present day lake acidity distribution, when the model is driven by a specified deposition.

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1. INTRODUCTION

The harmful effects on surface waters resulting from acidic deposition have been well documented in various parts of the Northern Hemisphere. The causal relationships leading to freshwater acidification are, however, complex and difficult to quantify. Hydrochemical models have provided one way of quantifying and integrating various processes in the entire catchments. Models have been used for simulating daily variations of water quality in streams, caused by variations in deposition, as well as in catchment hydrology and meteorology (e.g. Christophersen et al. 1982). However, many of these modeling approaches have been regarded as tools for data evaluation rather than tools for predicting long-term acidification of the catchments.

Recently the need to provide estimates of potential future impacts of acidic deposition has been emphasized. Scientific information can assist in evaluating policies for emission control by describing quantitative consequences of alternative scenarios. There are at present three basic methods for making projection of future water chemistry of sensitive areas. The first is an empirical approach which allows the estimation of future steady-state chemical composition of lakes resulting from changes in loading of strong acids on the basis of observed relationships in present conditions (e.g. Henriksen, 1980). The second method utilizes complex, process oriented submodels for catchment hydrology, canopy chemistry, soil chemistry as well as for stream and lake water quality to provide a scientific link between acidic deposition and lake acidification (e.g. Chen et al. 1983). The third method defines predictive algorithms that largely retain the simplicity

of the empirical models but that have mechanistic process oriented explanations incorporated in their structure, to allow a theoretical basis for establishing confidence in the estimates (Cosby et al. 1985).

Simple models can be applied as part of a regionalized model structure. At the beginning of the development of IIASA's lake acidification model, no suitable models were available for this purpose. Therefore, a number of existing process descriptions were simplified, modified to monthly time step and finally linked together to form a simple working method for the evaluation of lake acidification. This method will be used as a component of the IIASA Regional Acidification Information and Simulation (RAINS) model system. The objective of this model system is to provide decision makers with a tool, which can assist in evaluating policies for controlling the impact of acidic deposition in Europe. With the lake acidification model, the response of sensitive lake areas to alternative energy patterns and emission reduction measures will be analyzed.

In the IIASA acid rain study, the energy-emission model generates *sulfur emission scenarios* for Europe, assuming optional programs for energy development and emission control (Alcamo et al., 1985). Computed emissions are converted into *sulfur deposition scenarios* in the atmospheric transformation compartment of the model system by using the long-range transport model for air pollutants developed within the EMEP-program (see Eliassen and Saltbones, 1983). Sulfur deposition is finally transformed into an estimation of *acid stress* (Kauppi et al. 1985), which forms the basic input data for environmental impact submodels. Any long-range transport model from the Atmospheric Processes compartment may be linked to all models in the Environmental Impact compartment (Figure 1). Presently, the EMEP sulfur transport model forms the driving force of the forest soil acidity and lake acidity submodels.

The study includes model development and model application. In this paper, the overall strategy for the model application as well as the present model structure and some model experiments are described. The second part includes the model application with model results for different lake regions in Europe.

2. STRATEGY FOR MODEL APPLICATION

In simulation models of environmental systems, based upon physical, chemical and/or biological mechanisms, the model structure (the theory), model inputs, initial conditions as well as parameter values all necessarily include uncertainty. On a regional scale, the uncertainty is even greater. It has been emphasized in several studies that the analysis of models should concentrate on identifying ranges of inputs, rather than on traditional parameter estimation (e.g. Fedra 1983; Hornberger and Cosby 1985). Hornberger and Cosby (1985) have successfully investigated the ability of a simple catchment model of sulfate dynamics, run with the most probable ranges of inputs, to produce the *distribution* of measured, present-day stream sulfate concentrations for the White Oak Run region in Virginia, USA. Moreover, the same procedure has been applied to determine which parameter combinations produced acceptable predictions of soil properties when the

(a) COMPARTMENTS

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┌──────────────┐        ┌──────────────┐        ┌──────────────┐
│ Pollutant    │        │ Atmospheric  │        │ Environmental│
│ generation   │───────▶│ processes    │───────▶│ impact       │
│              │        │              │        │              │
└──────────────┘        └──────────────┘        └──────────────┘
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                                                    ┌──────────────┐
                                                    │ Forest soil  │
                                                    │ acidity      │
                                                    │              │
┌──────────────┐        ┌──────────────┐           └──────────────┘
│ Sulfur       │        │ EMEP sulfur  │          ╱
│ emissions    │───────▶│ transport    │─────────┤
│              │        │              │          ╲ ┌──────────────┐
└──────────────┘        └──────────────┘            │ Lake         │
                                                     │ acidity      │
                   (b) SUBMODELS                     │              │
                                                     └──────────────┘
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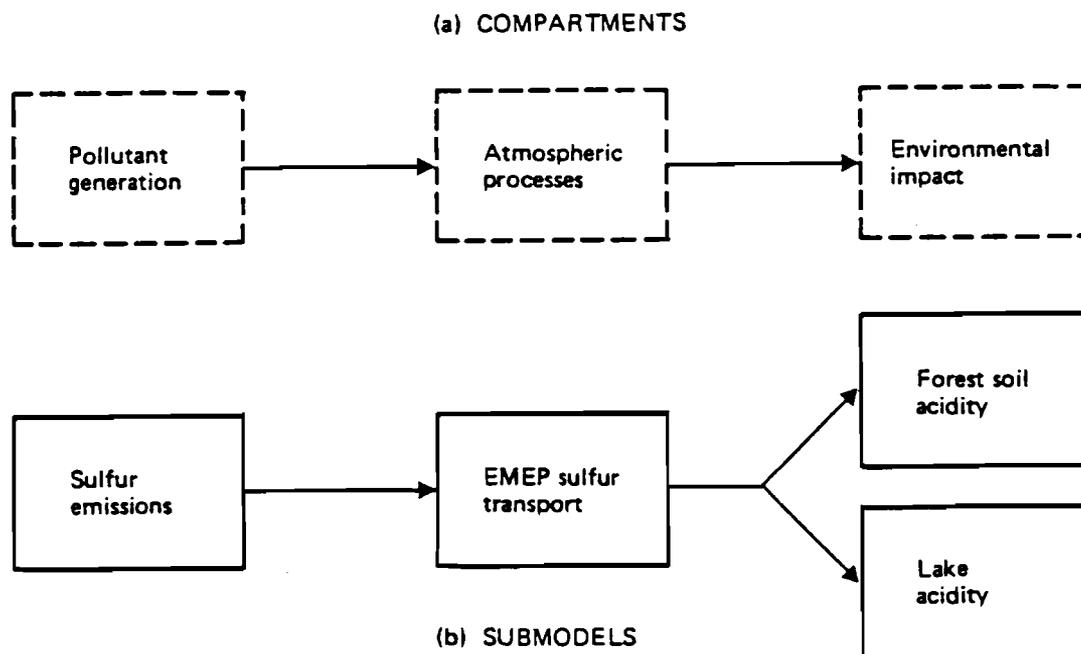
Figure 1.   Links in the IIASA Acid Rain Model.

model was driven by the observed stream chemistry (Cosby et al. 1985). The basic principle of their *Regionalized Sensitivity Analysis* has been to use Monte Carlo techniques for simulating the result of temporal evolution of a number of individual catchments with varying inputs. Hornberger and Cosby (1985) suggest that

> " ... it is appropriate and, in a sense, easier to predict conditions relating to *distributions* of uncertain systems than it is to predict conditions for an individual example of the system."

Our strategy for the application of the model for the regional scenario analysis has two distinct levels. At the first level the catchment model is able to analyze changes over time in the chemistry of a lake. The model can be run for any known system for which relevant lake, catchment and soil information is available. Examples of model experiments at the catchment level are shown and discussed in chapter 4 of this paper. In course of the regional model development the model is incorporated into a larger structure which scales the scenarios from individual systems up to a regional level. We apply the Monte Carlo parameter estimation procedure to the regional lake acidification assessment in order to model regional lake water quality distributions.

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

(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 the simulation.

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

In our regional model, the Monte Carlo method is used to determine the combinations of inputs that produce an acceptable distribution of output variables, observed in the study region. For all inputs, ranges are chosen broad enough so that any reasonable value for an input could be selected in the Monte Carlo simulations. In an ideal case, there should be *a priori* information on the shape of distributions of all parameters, initial conditions and catchment characteristics. In reality, however, this is not the case and several inputs have to be selected from uniform distributions.

Monte Carlo simulations are then carried out by randomly selecting a set of input values from within these designated ranges and integrating the equations from 1960 on using this particular set of values. A subset of accepted input values corresponding to the actual observed present-day frequency distribution in 1980 in each lake region, is obtained. The model, now calibrated for present-day conditions, provides a tool for future projections of regional lake water acidity. Assuming that the set of input values obtained in the calibration is representative of real catchments in the study region, this ensemble can be used for the scenario analysis of the response of lake systems to different patterns in acidic deposition.

As a result, this procedure will give new frequency distributions for model output variables which will serve as impact indicators. A critical acidity level has to be established, and according to this level, the number of lakes or the lake surface area threatened in each lake district can be estimated for any year and any energy-emission scenario desired.

Agricultural management practices as well as other sources of pollution in the catchment have an overwhelming influence on the ionic balance of surface waters. For example, liming and fertilizing practices cause eutrophication, high alkalinity and high pH-values in those surface waters receiving agricultural runoff. Therefore the evaluation of impacts will be restricted to sensitive lake regions that do not receive any significant anthropogenic input except atmospheric pollutants. The behavior of each sensitive lake-district is determined by distributions of regional soil, lake and catchment characteristics as well as by deposition, precipitation and air temperature. All information regarding this input data is stored into a computerized format. Simulations with 70 years time span (1960-2030) are performed for each sensitive lake region in Europe using a monthly time step.

3. MODEL STRUCTURE

During the development of the study our modeling philosophy 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 to allow a theoretical basis for assessing confidence in the scenarios. The model consists of four modules that are linked together as shown in Figure 2. The processes considered in each module are summarized in Table 1. The meteorologic module regulates the input flows of water and deposition to the soil and directly to the lake. The hydrologic and soil chemistry modules together determine the flow of ions leaching from the terrestrial catchment to the lake. New equilibrium concentrations in the lake water are then computed in the lake module.

Table 1.   Processes considered in the IIASA lake acidity model.

Process	Reference
Meteorology :	
Partitioning between snow and rain	Shih et al. 1972
Snow melt	Chow 1964
Release of deposition from snowpack	Johannessen and Henriksen 1978
Hydrology :	
Evapotranspiration	Christophersen et al. 1984
Percolation from upper to lower reservoir	Chen et al. 1982
Lateral flow	Chen et al. 1982
Soil chemistry :	
Carbonate weathering	Ulrich 1983
Silicate weathering	Ulrich 1983
Cation exchange	Ulrich 1983
Aluminum equilibrium with gibbsite	Christophersen et al. 1982
Lake :	
Inorganic carbon equilibrium	Stumm and Morgan 1981

3.1. Meteorologic Module

The purpose of the meteorologic module is to determine the volume of water and proportion of deposition entering the catchment within one time step, τ. The division of the total precipitation, P_{tot}^{τ}, into rain, P_r^{τ}, and snow, P_s^{τ}, is accomplished by Eqs.1a,b using threshold temperatures, T_s and T_r and the mean monthly temperature T^{τ} (Shih et al., 1972, Christophersen et al. 1984)

$$P_r^{\tau} = \begin{cases} 0 & \text{if } T^{\tau} < T_s \\[2ex] P_{tot}^{\tau} \dfrac{T^{\tau} - T_s}{T_r - T_s} & \text{if } T_s \le T^{\tau} \le T_r \\[2ex] P_{tot}^{\tau} & \text{if } T^{\tau} > T_r \end{cases} \tag{1a}$$
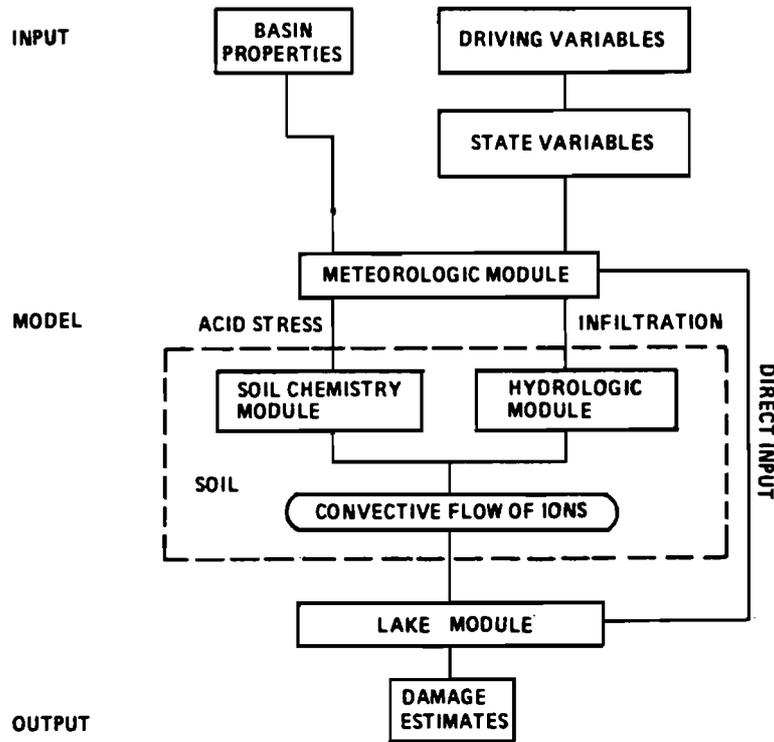
Figure 2.   The overall structure of the IIASA lake acidity model.

$$P_s^\tau = P_{tot}^\tau - P_r^\tau \tag{1b}$$

Snow accumulates, whereas all rain during the winter is assumed to run through the snowpack and enter the soil. Also, the melting of the snowpack, m^τ, is set to be proportional to the mean monthly temperature above the threshold temperature T_s, using a melting rate coefficient β (Chow, 1964; Chen et al. 1982)

$$m^\tau = \begin{cases} \beta(T^\tau - T_s) & \text{if } T^\tau > T_s \\ \\ 0 & \text{if } T^\tau \le T_s \end{cases} \tag{2}$$

The snowpack, SP^τ, is obtained by summing the individual P_s^τ-values and subtracting the m^τ-values, as long as SP^τ stays above zero (Eqs. 3 a and b; here and thereafter primes refer refer to an intermediate step, which is used for computational purposes only)

$$SP' = SP^{\tau-1} + P_s^{\tau} \tag{3a}$$

$$SP^{\tau} = SP' - m^{\tau} \tag{3b}$$

Deposition is assumed to accumulate when snow accumulates, the rate for deposition accumulation being D_s^{τ}. The same fraction of total deposition, D_{tot}^{τ}, as of total precipitation is retained in the snowpack each month as accumulated deposition, DP^{τ} (Eqs.4a,b)

$$D_s^{\tau} = D_{tot}^{\tau} \cdot P_s^{\tau} / P_{tot}^{\tau} \tag{4a}$$

$$DP' = DP^{\tau-1} + D_s^{\tau} \tag{4b}$$

During the snowmelt, the rate for the release of deposition from the snowpack, D_m^{τ}, is assumed to be two times higher than meltwater (Eqs.5 a and b). The fractionation effect observed during the snowmelt (Johannessen and Henriksen, 1978) implies that most of the impurities in the snowpack are found in the first meltwater.

$$D_m^{\tau} = \begin{cases} 2m^{\tau}DP' / SP' & \text{if} \quad m^{\tau} < \frac{1}{2}SP' \\[2ex] DP' & \text{if} \quad m^{\tau} \geq \frac{1}{2}SP' \end{cases} \tag{5a}$$

$$DP^{\tau} = DP' - D_m^{\tau} \tag{5b}$$

The deposition entering the soil or the lake will be called *acid stress*, as^{τ}, in the sequel

$$as^{\tau} = D_{tot}^{\tau} - D_s^{\tau} + D_m^{\tau} \tag{6}$$

3.2. Hydrologic Module

The flowpaths of rain and snowmelt water through the terrestrial system are important factors in determining the susceptibility of lakes to acidification by atmospheric deposition (Chen et al. 1982). To provide a method for simulating the routing of internal flows, a simple hydrologic model is applied. A combined version of hydrologic models, Birkenes model and ILWAS model, presented by Christophersen et al. (1982) and Chen et al. (1982) respectively, is used.

The IIASA framework sets the prerequisite of a large spatial scale. The ILWAS model is highly mechanistic and contains descriptions of the processes both in the canopy and in several soil layers. There is thus rather little curve-fitting involved. The Birkenes model is very site specific and must be calibrated against the typical features of a given catchment

before it can be applied. For the IIASA context, the simple two-layer structure of the Birkenes model is applied. Most of the physical descriptions of the processes for routing the water through these two layers and out of the system are simplified from the ILWAS model.

The terrestrial catchment is vertically segmented into snowpack and two soil layers (A- and B-reservoirs; Figure 3). The A-reservoir is defined to be identical with the uppermost 0.5 meter soil layer modeled by the soil impact model (Kauppi et al. 1985), which is used later to account for soil solution chemistry. Physically, the flow from the upper reservoir can be thought of as *quickflow*, which drains down the hillsides as piped flow or fast throughflow and enters the brooks directly (Christophersen and Wright, 1981). This water is mainly in contact with humus and the upper mineral layer. The B-reservoir in the model provides the *baseflow*, which presumably comes largely from deeper (> 0.5 m) soil layers (c.f. Christophersen and Wright, 1981).
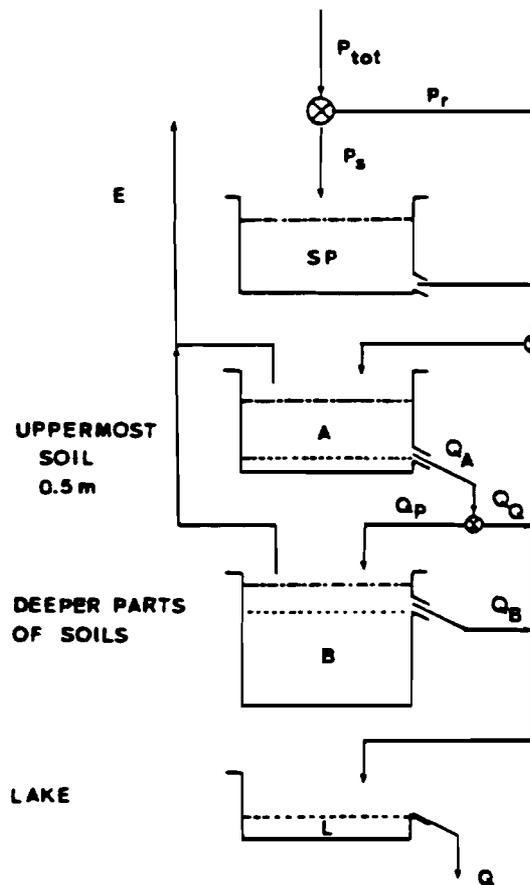

Figure 3.   Simulating the routing of water flows from precipitation to lake discharge; see text for explanation (modified from Christophersen et al. 1984).

The basic assumption governing the soil hydraulics is that rainfall or meltwater infiltrates as a whole into the A-reservoir (c.f. Christophersen and Wright, 1981). Evapotranspiration, E^τ, is set proportional to the mean monthly temperature, T^τ, above $0\ ^\circ C$, using a evapotranspiration coefficient ε (c.f. Christophersen et al. 1984)

$$E^\tau = \begin{cases} \varepsilon \cdot T^\tau & \text{if } T^\tau > 0 \\ 0 & \text{if } T^\tau \leq 0 \end{cases} \tag{7}$$

The actual evapotranspiration rate is assumed to be equal to the potential from the A-reservoir, and if A becomes empty, from the B-reservoir. The intermediate water balance is given by Eq.12, which considers the water fluxes between the A-reservoir, the atmosphere and the snowpack

$$V_A{}' = V_A^{\tau-1} + m^\tau + P_r^\tau - E^\tau \tag{8}$$

The percolation of water into the B-reservoir is controlled by the maximum possible percolation rate, $Q_p^{(1)}$, the water volume available in the A-reservoir, $Q_p^{(2)}$, and the space left in the B-reservoir, $Q_p^{(3)}$. Any one of these three factors can be a limiting factor for percolation. Therefore the actual percolation rate, Q_p^τ, is set equal to the minimum of these three,

$$Q_p^{(1)} = K_s \frac{V_A{}' - \theta_{f,A}}{\theta_{s,A} - \theta_{f,A}} \tag{9a}$$

$$Q_p^{(2)} = V_A{}' - \theta_{f,A} \tag{9b}$$

$$Q_p^{(3)} = \theta_{s,B} - (V_B^{\tau-1} - Q_B^\tau) \tag{9c}$$

$$Q_p^\tau = \min\left\{ Q_p^{(1)}, Q_p^{(2)}, Q_p^{(3)} \right\} \tag{9d}$$

and

$$V_A{}'' = V_A{}' - Q_p^\tau \tag{10a}$$

$$V_B{}' = V_B^{\tau-1} + Q_p^\tau \tag{10b}$$

where K_s is the hydraulic conductivity at saturation, $\theta_{f,A}$, $\theta_{f,B}$ the soil moisture content at field capacity in A- and B-layer, resp. and $\theta_{s,A}$, $\theta_{s,B}$ the soil moisture content at saturation in A- and B-layer, resp.

Lateral flow, Q_B^τ, is the limiting factor for the rate with which the water is discharged from the B-reservoir to streams and lakes. It is a function of hydraulic conductivity, K_s, surface slope, S, soil moisture content above field capacity, catchment width, W, and the terrestrial catchment area, A_c (Chen et al., 1982)

$$Q_B^\tau = \begin{cases} K_s \, S \, W \, (V_B' - \theta_{f,B})/A_c & \text{if} \quad \theta_{f,B} < V_B' \leq \theta_{s,B} \\ 0 & \text{if} \quad 0 < V_B' \leq \theta_{f,B} \end{cases} \tag{11}$$

Quickflow is formed from two fractions; (i) if the soil moisture exceeds the saturation value, the exceeding volume is assumed to enter the brooks directly, $Q_q^{(1)}$, and (ii) if the soil moisture exceeds the field capacity value, a fraction of the exceeding volume is discharged from the A-reservoir as lateral flow, $Q_q^{(2)}$. The total quickflow at time step τ is then the sum of these two,

$$Q_q^{(1)} = \begin{cases} V_A'' - \theta_{s,A} & \text{if} \quad V_A'' > \theta_{s,A} \\ 0 & \text{if} \quad V_A'' \leq \theta_{s,A} \end{cases} \tag{12a}$$

$$V_A''' = V_A'' - Q_q^{(1)} \tag{12b}$$

$$Q_q^{(2)} = \begin{cases} K_s S \, W \, (V_A''' - \theta_{f,A})/A_c & \text{if} \quad V_A''' > \theta_{f,A} \\ 0 & \text{if} \quad V_A''' \leq \theta_{f,A} \end{cases} \tag{12c}$$

$$Q_q^\tau = Q_q^{(1)} + Q_q^{(2)} \tag{13}$$

The volume of water retained in both reservoirs is then the balance between incoming and outgoing water volumes,

$$V_A^\tau = V_A^{\tau-1} + m^\tau - P_\tau^\tau - E^\tau - Q_p^\tau - Q_q^\tau \tag{14}$$

$$V_B^\tau = V_B^{\tau-1} - Q_B^\tau + Q_p^\tau \tag{15}$$

As a result, the hydrologic module simulates discharges from all reservoirs: snowpack and soil reservoirs A and B. The water from these three reservoirs mixes in the lake within the mixing volume before running out from the outlet.

3.3. Soil Chemistry Module

IIASA's soil acidification model is applied as a component of this model to compute the ion concentrations of the internal flows. Ideal mixing is assumed in the reservoirs and equilibrium is assumed to be reached according to computed H^+-concentration. The buffer mechanisms incorporated in the soil model are explained in detail elsewhere (Kauppi et al. 1985). In this paper only the basic principles of the soil model are described.

It is assumed that soils containing free carbonates (calcareous soils) always have a buffer rate high enough to neutralize any acid stress. In non-calcareous soils, however, neutralization depends on the intensity of silicate weathering (silicate buffer rate). As long as this buffer rate is larger than the acid stress there will be no change in the H^+-concentration of soil or in the quality of drainage. If acid stress exceeds the actual buffer rate of the silicates, the soil is shifted to cation exchange buffer range. Then the capacity of the cation exchange buffer system, BC_{CE}^τ, is depleted with the rate of acid stress, as^τ, minus the buffer rate of silicates, br_{St} (Eq.16). A non-linear relationship is assumed between the base saturation and the soil pH within the silicate, cation exchange and the upper aluminum buffer range, as long as $BC_{CE}^\tau \geq 0$, at pH from 5.6 to 4.0 (Eq.17).

$$BC_{CE}^\tau = BC_{CE}^{\tau-1} - (as^\tau - br_{St}) \tag{16}$$

$$-log_{10}[H^+]^\tau = 4.0 + 1.6 \, (BC_{CE}^\tau / CEC_{tot})^{3/4} \tag{17}$$

The shape of the pH - base saturation relationship has been adopted from results of an equilibrium model by Reuss (1983).

The assumption that water discharged from the soil is in equilibrium with a solid aluminum phase has been widely used to calculate the dissolved aluminum concentrations (see e.g. Christophersen et al. 1982). The same assumption may then be applied also to compute the buffering through dissolution of solid aluminum compounds. Gibbsite $(Al \, (OH)_3)$ is one mineral often assumed to control the equilibrium concentration of free aluminum ions and mononuclear hydroxy species in freshwaters. We assume the equilibrium with gibbsite to control buffering in soil after there is no buffer capacity left in the cation exchange buffer range, i.e. $BC_{CE}^\tau = 0$. As precipitation infiltrates into the soil and mixes with the soil solution, disequilibrium concentrations $[H^+]_s$ and $[Al^{3+}]_s$ are obtained,

$$[Al^{3+}]_s = V_f [Al^{3+}]^{\tau-1} / \left[V_f + m^\tau + P_\tau^\tau - E^\tau \right] \tag{18}$$

$$[H^+]_s = \left[V_f [H^+]^{\tau-1} + (as^\tau - br_{St}) \right] / \left[V_f + m^\tau + P_\tau^\tau - E^\tau \right] \tag{19}$$

where V_f is the volume of soil solution at field capacity and the infiltrating water volume is assumed to equal $P_r^T + m^T - E^T$. The soil solution volume is simply defined by

$$V_f = \theta_f z_A \tag{20}$$

The soil thickness of the A layer, z_A, is fixed to 50 cm and the volumetric water content value at field capacity, θ_f, is estimated separately for each soil type based on the grain size distribution in soil. Aluminum is dissolved or precipitated until the gibbsite equilibrium state is reached (Eq.26). This process involves a change from disequilibrium concentrations as defined in Eq.27

$$[Al^{3+}]_A^T / \left[[H^+]_A^T \right]^3 = K_{so} \tag{21}$$

$$3\left[[Al^{3+}]_s - [Al^{3+}]_A^T \right] = [H^+]_A^T - [H^+]_s \tag{22}$$

Combining Eqs.21 and 22 yields a third order equation which has a single real root

$$3K_{so}\left[[H^+]_A^T \right]^3 + [H^+]_A^T - 3[Al^{3+}]_s - [H^+]_s = 0 \tag{23}$$

The comparison between the rate of acid stress and the buffer rate takes place at each time step in both reservoirs before the chemical status of the soil solution is computed. The water entering the B-reservoir has the quality of the soil solution leaving the A-reservoir. Acid stress to the B-reservoir, as_B^T, is then

$$as_B^T = Q_p^T [H^+]_A^T \tag{31}$$

where $[H^+]_A^T$ is the H^+-concentration in the water leaving the A-reservoir.

Depending upon the acid stress there is either a net production of base cations or there is an exhaustion of cation exchange capacity. In case the deposition rate of H^+ is lower than the silicate buffer rate, the weathering first has to fill up the cation exchange complex and after that an excess supply of base cations occurs. The contribution of the soil reservoir to the alkalinity of the surface water is assumed to equal the amount of the excess base cations (Eq.30).

$$M_{HCO_3}^T = -(as^T - br_{Si})A_c \tag{30}$$

The monthly leaching of hydrogen ions is simulated on the basis of the simulated hydrogen ion concentrations and the simulated monthly discharges from both reservoirs. Additionally, part of deposition and impurities in the meltwater fall directly on the lake. This source of acidity is simply computed from acid stress and lake area. As a result, the chemistry module gives the quantity of acidity, M_H, and alkalinity, $M_{HCO_3}^T$, from all sources to the lake

$$M_H^T = Q_q^T [H^+]_A^T + Q_B^T [H^+]_B^T + as^{T} \cdot A_l \qquad (32)$$

3.4. Lake Module

The lake module computes the time pattern of water quality in the lake. The impact on aquatic life will be estimated on the basis of simple threshold pH-values and aluminum concentrations. These characteristics are most likely to indicate damage to fish populations and other aquatic organisms.

The change in lake water chemistry will be predicted by means of titration of the base content of the lake with strong acid originating from the atmosphere. The initial conditions — the preacidification water quality — has to be determined for a given lake. The water quality variable of great importance is alkalinity, which expresses the total buffering capacity of the lake water.

In preacidification conditions the only affecting process is assumed to be the weathering of carbonates or silicates. In case the soil contains free carbonate bearing minerals, the lake water can be assumed to be very high in alkalinity due to the high rate of carbonate weathering. For silicate rocks, Ulrich (1983) has defined weathering rates between 0.2-2.0 $keq\ ha^{-1} m^{-1} yr^{-1}$. The original bicarbonate concentration, $[HCO_3^-]_0$, of the lake water is computed by the available information on:

- the annual weathering rate of the mineral matter (br);
- the volume of soil through which the incoming water drains $(A_c \cdot (z_A + z_B))$;
- the mean annual runoff to which produced HCO_3^- is mixed $(P-E)$.

The following steady-state bicarbonate concentration in the outlet of the lake may then be calculated based on that information. The bicarbonate concentration obtained is used as the initial alkalinity for the model runs.

$$[HCO_3^-]_0 = A_c(z_A + z_B)br / (A_c + A_l)(P - E) \qquad (34)$$

In clearwater lakes the carbonate alkalinity can be assumed to be the only significant buffering agent, mainly with reaction (Eq.35). Reaction (Eq.36) can be neglected since the naturally sensitive surface waters contain only negligible concentrations of carbonate ions.

$$HCO_3^- + H^+ = H_2CO_3 = CO_{2_{(aq)}} + H_2O \qquad (35)$$

$$CO_3^{2-} + H^+ = HCO_3^- \qquad (36)$$
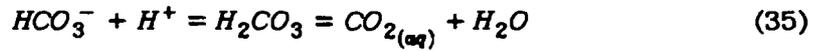
Reaction (Eq.35) yields an expression for the equilibrium (Eq.37), where $[H_2CO_3^*]$ represents the sum of $[CO_2]$ and $[H_2CO_3]$.

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3^*]} = K_1 \qquad (37)$$

Combining this with Henry's Law (Stumm and Morgan, 1981)

$$[H_2CO_3^*] = K_H \cdot p_{CO_2} \qquad (38)$$

one finally gets

$$[HCO_3^-] = \frac{K_1 \cdot K_H \cdot p_{CO_2}}{[H^+]} \qquad (39)$$

where K_1 and K_H are thermodynamic equilibrium constants, which depend on temperature.

When the drainage water, $Q_q^T + Q_B^T$, together with the direct water input as rain on the lake, Q_d^T, enter the lake and mix within the mixing layer, z_0, disequilibrium concentrations (Eqs.40 and 41) result,

$$[H^+]' = \frac{M_{H^+}^T + [H^+]^{T-1} \cdot z_0^T \cdot A_l}{Q_q^T + Q_B^T + Q_d^T + z_0^T \cdot A_l} \qquad (40)$$

$$[HCO_3^-]' = \frac{M_{HCO_3^-}^T + [HCO_3^-]^{T-1} \cdot z_0^T \cdot A_l}{Q_q^T + Q_B^T + Q_d^T + z_0^T \cdot A_l} \qquad (41)$$

During the snowmelt the mixing layer is assumed to be the topmost water layer. The meltwater is colder than most of the lake volume and therefore lighter than the $4°C$ water at the bottom. In this way the episodic spring time alkalinity and pH declines in the epilimnion can be estimated. The two water layers are then mixed together after there is no snow left in the catchment. During the summer, the incoming acidity is mixed with the whole lake water body.

The buffer reaction (Eq.35) continues until a new equilibrium state according to Eq.37 is accomplished. Equal amounts of hydrogen and bicarbonate ions are consumed

$$[H^+]^\tau - [H^+]' = [HCO_3^-]^\tau - [HCO_3^-]' \qquad (42)$$

The new equilibrium concentrations, $[H^+]^\tau$ and $[HCO_3^-]^\tau$, can be obtained by solving Eqs.39-41. A second order equation is obtained, from which the positive root for bicarbonate concentration is accepted. The equilibrium hydrogen ion concentration is then calculated from Eq.42

$$([HCO_3^-]^\tau)^2 + ([H^+]' - [HCO_3^-]')[HCO_3^-]^\tau - K_H \cdot K_1 \cdot p_{CO_2} = 0 \qquad (43)$$

Finally, the equilibrium total alkalinity is given based on the definition by Stumm and Morgan (1981),

$$[Alk] = [HCO_3^-]^\tau - [H^+]^\tau - [Al^{3+}]^\tau \qquad (44)$$

where the dissolved aluminum concentration is set proportional to the hydrogen ion concentration according to the gibbsite equilibrium in Eq.28.

4. MODEL TESTING

The complexity of environmental systems and the lack of comprehensive theoretical background make it difficult to test any conceptualization of a given system. In most applications of mathematical formulations describing physicochemical systems, the predictions are compared with measurements or samples of the system. In case the processes under study are very slow, it is practically impossible to test the conceptualization of the system by comparing the outcome with measurements. Long time series of, e.g., lake acidity measurements quite rarely exist.

Recently, a need has been recognized in several environmental management and planning programs to construct policy oriented computerized tools to be used in the decision making process. These formalized mathematical constructs usually have the best current knowledge incorporated in their structure. Such models, viewed as scientific theories, have to be testable in order to allow their use for management. A formal approach to theory testing, based on numerical simulation and Monte Carlo methods, has been proposed by Fedra (1983). His analysis allows conclusions to be drawn on the adequacy of both, the theory and the uncertain inputs, and provides some guidance on how to improve a certain conceptualization, even in the presence of a high degree of uncertainty (Fedra, 1983).

The first tests of the conceptualization of lake water acidification have been performed by simulating long term trends in freshwater acidity of a number of individual Finnish lakes (see Kämäri et al., 1985). In this model application, crude estimates for parameters and initial conditions were derived for 40 lakes in Southern Finland from a variety of sources including soil and geologic maps and the water quality data base of the Finnish National Board of Waters. The aim of the test runs was to evaluate whether the model could correctly distinguish between acidified lakes and lakes where no indications of acidification had been observed, when driven with an assumed historical deposition pattern (see Figure 6). The deposition pattern from 1960 to 1980 was obtained from the RAINS model, in which the upstream submodels, the energy-emissions submodel and the EMEP sulfur long-range transport submodel, supplied the input for the environmental impact submodels (see Alcamo et al., 1985). The other environmental driving variables, ambient air temperature and precipitation, were obtained from the thirty year climatic means presented in Müller (1982). Example model runs are shown for two lakes in this paper. Catchment characteristics as well as values for initial conditions and parameters used in the application are summarized in Table 2.

These first results suggested that the model was able to generate an allowable outcome. For example, a strongly decreasing lake pH was estimated for lake Orajärvi, a typical acidic lake with an observed summer pH below 5.0 (Figure 4). Moreover, a correct pH-level in 1980 was predicted for lake Venjärvi, which is a circumneutral lake in South-East Finland (Figure 5). Therefore, these model results were considered promising for further applications and as a next step Fedra's (1983) formal approach for model testing was utilized.

The logical structure of testing a proposed model (a theory), i.e. comparison of outcomes with observations, was retained but at the same time an appropriate way of describing uncertain inputs as well as somewhat uncertain expected outcome was included. Instead of giving the inputs and outputs as specific values, these two data points were extended to regions in their respective spaces. In the presence of uncertainty, one has to deal with a set of vectors instead of one vector in the n-dimensional input and output vector spaces (Fedra, 1983).

To test a specific model, it is examined whether, for a set of ranges of initial conditions and parameters, allowable outcomes can be produced. The model has to be rejected, if no allowable outcome can be generated from a statistically sufficient number of trials. If a simple model version fails to give an acceptable behavior over the allowable input ranges, it can be modified by adding more complex process descriptions to the model. In our case, however, we wish to keep the model as simple as possible in order to minimize the computational steps required. For the regional application, one objective is to retain the simplicity of the model to allow its interactive use,

The lake acidification model version described above was subjected to the testing procedure. The catchments studied in this application were the same as for the first model application to individual basins. The model was incorporated into a Monte Carlo framework, which randomly sampled a

Table 2.   Catchment characteristics, initial conditions and parameter values chosen for the two example catchments.

Lake Orajärvi		Lake Venjärvi	
A_l (m^{-2})	$= 2.2 \cdot 10^5$	A_l (m^{-2})	$= 4.3 \cdot 10^5$
A_c (m^{-2})	$= 5.6 \cdot 10^5$	A_c (m^{-2})	$= 3.3 \cdot 10^6$
z_A (m)	$= 0.50$	z_A (m)	$= 0.50$
z_B (m)	$= 0.98$	z_B (m)	$= 1.91$
z_0 (m)	$= 2.00$	z_0 (m)	$= 2.00$
z (m)	$= 3.93$	z (m)	$= 3.53$
W (m)	$= 2.2 \cdot 10^3$	W (m)	$= 4.4 \cdot 10^3$
S (m/m)	$= 0.06$	S (m/m)	$= 0.01$
$CEC_{tot,A}$ $(eq\ m^{-2})$	$= 61.05$	$CEC_{tot,A}$ $(eq\ m^{-2})$	$= 73.75$
$BC_{CE,A}$ $(eq\ m^{-2})$	$= 9.16$	$BC_{CE,A}$ $(eq\ m^{-2})$	$= 11.06$
$CEC_{tot,B}$ $(eq\ m^{-2})$	$= 119.0$	$CEC_{tot,B}$ $(eq\ m^{-2})$	$= 281.9$
$BC_{CE,B}$ $(eq\ m^{-2})$	$= 29.80$	$BC_{CE,B}$ $(eq\ m^{-2})$	$= 70.47$
br_{St} $(eq\ m^{-3} yr^{-1})$	$= 0.035$	br_{St} $(eq\ m^{-3} yr^{-1})$	$= 0.030$
θ_f	$= 0.33$	θ_f	$= 0.33$
θ_s	$= 0.45$	θ_s	$= 0.45$
p_{CO_2}	$= 10^{-2.8}$	p_{CO_2}	$= 10^{-2.8}$
T_r $(^o C)$	$= 2.0$	T_r $(^o C)$	$= 2.0$
T_s $(^o C)$	$= -1.0$	T_s $(^o C)$	$= -1.0$
ε $(m\ mo^{-1})$	$= 0.0039$	ε $(m\ mo^{-1})$	$= 0.0039$
β $(m\ ^o C^{-1} mo^{-1})$	$= 0.0213$	β $(m\ ^o C^{-1} mo^{-1})$	$= 0.0213$
K_s $(m\ mo^{-1})$	$= 25.50$	K_s $(m\ mo^{-1})$	$= 0.45$
K_{so}	$= 10^{8.5}$	K_{so}	$= 10^{8.5}$
K_1	$= 10^{-6.3}$	K_1	$= 10^{-6.3}$
K_H	$= 10^{-1.5}$	K_H	$= 10^{-1.5}$

parameter vector from the assigned allowable ranges (Table 3). The model was run with a constant deposition pattern through a period of ten years to allow the arbitrary initial values of the state variables to adjust. Next, a simulation of twenty years was performed assuming a historical deposition pattern shown in Figure 6 and all information about the run was stored. This process was repeated for a large number of trials (500 times for each lake). Finally, the set of runs obtained was analyzed for violations of the constraint conditions in the course of the simulations.

The uncertainty in the measurements and the representativeness of the sample for the whole season was considered when assigning the constraint ranges on the basis of observations. The generalized conditions compiled in Table 4 were formulated.
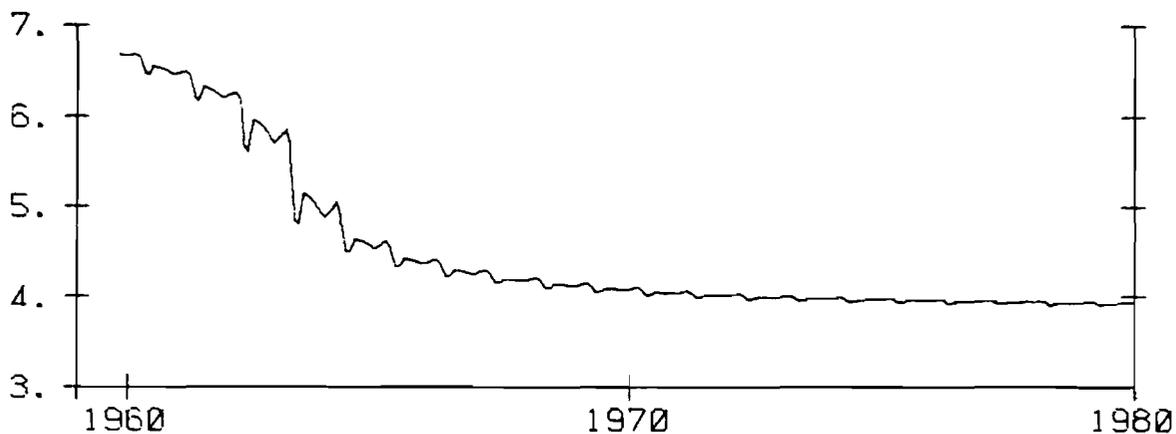
Figure 4. Simulation of the lake-pH of lake Orajärvi driven by the historical deposition pattern.

Figure 5. Simulation of the lake-pH of lake Venjärvi driven by the historical deposition pattern.

The model was expected to predict correctly the observed long term development of lake water acidification together with the observed seasonal variation of lake acidity. The reproduction of these two parts of the systems behavior was considered relevant to the regional application of the model. If the model structure could fulfill the formulated behavior definition, it can also be assumed to describe satisfactorily the development of pH- and alkalinity-distributions in different *lake regions* in Europe.

Table 3.   Assigned allowable input ranges for the two catchments studied.

Lake Orajärvi			Lake Venjärvi		
Parameter	Min.	Max.	Parameter	Min.	Max.
K_s $(m\ mo^{-1})$	2.548	254.8	K_s $(m\ mo^{-1})$	0.045	4.530
$z_A + z_B$ (m)	0.675	2.275	$z_A + z_B$ (m)	1.611	3.211
br_{St} $(eq\ m^{-3}yr^{-1})$	0.035	0.070	br_{St} $(eq\ m^{-3}yr^{-1})$	0.030	0.060
$BC_{CE,A} / CEC_{tot,A}$	0.10	0.20	$BC_{CE,A} / CEC_{tot,A}$	0.10	0.20
$BC_{CE,B} / CEC_{tot,B}$	0.25	0.60	$BC_{CE,B} / CEC_{tot,B}$	0.25	0.60
S (m/m)	0.030	0.090	S (m/m)	0.005	0.015
θ_f	0.23	0.42	θ_f	0.23	0.42
θ_s	0.32	0.59	θ_s	0.32	0.59
z_0 (m)	1.40	2.60	z_0 (m)	1.40	2.60
z (m)	2.75	5.11	z (m)	2.47	4.59

Figure 6.   Sulfur deposition scenarios assumed for the studied catchments; (a) high and (b) low deposition scenario.

Results of the Monte-Carlo runs indicated that the model could fulfill all of the assigned constraint conditions. For lake Venjärvi 18 runs out of 500 were found to pro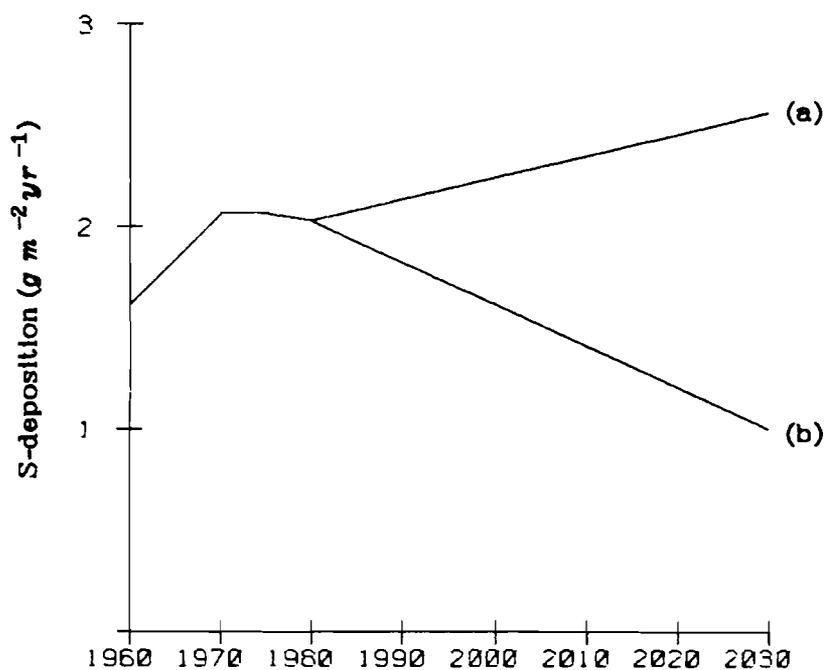duce an acceptable outcome. For lake Orajärvi only 5 runs out of 500 gave an acceptable behavior. The model seems to be able to

Table 4.   Constraint conditions for the two catchments studied.

Lake Orajärvi	Lake Venjärvi
[1] The mean summer pH in 1965 between 5.1 and 5.7	[1] The mean summer pH in 1965 between 6.4 and 7.0
[2] The mean summer pH in 1980 between 4.4 and 5.0	[2] The mean summer pH in 1980 between 6.3 and 6.9
[3] The mean spring pH in 1980 between 4.2 and 4.8	[3] The mean spring pH in 1980 between 5.8 and 6.4

generate the general trend in lake acidity, but many of the runs had to be rejected, because the model gave too low pH-values or the seasonal dynamics was not predicted accurately enough.

There are three possible explanations for getting so few sets of input values to match the observed water quality. The first and most appealing is, that the historical deposition pattern — given by the upstream models — is biased; i.e. the emission estimates for the period 1960 to 1980 maybe somewhat too high. The second reason could be the uncertainty in assigning input ranges, they may be too narrow and badly placed. On the other hand, the allowable ranges for input values should be constrained as much as possible in order to avoid unrealistic combinations of input values. The third explanation could be the model itself: the proposed model structure does not try to be a final description of the lake acidification phenomena. Some additional processes may have to be included in the course of a further development of the model. For example, there is recent evidence that the carbonate system is not the only buffering system operating in lakes against acidification. Schindler et al. (1985) have reported that a significant proportion of the acid neutralization in lakes in different parts of the world has been accounted for by auxiliary buffering (sulfate reduction, denitrification, etc.). Up to now the model has been kept simple; nevertheless it consists of numerous mathematical descriptions, each of them being a theory by itself. Their dynamic nonlinear interactions make it difficult to relate a failure in the overall performance of the model to any of the individual modules used.

The model could, thus, reproduce the required behavior, which is not to say that it is validated now. Rather, one could say that the model could not be falsified yet. Meanwhile one can use the model cautiously as a tool for scenario analysis, representing one interpretation of the current understanding of long term lake acidification. The constraint conditions had to be formulated so broad, that several possible conceptualizations of lake acidification necessarily exist, which are able to reproduce the allowable systems behavior. The differences may only arise when the models are applied for future projections (Fedra, 1983). We consider model validation a iterative process, which should also provide guidance on how to improve the model.

The set of inputs, which yielded accepted simulations, .i.e. model runs fulfilling the constraint conditions, can be used for future projections of the response of the catchments to different deposition scenarios. Two example scenarios were introduced using the IIASA RAINS model (Figure 6; see Alcamo et al., 1985). From 1960 to 1980 the scenarios assumed identical historical energy-emission trends. From 1980 on the scenarios departed so that the *high* deposition scenario assumed an increasing rate of energy use throughout Europe, as defined by the ECE *'trends continued'* scenario (ECE, 1983), linearly extrapolated to 2030. The *low* deposition scenario was constructed from the ECE *'conservation'* scenario, assuming lower rates of energy use and in addition to that, effective measures taken for the control of sulfur emissions.

The model can be used for any deposition scenario for producing a series of lake simulations with the accepted set of input values. The variability of the individual runs can be interpreted as the uncertainty in the model results due to the uncertainty in the input data. This means that some of the initial uncertainty is taken into account throughout the long term simulation. The model behavior is demonstrated in Figures 7 and 8, in which simulations are continued from 1980 on using only the 'accepted' input data. The constraints can be looked at as windows through which the future scenarios are forced to pass.

Results of the model runs of lake Venjärvi show a clear increase in time in the uncertainty of scenarios (Figure 7). However, the degree of uncertainty seems to depend on the type of scenario used as well as on the type of lake studied. Running lake Orajärvi with the high scenario the five accepted runs show very little variability, whereas with the low scenario there are clear differences in the rate of recovery (Figure 8). Nevertheless, the scenarios yield a mean summer-pH quite close to 6.0 in 2030. Fedra (1981) has concluded, that the prediction uncertainty (measured as the coefficient of variation of Monte Carlo outputs) increases with the prediction time as well as with the amount of change in the driving variables. The results from out preliminary analysis on scenario uncertainty suggest a similar pattern. The magnitude of uncertainty may, however, vary, depending on the model and the data used. Therefore, besides a more comprehensive uncertainty analysis, also a better understanding of the model structure is essential.
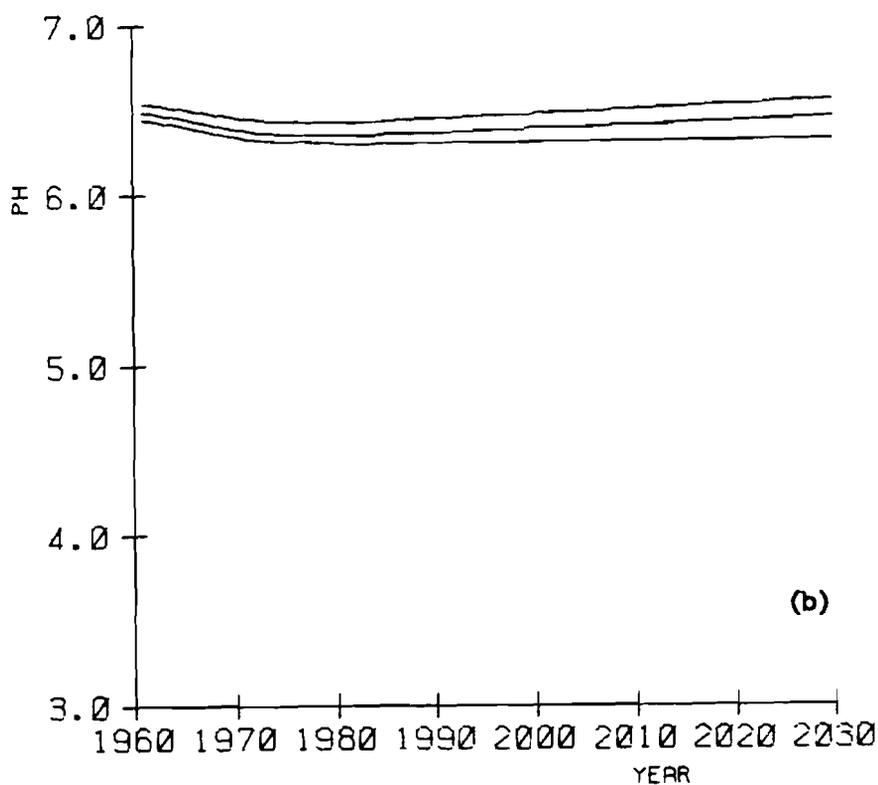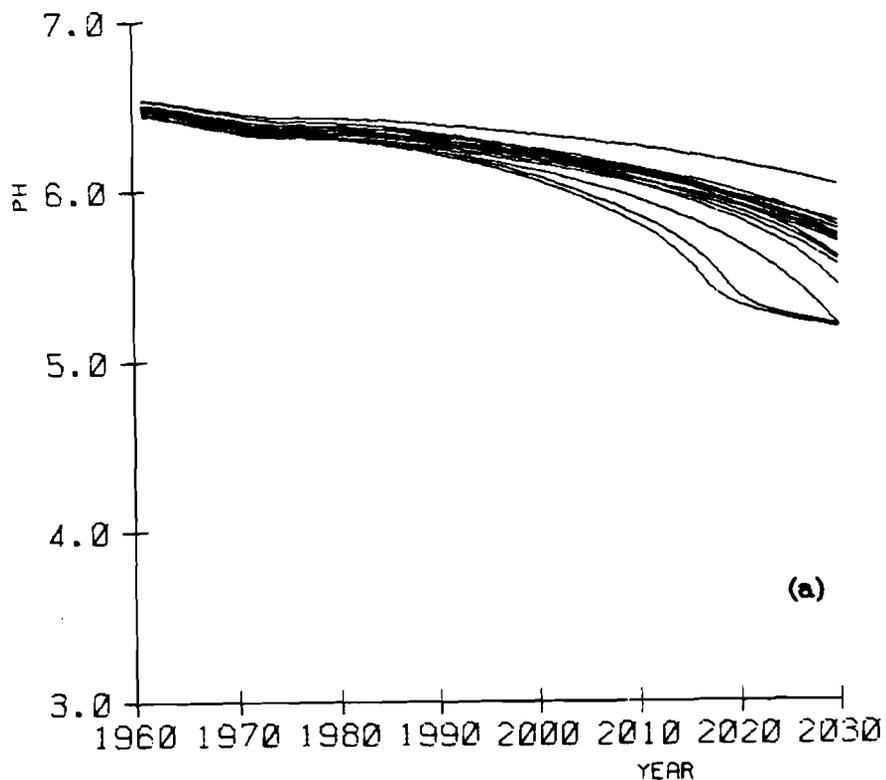
Figure 7.   Lake acidity scenarios for lake Venjärvi generated by using
the set of input data combinations, which fulfilled the con-
straint conditions (see Table 4). In (a) the high scenario was
used and all 35 runs are displayed; in (b), using the low
scenario, the mean and the minimum-maximum envelope is
displayed.
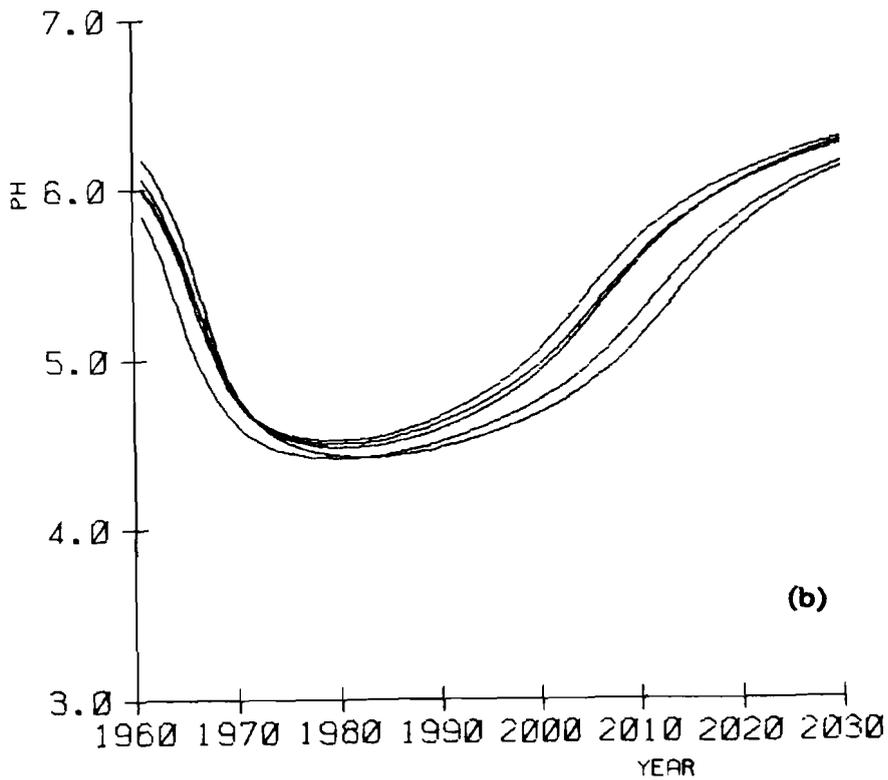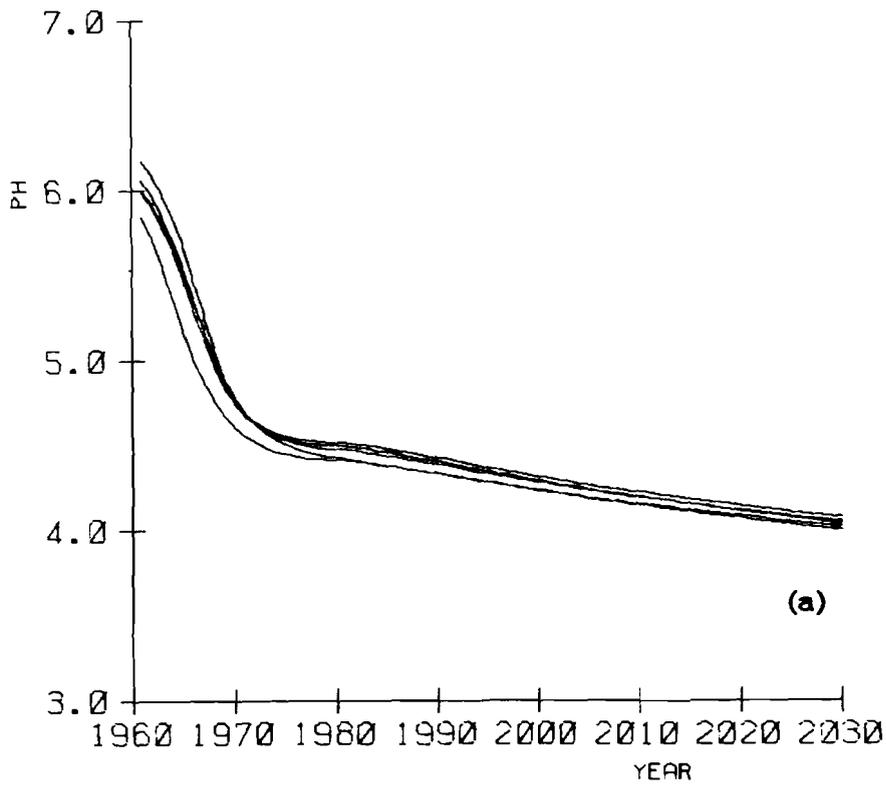
Figure 8.   Lake acidity scenarios for lake Orajärvi generated by using
the set of input data combinations, which fulfilled the con-
straint conditions (see Table 4). In (a) the high scenario and in
(b) the low scenario was used. All 5 runs are displayed.

LIST OF SYMBOLS

In this list of symbols the superscript τ — the time step index — is suppressed.

τ	time step index
β	melting rate coefficient for forested area
ε	evapotranspiration rate coefficient
θ_A	actual soil moisture content
θ_f	soil moisture content at field capacity
θ_s	soil moisture content at saturation
A_l	lake area
A_c	catchment area
as	acid stress rate
BC_{CE}	actual cation exchange capacity
br_{Si}	silicate buffer rate
CEC_{tot}	total cation exchange capacity
D_{tot}	total deposition
D_m	deposition released from the snowpack
D_s	deposition retained in the snowpack
DP	accumulated deposition
E	monthly evapotranspiration
E_a	mean annual evapotranspiration
K_1	first dissociation constant for carbonic acid
K_H	constant of Henry's law
K_s	hydraulic conductivity at saturation
K_{so}	gibbsite equilibrium constant
M_{H^+}	flow of hydrogen ions to the lake
$M_{HCO_3^-}$	flow of bicarbonate ions to the lake
m	melting rate of snow
P_a	mean annual precipitation
P_r	monthly rainfall
P_s	monthly snowfall
P_{tot}	total monthly precipitation
p_{CO_2}	partial pressure of CO_2 in lake water
Q_B	lateral flow from the B-layer

Q_d	precipitation onto the lake
Q_p	percolation flow from A-layer into B-layer
$Q_p^{(1)}$	maximum possible percolation rate
$Q_p^{(2)}$	water volume available in the A-layer
$Q_p^{(3)}$	space left in the B-reservoir
Q_q	quickflow from the catchment
$Q_q^{(1)}$	surface runoff
$Q_q^{(2)}$	lateral flow from the A-layer
S	surface slope
SP	snowpack
T	mean monthly temperature
T_r	threshold temperature above which all precipitation falls as rain
T_s	threshold temperature below which all precipitation falls as snow
V_f	soil water volume of field capacity
V_A	total water volume in A-layer
V_B	total water volume in B-layer
W	catchment width
z_A	thickness of A-layer
z_B	thickness of B-layer
z	mean depth of the lake
z_0	mixing layer of the lake
$z_{0,s}$	mixing layer of the lake in spring
$[Alk]$	equilibrium total alkalinity in lake water
$[HCO_3^-]_0$	initial alkalinity in lake water
$[H_2CO_3^*]$	sum of $[CO_2]$ and $[H_2CO_3]$
$[Al^{3+}]$	aluminum ion concentration
$[H^+]$	hydrogen ion concentration
$[HCO_3^-]$	bicarbonate ion concentration

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APPENDIX

In this Appendix a listing of the FORTRAN-77 code of the lake acidification model is presented. The model is programmed as a subroutine — called *watsim* — which enables its use for the simulation of an individual lake (one subroutine call) as well as its application in a Monte-Carlo framework (repeated calls with randomized input variables). *watsim* itself calls four different subroutines — *met, hydro, soil* and *lake* — which correspond to the four modules described in chapter 3.

```
1    c
2    c
3             subroutine  w a t s i m  (nyears,nvartp,rv,mxvar,
4          2                            bcca,cect,areal,areac,
5          3                            tempm,precm,sm,vpr,maxvar)
6    c
7    c
8    c       This subroutine simulates the acidification of a lake.
9    c
10   c       INPUT variables:
11   c
12   c       nyears ....... number of years to be simulated.
13   c       nvartp = 1 ... temperature and precipitation randomized.
14   c              = 0 ... temperature and precipitation NOT randomized.
15   c
16   c       The array 'rv' (mxvar=10 elements)
17   c          contains the following (randomized) variables:
18   c
19   c       rv(1) = thick ... mean soil thickness (m)
20   c       rv(2) = cond .... hydraulic conductivity (m per mo)
21   c       rv(3) = brsi .... Si-buffer rate (eq per m3 and mo)
22   c       rv(4) = bsata ... base saturation in A-layer (fraction)
23   c       rv(5) = bsatb ... base saturation in B-layer (fraction)
24   c       rv(6) = slope ... mean surface slope (m per m)
25   c       rv(7) = fcap .... soil moisture content at field capacity (fraction)
26   c       rv(8) = fsat .... soil moisture content at saturation (fraction)
27   c       rv(9) = z0 ...... depth of springtime mixing layer (m)
28   c       rv(10) = z ...... mean lake depth (m)
29   c
30   c       bcca .... Ca-buffer capacity (eq per m3)
31   c       cect .... total CEC (eq per m3)
32   c       areal ... lake area (m2)
33   c       areac ... catchment area (m2)
34   c       tempm(12) ... mean monthly temperature (degrees Celsius)
35   c       precm(12) ... monthly precipitation (m)
36   c       sm(12*(nyears+1)) ... monthly acid stress for years '0' thru 'nyears'
37   c                             (eq per m2 and mo)
38   c
39   c       OUTPUT variables:
40   c
41   c       The array 'vpr' (maxvar=18 elements) contains
42   c       the following output variables (for every time step):
43   c
44   c       vpr(1,.) = depth of snow cover (m)
45   c       vpr(2,.) = depth of water entering the soil (m)
46   c       vpr(3,.) = depth of water in A-layer (m)
47   c       vpr(4,.) = depth of water in B-layer (m)
48   c       vpr(5,.) = water discharged from A-layer (m)
49   c       vpr(6,.) = water discharged from B-layer (m)
50   c       vpr(7,.) = H+ concentration in A-layer (eq per m3)
51   c       vpr(8,.) = actual CEC in A-layer (eq per m2)
52   c       vpr(9,.) = H+ concentration in B-layer (eq per m3)
53   c       vpr(10,.) = actual CEC in B-layer (eq per m2)
54   c       vpr(11,.) = H+ concentration in the lake (eq per m3)
55   c       vpr(12,.) = total alkalinity in the lake (eq per m3)
56   c       vpr(13,.) = water volume entering the lake (m3)
57   c       vpr(14,.) = lake volume (m3)
58   c       vpr(15,.) = lake mixing volume (m3)
59   c       vpr(16,.) = protons discharged from A-layer (eq)
60   c       vpr(17,.) = protons discharged from B-layer (eq)
```

```
61   c       vpr(18,.) = protons entering the lake directly (eq)
62   c
63           logical            melt, melto
64           real               rv(mxvar)
65           real               tempm(12),  precm(12),  revapm(12)
66           real               rtempm(12),  rtmin(12),  rtmax(12)
67           real               rprecm(12),  rpmin(12),  rpmax(12)
68           real               sm(*),  vpr(maxvar,*)
69   c
70   c       spi = sqrt(pi)
71   c       eps = 0.0039 ... evapotranspiration coefficient (m per deg.C and mo)
72   c       calk ... 1st dissociation constant x Henry's law constant x
73   c                   partial CO2-pressure in water
74   c                   (10**-6.3 x 10**-1.5 x 10**-3.5 for eq/l)
75   c                   calk = calk*10**6 = 10**-5.3 = 5.01187235e-6 for eq/m3
76   c                   or
77   c                   empirical derived by Wright and Henriksen
78   c                   (Nature 305, pp.422-424, 1984)
79   c                   calk = 1.94984459e-5 for eq/m3
80   c       gibbs =10**8.5/10**6 ... gibbsite equilibrium constant for eq/m3
81   c       hporig = 10**-4 ... original H+ conc. in the soil (eq per m3)
82   c                       (corresponds to pH = 7!)
83   c       alorig = gibbs*(H+ at ph=4)**3
84   c           ... original Al3+ conc. in the soil (eq per m3)
85   c               alorig = 10**2.5*(10**-1)**3 = 0.316227766
86   c
87           data  spi /1.77245385/
88           data  eps /0.0039/
89           data  calk /1.94984459e-5/,  gibbs /3.1622776e+2/
90           data  hporig /1.e-4/,  alorig /0.316227766/
91   c
92   c       Compute additional variables:
93   c
94   c       area ..... terrestrial catchment area (m2)
95   c       width .... catchment width (m);
96   c                   assuming a circular lake centered in a circular catchment
97   c       dw0 ...... mean annual water level variation (m);
98   c                   empirical formula taken from
99   c                   E. Kuusisto, 'Conceptual Modelling of Inflow into Lake
100  c                   Suur-Saimaa from the Surrounding Watersheds' (in Finnish),
101  c                   Publ. of the Fin. Water Res. Inst. 26, Helsinki 1978
102  c       dw ....... actual water level variation (m);
103  c                   maximum: half of mean lake depth
104  c       zh ....... maximum water level (m)
105  c       zl ....... minimum water level (m)
106  c       thicka ... thickness of A-layer (m); maximum: 0.5 m
107  c       thickb ... thickness of B-layer (m); might be zero!
108  c       bccaa .... Ca-buffer capacity in A-layer (eq per m2)
109  c       brsia .... Si-buffer rate in A-layer (eq per m2 and mo)
110  c       cecta .... total CEC in A-layer (eq per m2)
111  c       bccea .... actual CEC in A-layer (eq per m2)
112  c       bccab .... Ca-buffer capacity in B-layer (eq per m2)
113  c       brsib .... Si-buffer rate in B-layer (eq per m2 and mo)
114  c       cectb .... total CEC in B-layer (eq per m2)
115  c       bcceb .... actual CEC in B-layer (eq per m2)
116  c       fcapa .... soil moisture content at field capacity in A-layer (m)
117  c       fcapb .... soil moisture content at field capacity in B-layer (m)
118  c       fsata .... soil moisture content at saturation in A-layer (m)
119  c       fsatb .... soil moisture content at saturation in B-layer (m)
120  c       beta = cond*width*slope/area (per mo)
```

```
121    c
122           area = areac-areal
123           width = spi*(sqrt(areac)+sqrt(areal))
124           dw0 = 4.69*(100.*areal/areac)**(-0.73)
125           dw = amin1(dw0,0.5*rv(10))
126           zh = rv(10)+0.5*dw
127           zl = zh-dw
128           thicka = amin1(rv(1),0.5)
129           thickb = amax1(rv(1)-0.5,0.)
130           bccaa = bcca*thicka
131           brsia = rv(3)*thicka
132           cecta = cect*thicka
133           bccea = rv(4)*cecta
134           bccab = bcca*thickb
135           brsib = rv(3)*thickb
136           cectb = cect*thickb
137           bcceb = rv(5)*cectb
138           fcapa = rv(7)*thicka
139           fcapb = rv(7)*thickb
140           fsata = rv(8)*thicka
141           fsatb = rv(8)*thickb
142           beta = rv(2)*width*rv(6)/area
143           if (beta .gt. 1.) beta = 1.
144    c
145    c      Initialize variables:
146    c
147    c      hpa ...... H+ conc. in A-layer (eq per m3)
148    c      alua ..... Al3+ conc. in A-layer (eq per m3)
149    c      hpb ...... H+ conc. in B-layer (eq per m3)
150    c      alub ..... Al3+ conc. in B-layer (eq per m3)
151    c      protb .... H+ concentration released from B-layer (eq per m2)
152    c      bicarb ... bicarbonate conc. released from B-layer (eq per m2)
153    c      voll ..... lake volume (m3)
154    c      vmix ..... lake mixing volume (m3)
155    c      vola ..... water depth in A-layer (m)
156    c      volb ..... water depth in B-layer (m)
157    c      snow ..... depth of snowpack at t-1 (m)
158    c      depack ... acid stress stored in the snowpack at t-1 (eq per m3)
159    c      melto = true .... snowmelt at t-1
160    c            = false ... NO snowmelt at t-1
161    c
162           hpa = hporig
163           alua = alorig
164           hpb = hporig
165           alub = alorig
166           protb = 0.
167           bicarb = 0.
168           voll = rv(10)*area!
169           vmix = voll
170           vola = fsata
171           volb = fsatb
172           snow = 0.
173           depack = 0.
174           melto = .false.
175    c
176           do 10 m = 1,12
177               rtempm(m) = tempm(m)
178               rprecm(m) = precm(m)
179    10     continue
180           if (nvartp .ne. 1)                    goto 30
```

```
181    c
182    c         Randomize first year's temperature and precipitation:
183    c
184              do 20 m = 1,12
185                  rtmin(m) = 0.8*tempm(m)
186                  rtmax(m) = 1.2*tempm(m)
187                  rtempm(m) =  v r a n d  (rtmin(m),rtmax(m),1)
188                  rpmin(m) = 0.8*precm(m)
189                  rpmax(m) = 1.2*precm(m)
190                  rprecm(m) =  v r a n d  (rpmin(m),rpmax(m),1)
191    20        continue
192    c
193    30        continue
194    c
195    c         rain ... mean annual runoff (m)
196    c         vout ... mean monthly lake outflow (m3 per mo)
197    c         alko ... original lake alkalinity (eq per m3)
198    c         hpo .... original H+ conc. in the lake (eq per m3)
199    c
200              rain = 0.
201              do 40 m = 1,12
202                  revapm(m) = 0.
203                  if (rtempm(m) .gt. 0.) revapm(m) = eps*rtempm(m)
204                  rain = rain+rprecm(m)-revapm(m)
205    40        continue
206              vout = areac*rain/12.
207              alko = 12.*rv(1)*rv(3)*area/(rain*areac)
208              hpo = calk/alko
209    c
210    c         ***** Start loop over years *****
211    c
212              iyr = -1
213    1000      continue
214              iyr = iyr+1
215              if (iyr .gt. nyears)                 goto 9999
216              iyr12 = 12*iyr
217    c
218    c         Randomize temperature and precipitation:
219    c
220              if (iyr .eq. 0 .or. nvartp .ne. 1) goto 1150
221              rain = 0.
222              do 1120 m = 1,12
223                  rtempm(m) =  v r a n d  (rtmin(m),rtmax(m),1)
224                  rprecm(m) =  v r a n d  (rpmin(m),rpmax(m),1)
225                  revapm(m) = 0.
226                  if (rtempm(m) .gt. 0.) revapm(m) = eps*rtempm(m)
227                  rain = rain+rprecm(m)-revapm(m)
228    1120      continue
229              vout = areac*rain/12.
230    1150      continue
231    c
232    c         ***** Loop over months *****
233    c
234    c         Actual simulation starts in October of year '0'!
235    c
236              do 2000 m = 1,12
237                  index = iyr12+m
238                  if (index .lt. 10)                 goto 2000
239    c
240    c         Meteorology:
```

```
241   c
242   c        wat ...... depth of water entering the soil (m)
243   c        stress ... H+ conc. entering the A-layer (eq per m3 and mo)
244   c        melt = true .... snowmelt at t
245   c             = false ... NO snowmelt at t
246   c
247              call  m e t  (rtempm(m),rprecm(m),sm(index),
248          2                   snow,depack,wat,stress,melt)
249   c
250   c        Hydrology:
251   c
252   c        qq ....... quickflow (out of A-layer) (m)
253   c        qb ....... lateral flow out of B-layer (m)
254   c        qp ....... percolation flow from A- to B-layer (m)
255   c
256              call  h y d r o  (wat,revapm(m),fcapa,fsata,
257          2                   fcapb,fsatb,rv(2),beta,thickb,
258          3                   vola,volb,qq,qb,qp)
259   c
260   c        Soil chemistry:
261   c
262   c        A-layer:
263   c
264   c        prota .... H+ concentration released from A-layer (eq per m2)
265   c        bicara ... bicarbonate conc. released from A-layer (eq per m2)
266   c
267              call  s o i l  (brsia,cecta,stress,rprecm(m),qq,fcapa,
268          2                   bccaa,bccea,hpa,alua,prota,bicara)
269   c
270   c        B-layer (if existent):
271   c
272   c        protb .... H+ concentration released from B-layer (eq per m2)
273   c        bicarb ... bicarbonate conc. released from B-layer (eq per m2)
274   c
275              if (thickb .gt. 0.) then
276                 stresb = qp*hpa
277                 call  s o i l  (brsib,cectb,stresb,qp,qb,fcapb,
278          2                      bccab,bcceb,hpb,alub,protb,bicarb)
279              endif
280   c
281   c        Lake chemistry:
282   c
283   c        In first month after snowmelt mix epilimnion
284   c        with rest of the lake volume (if there is one):
285   c
286   c        vol ...... water volume entering the lake (m3)
287   c        cprot .... amount of H+ entering the lake (eq)
288   c        cbicar ... amount of bicarbonate entering the lake (eq)
289   c        hpoo ..... H+ conc. from the last month without melting (eq/m3)
290   c        alkoo .... alkalinity from the last month without melting (eq/m3)
291   c
292              if (.not.melt .and. melto .and.
293          2       voll .gt. vmix .and. m .lt. 7) then
294                 vol0 = vmix
295                 vmix0 = voll-vmix
296                 cprot = hpn*vmix
297                 cbicar = alkn*vmix
298   c
299              call  l a k e  (vol0,vmix0,cprot,cbicar,
300          2                   hpoo,alkoo,hpo,alko)
```

```fortran
301            endif
302    c
303    c      Compute new lake and mixing volume:
304    c
305            vol = (qq+qb)*area+(wat-revapm(m))*area
306            voll = voll+vol-vout
307            if (voll .lt. zl*area) voll = zl*area
308            if (voll .gt. zh*area) voll = zh*area
309            vmix = voll
310            if (melt .and. zl .gt. rv(9) .and. m .lt. 7) vmix = rv(9)*area
311            cprot = (prota+protb)*area+stress*area
312            cbicar = (bicara+bicarb)*area
313    c
314            call  l a k e  (vol,vmix,cprot,cbicar,hpo,alko,hpn,alkn)
315    c
316            alko = alkn
317            hpo = hpn
318            if (melt .and. .not.melto .and. m .lt. 7) then
319               alkoo = alko
320               hpoo = hpo
321            endif
322            melto = melt
323    c
324    c      Store variables for output:
325    c
326            vpr(1,index) = snow
327            vpr(2,index) = wat
328            vpr(3,index) = vola
329            vpr(4,index) = volb
330            vpr(5,index) = qq
331            vpr(6,index) = qb
332            vpr(7,index) = hpa
333            vpr(8,index) = bccea
334            vpr(9,index) = hpb
335            vpr(10,index) = bcceb
336            vpr(11,index) = hpn
337            vpr(12,index) = alkn
338            vpr(13,index) = vol
339            vpr(14,index) = voll
340            vpr(15,index) = vmix
341            vpr(16,index) = prota*area
342            vpr(17,index) = protb*area
343            vpr(18,index) = stress*area
344    2000  continue
345                                              goto 1000
346    9999                                      return
347            end
```

```fortran
1     c
2     c
3               subroutine  m e t  (temp,prec,dep,snow,depack,wat,stress,melt)
4     c
5     c
6     c         This subroutine is the FORTRAN-version of the
7     c         'Meteorologic Module' of the IIASA Lake Acidification Model.
8     c
9     c         Input variables:
10    c
11    c         temp ... mean temperature (degrees Celsius)
12    c         prec ... precipitation (m)
13    c         dep .... acid stress (eq per m3 and mo)
14    c
15    c         Input & Output variables:
16    c
17    c         snow ..... depth of snowpack (m)
18    c         depack ... acid stress stored in the snowpack (eq per m3)
19    c
20    c         Output variables:
21    c
22    c         wat ...... depth of water entering the soil (m)
23    c         stress ... H+ conc. entering the A-layer (eq per m3 and mo)
24    c         melt = true .... snowmelt
25    c              = false ... NO snowmelt
26    c
27    c         logical           melt
28    c
29    c         ts = -1 ... threshold temperature (deg.C)
30    c         tr = +2 ... threshold temperature (deg.C)
31    c         rate = 0.0213 ... melting rate coefficient (m per deg.C and mo)
32    c
33              data  ts  /-1./,  tr  /2./,  rate  /0.0213/
34    c
35    c         Fractionation of precipitation into rain and snow:
36    c
37              if (temp .le. ts) wat = 0.
38              if (temp .gt. ts .and. temp .lt. tr) wat = prec*(temp-ts)/(tr-ts)
39              if (temp .ge. tr) wat = prec
40              ps = prec-wat
41    c
42    c         Snow accumulation and melting:
43    c
44              snow = snow+ps
45              melt = .false.
46              frac = 0.
47              if (temp .gt. ts .and. snow .gt. 0.) then
48                 melt = .true.
49                 rmt = amin1(rate*(temp-ts),snow)
50                 frac = amin1(2.*rmt/snow,1.)
51                 snow = snow-rmt
52                 wat = wat+rmt
53              endif
54    c
55    c         Acid stress accumulation and release:
56    c
57              ds = dep*ps/prec
58              depack = depack+ds
59              stress = dep-ds+frac*depack
60              depack = (1.-frac)*depack
```

```
61                                    return
62          end
```

```
1     c
2     c
3           subroutine  h y d r o   (wat,evap,fcapa,fsata,
4          2                 fcapb,fsatb,cond,beta,thickb,
5          3                 vola,volb,qq,qb,qp)
6     c
7     c
8     c     This subroutine is the FORTRAN-version of the
9     c     'Hydrologic Module' of the IIASA Lake Acidification Model.
10    c
11    c     Input variables:
12    c
13    c     wat ...... depth of water entering the soil (m)
14    c     evap ..... depth of water evapotranspirating (m)
15    c     fcapa .... soil moisture content at field capacity in A-layer (m)
16    c     fsata .... soil moisture content at saturation in A-layer (m)
17    c     fcapb .... soil moisture content at field capacity in B-layer (m)
18    c     fsatb .... soil moisture content at saturation in B-layer (m)
19    c     cond ..... hydraulic conductivity (m per mo)
20    c     beta = cond*width*slope/area (per mo)
21    c     thickb ... thickness of B-layer (m)
22    c
23    c     Input & Output variables:
24    c
25    c     vola .... water depth in A-layer (m)
26    c     volb .... water depth in B-layer (m)
27    c
28    c     Output variables:
29    c
30    c     qq ....... quickflow (out of A-layer) (m)
31    c     qb ....... lateral flow out of B-layer (m)
32    c     qp ....... percolation flow from A- to B-layer (m)
33    c
34          vola = vola+wat-evap
35          if (thickb .gt. 0.) then
36             qp = amin1(vola-fcapa,cond*(vola-fcapa)/(fsata-fcapa),
37         2            fsatb-volb)
38             if (qp .lt. 0.) qp = 0.
39             vola = vola-qp
40             volb = volb+qp
41             qb = amax1(beta*(volb-fcapb),0.)
42             volb = volb-qb
43          else
44             qp = 0.
45             qb = 0.
46          endif
47          qq1 = amax1(vola-fsata,0.)
48          vola = vola-qq1
49          qq2 = amax1(beta*(vola-fcapa),0.)
50          vola = vola-qq2
51          qq = qq1+qq2
52                                          return
53          end
```

```
   1   c
   2   c
   3           subroutine  s o i l  (brsi,cect,stress,prec,dis,fcap,
   4          2                      bcca,bcce,hplus,alu,prot,bicar)
   5   c
   6   c
   7   c       This subroutine is the FORTRAN-version of the
   8   c       IIASA Soil Acidification Model.
   9   c
  10   c       Input variables:
  11   c
  12   c       brsi ..... Si-buffer rate (eq per m2 and mo)
  13   c       cect ..... total CEC (eq per m2)
  14   c       stress ... monthly acid stress (eq per m2 and mo)
  15   c       prec ..... monthly precipitation (m)
  16   c       fcap ..... soil moisture content at field capacity (m)
  17   c       dis ...... water discharged from soil (m)
  18   c
  19   c       Input & Output variables:
  20   c
  21   c       bcca ..... Ca-buffer capacity (eq per m2)
  22   c       bcce ..... actual CEC (eq per m2)
  23   c       hplus .... H+ concentration (eq per m3)
  24   c       alu ...... Al3+ concentration (eq per m3)
  25   c
  26   c       Output variables:
  27   c
  28   c       prot ..... H+ concentration released from soil (eq per m2)
  29   c       bicar .... bicarbonate conc. released from soil (eq per m2)
  30   c
  31   c       3-log10(hca) = 6.2;  hca in eq/m3 = meq/l
  32   c       gibbs =10**8.5/10**6 ... gibbsite equilibrium constant for eq/m3
  33   c       ppp = p**3, where p = 1./(9.*gibbs)
  34   c       third = 1/3
  35   c
  36           data  hca /0.000631/
  37           data  gibbs /3.1622776e+2/,  ppp /4.3378298e-11/
  38           data  third /0.3333333/
  39   c
  40   c       Carbonate-range:
  41   c
  42           if (bcca .le. 0.)                    goto 20
  43           bcca = amax1(bcca-stress,0.)
  44           hplusn = hca
  45                                               goto 90
  46   20      continue
  47   c
  48   c       Silicate- and Cation-Exchange-range:
  49   c
  50           stresx = stress-brsi
  51           if (hplus .ge. 0.1)                 goto 30
  52           bcce = amax1(amin1(bcce-stresx,cect),0.)
  53           hplus = 10.**(-1.-1.6*(bcce/cect)**0.75)
  54                                               goto 90
  55   30      continue
  56   c
  57   c       Aluminum-range:
  58   c
  59           strexx = amax1(stresx,0.)
  60   c
```

```fortran
61    c       Disequilibrium concentrations:
62    c
63            hpluss = (fcap*hplus+strexx)/(fcap+prec)
64            alus = fcap*alu/(fcap+prec)
65    c
66    c       Equilibrium concentrations:
67    c
68            c = hpluss+3.*als
69            q = -c/(6.*gibbs)
70            diss = sqrt(q*q+ppp)
71            hplus = (-q+diss)**third-(q+diss)**third
72            alu = third*(c-hplus)
73            if (hplus .lt. 0.1) then
74               if (strexx .gt. 0.) hplus = 0.1
75               if (strexx .le. 0.) hplus = 0.101
76            endif
77    90      continue
78    c
79    c       Compute release of protons and bicarbonate (per m2):
80    c
81            prot = dis*hplus
82            bicar = amax1(brsi-stress,0.)
83                                             return
84            end
```

```
1    c
2    c
3            subroutine  l a k e  (vol,vmix,cprot,cbicar,hpluso,alko,
4          2                 hplusn,alkn)
5    c
6    c
7    c       This subroutine is the FORTRAN-version of the
8    c       'Lake Module' of the IIASA Lake Acidification Model.
9    c
10   c       Input variables:
11   c
12   c       vol ...... water volume entering the lake (m3)
13   c       vmix ..... lake mixing volume (m3)
14   c       cprot .... amount of H+ entering the lake (eq)
15   c       cbicar ... amount of bicarbonate entering the lake (eq)
16   c       hpluso ... H+ concentration at t-1 (eq/m3)
17   c       alko ..... alkalinity at t-1 (eq/m3)
18   c
19   c       Output variables:
20   c
21   c       hplusn ... H+ concentration at t (eq/m3)
22   c       alkn ..... alkalinity at t (eq/m3)
23   c
24   c       calk ... 1st dissociation constant x Henry's law constant x
25   c                partial CO2-pressure in water
26   c                (10**-6.3 x 10**-1.5 x 10**-3.5 for eq/l)
27   c                calk = calk*10**6 = 10**-5.3 = 5.01187235e-6 for eq/m3
28   c                or
29   c                empirical derived by Wright and Henriksen
30   c                (Nature 305, pp.422-424, 1984)
31   c                calk = 1.94984459e-5 for eq/m3
32   c
33           data  calk /1.94984459e-5/
34   c
35           dd = 0.5*(cbicar-cprot+vmix*(alko-hpluso))/(vol+vmix)
36           alkn = dd+sqrt(dd*dd+calk)
37           hplusn = calk/alkn
38                                        return
39           end
```