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METHODS FOR PREDICTING FRESHWATER ACIDIFICATION

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PREFACE

Scientists are becoming increasingly aware that air pollution is creating significant changes in the quality of freshwaters. An important example is the established connection between the deposition of air pollutants and acidification of freshwater lakes in Nordic countries and parts of North America.

Scientists have responded to the need for greater understanding of the problem by developing mathematical models which describe the relationship between air pollution and acidification of lakes and streams. This paper reviews these mathematical approaches and will serve as a basis for developing IIASA's own strategy for linking air pollutant emissions with damage to aquatic ecosystems.

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METHODS FOR PREDICTING FRESHWATER ACIDIFICATION

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1. INTRODUCTION

The Extensive OECD research studies have indicated that levels of atmospheric sulphur compounds over large areas of Europe greatly exceed natural levels (OECD, 1979). IIASA's Acid Rain Project has the general objective of assisting in selecting emission policies which would be effective in decreasing harmful impacts of air pollution and yet remain economically feasible. With this end in view, efforts have been made at IIASA to build a model system for analyzing different aspects of transboundary air pollution in Europe. The results of the model system will provide the input data for a cost-benefit analysis and related policy tools.

The main objective of IIASA's impact submodels is to estimate the damage corresponding to different deposition patterns produced by the

energy and transport submodels. IIASA's work so far has concentrated on the emission transport and on the impact of acid deposition on terrestrial ecosystems. The next step in completing the model system is to quantify lake impact in terms of change in lake pH level. This factor is most likely to indicate damage to aquatic life.

The objective of this paper is to form a basis for IIASA's future efforts to develop a European-scale long time horizon simulation model of freshwater acidification. This paper reviews several approaches for estimating the quantity and/or the geographic extent of the impact of acid precipitation on aquatic resources.

2. SENSITIVITY TO ACIDIFICATION

2.1. Sensitivity Classification based on Water Quality Data

General patterns of surface water sensitivity to acidification have been identified on the basis of alkalinity. Total alkalinity can be used as an index of sensitivity because it reflects the acid neutralizing capacity of water bodies and thus their relative sensitivity to acid inputs.

Although there is general agreement that total alkalinity expresses acid sensitivity of surface water, there are differences of opinion as to exactly where the breaking points exist between sensitive and insensitive waters.

A map illustrating the regional patterns of mean annual alkalinity of surface waters has been prepared for the United States (Omernik and Powers, 1982). This approach affords a qualitative graphic overview of the sensitivity of surface waters to acidification on a regional scale.

It is important to form an understanding of relative sensitivity of surface waters in different regions in order to (1) provide a national perspective on the extent of the problem, (2) provide logic and/or rationale for selecting geographic areas for more detailed studies, and (3) allow more accurate regional economic assessment of acid precipitation impact on aquatic ecosystems (Omernik and Powers, 1982).

2.2. Sensitivity of Regions

Efforts to identify areas where soils and fresh waters might be sensitive to acidification have proceeded from the analyses of large-scale geological maps, mainly in North America. The ranking of sensitivity is not intended to predict severity of the effects but to guide the selection of terrestrial and aquatic sites which have the greatest potential for adverse consequences of long-term atmospheric deposition is greatest. A closer investigation of the surrounding geology should make it possible to predict the occurrence of lakes with particular buffering properties and therefore with particular sensitivity to acidification without having to sample every lake in the area.

The buffering properties of geological formations have a quantitative (capacity) and a qualitative (intensity) aspect. The buffering capacity can be defined as the equivalent sum of bases which can be titrated by addition of a strong acid during infinite time. The intensity can be expressed as the rate of the buffer reaction (cf. Ulrich, 1983). Buffer ranges, defined by pH-values, have been distinguished according to buffer reactions occurring in soils (Ulrich et al, 1979): (1) Carbonate buffer range (pH > 8.0 - 6.2), (2) Silicate buffer range (pH 6.2 - 5.0), (3)

Cation exchange buffer range (pH 5.0 - 4.2), (4) Aluminum buffer range (pH 4.2 - 2.8), (5) Iron buffer range (pH 3.8 - 2.4).

The chemical composition of the rock formations has been shown to match the actual sensitivity of sampled lakes to acidification in North America by Hendrey et al., (1980a). In their survey, over 80% of low alkalinity sites ($\leq 200\ \mu$ eq/l) were located in the sensitive areas defined by the sensitivity map. The characteristics of the bedrock are therefore considered largely to determine the impact of acid precipitation on aquatic ecosystems (Norton, 1979; Zimmerman, 1982).

Rock formations have been classified according to their potential acid-neutralizing property (Norton, 1979; Hendrey et al., 1980a, b) (Table 1).

Table 1: Rock types used to distinguish geological sensitivity (Norton 1979; Hendrey *et al.* 1980 a,b)

Type 1.	Low to no buffering intensity, Granite/syenite, granitic gneisses, quartz sandstones, or metamorphic equivalents.
Type 2.	Medium/low buffering intensity. Sandstones, shales, conglomerates, high-grade metamorphic felsite to intermediate igneous rocks, calcsilicate gneisses (no free carbonates).
Type 3.	Medium/high buffering intensity. Slightly calcareous, lowgrade, intermediate to mafic volcanic, ultra mafic and glassy volcanic rocks.
Type 4.	High buffering intensity. Highly fossiliferous sediments or metamorphic equivalents. Limestones or dolostones.

The most effective minerals for neutralizing acidic waters are carbonate minerals (e.g. calcite). The solution of this mineral at low and intermediate pH is given by:

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3 \quad (1)$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \quad (2)$$

These reactions are rapid and the dissolution rate of minerals containing free carbonate is never exceeded by the deposition rate of H^+–ions (Ulrich, 1983).

The factors controlling the chemical weathering of silicate minerals are the concentration of dissolved carbon dioxide and the activity of hydrogen ions (Feth et al., 1964):

$$2KAlSi_3O_8 + 2CO_2 + 3H_2O = Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 2K^+ + 4SiO_2 \quad (3)$$

$$KAlSi_3O_8 + 4H^+ + 4H_2O = K^+ + Al^{3+} + 3H_4SiO_4 \quad (4)$$

In reality these reactions are not straightforward processes but have passed through several stages. Reaction (4) occurring at pH under 5.0 consumes H^+ ions but does not contribute HCO_3^- for buffering. Bicarbonate produced in reaction (3) reacts with hydrogen ions and buffers the drainage.

$$HCO_3^- + H^+ = H_2O + CO_2 \quad (5)$$

Lithology can thus be an important predictive index for the sensitivity of lakes to acidification, although the mineralogy of the surficial deposits often differs from that of the bedrock. However, the actual sensitivity of fresh waters to acidification cannot be determined without considering the hydrologic characteristics, vegetation, and deposition rate, as well as the type and thickness of soil of the watershed.

Sensitivities of soil regions to acidification have been charted according to the cation exchange capacity (CEC) or the total amount of exchangeable cations in soil (Klopatek et al., 1980; McFee, 1980).

2.3. Sensitivity of Individual Watersheds

The scale of variability of rock types is such that in order to gain predictive value for individual lakes, one must look at the geology on a drainage basin basis. This approach was applied in Finland, where data of 375 small, oligotrophic, clear water lakes were analyzed and the sensitivity to acidification of watersheds was estimated (Kämäri, 1983). Stepwise multiple regression analysis was used to show the relative importance of watershed factors (independent variables) in explaining the variability in the water quality data (alkalinity, dependent variable).

The bedrock of Finland consists of granitic or highly siliceous prequaternary rock formations. The relative buffering rates of these silicate rocks (Table 2) were classified according to the average Ca+Mg–content of each rock type. The actual buffering rate (BR) values were estimated on the basis of Ulrich et al. (1979). Soil classes were determined accord-

ing to the texture and type of the soil. The value for the soil and rock variables was given by the percentage of the land area of drainage basins lying on each soil and rock class.

Table 2. Watershed factors as independent variables used to distinguish the sensitivity of lakes to acidification

ROCK 1		Quartzite
		Granites
	$CaO + MgO = 0 - 2$ % (wt)	Quartz-feldspar-gneisses
	$BR < 0.5$ keq ha^{-1} yr^{-1}	Quartz sandstones
ROCK 2		Granite gneisses
		Grano-diorites
	$CaO + MgO = 2 - 7$ % (wt)	Quartz diorites
	$BR = 0.5 - 1.0$ keq ha^{-1} yr^{-1}	Rapakivi granites
		Mica schists
		Phyllites
ROCK 3		Diorites
		Tuffites
	$CaO + MgO = 7\text{-}12$ % (wt)	Horblende gneisses
	$BR = 1.0 - 1.5$ keq ha^{-1} yr^{-1}	Plagioklase porfyrites
ROCK 4		Amfibolites
		Gabbros
	$CaO + MgO > 12$ % (wt)	Peridotite
	$BR = 1.5 - 2.0$ keq ha^{-1} yr^{-1}	Anorthosite
		Serpentinite
SOIL 1		Moraine
SOIL 2		Gravel, sand
SOIL 3		clay, silt
SOIL 4		Barren bedrock
SOIL 5		Peat
AL		Lake area (ha)
AW		Land area of drainage basin (ha)
ELEV		Elevation (m) above sealevel

The watershed factors explained approximately 60% of the variance in the observed values of alkalinity. In southern Finland, the bedrock was not significant in determining the sensitivity of small oligotrophic lakes to acidification. However, in the reference area - northern Finland - where the deposition rate is much lower, the weathering rate of silicate

rocks plays a major role. The amount of easily weathered rock types (ROCK 4) in the catchment largely determines the alkalinity of lake water.

In southern Finland the rate of H^+ load exceeds the silicate buffering rate. The buffer system has switched over to the next buffer range following at lower pH - the cation exchange. The rate of H^+ ion load to cation exchange system in silicate soils can be defined as the difference between the deposition rate and the weathering rate of silicate material. The buffer rate of the cation exchange complex is high. The limiting factor for the neutralization of acid inputs is the buffer capacity of this buffer system. It is therefore the capacity of the cation exchange buffer range that determines the sensitivity of the drainage basins to acidification in southern Finland.

The capacity of the cation exchange buffer system - the cation exchange capacity (CEC) - is dependent on the amount of fine-textured material (clays, organics) in the soil. This was reflected in the water quality of small, oligotrophic lakes in southern Finland. The most critical independent variable for the sensitivity of lakes to acidification was the percentage of barren bedrock in the drainage area (SOIL 4). In these areas the soil was thin or there was no soil on the bedrock. Thus the total cation exchange capacity of these soils was negligible and the watersheds could not neutralize the acidic drainage. The lakes with the highest pH - values in southern Finland were found to lie on soils formed entirely of fine-textured parent material; clay and silt.

3. ACIDIFICATION MODELS

3.1. Mobile Anion Concept

Sulfate is a mobile conservative anion - it shows nearly an input-output balance in catchments, if periods of several years are considered. The importance of sulfate anions for the transport of cations through the soil, the mobile anion concept, has been discussed widely with regard to acidification of soils and waters. (e.g.Johnson & Cole, 1977; Seip, 1980).

3.1.1. Birkenes Model

The model for sulfate chemistry in streamwater (Christophersen and Wright, 1981) forms the basis for the model for cation chemistry in streamwater (Christophersen et al., 1982). The objective of the model is to account quantitatively for some characteristics of streamwater chemistry by including only a small number of physically realistic processes.

MODEL FOR SULFATE CONCENTRATIONS

Birkenes sulfate model uses a mathematical approach to simulate the processes involving accumulation and release of sulfate in soil. The model is based on a hydrologic two-reservoir model that was developed by Lundqvist (1976) for natural catchments with the intention of applying it to water quality simulations (Figure 1).

The hydrologic submodel tells when the flow from a given part of the soil dominates the runoff, and in such periods the chemistry of this reservoir becomes observable. Basically, the upper reservoir supplies quick flow, and can be thought of as water mainly in contact with the

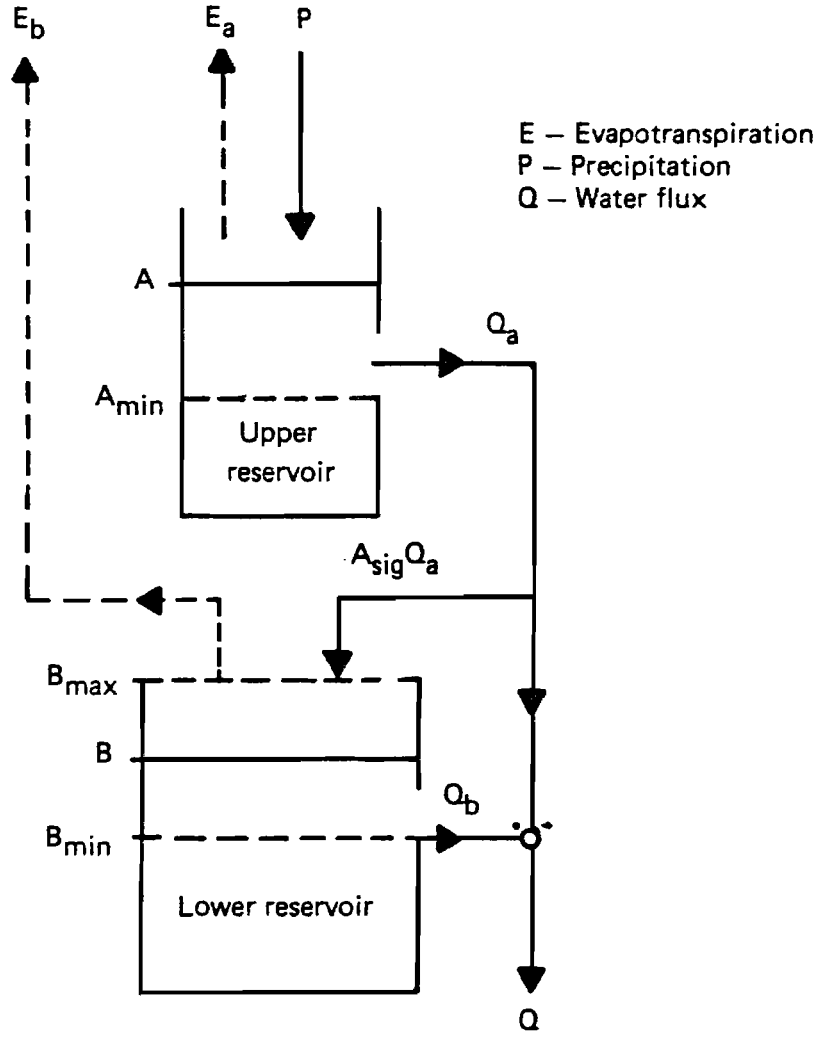

Figure 1. Hydrologic submodel of the Birkenes model (from Christophersen and Wright 1981; Christophersen et al. 1982)

upper soil horizons. The lower reservoir provides the base flow. The parameter values are determined by hydrogramme analyses and by trial and error. Data inputs to the model are daily precipitation volume and daily mean temperature. Runoff for a given summer half-year is then simulated (Christophersen, 1983; Christophersen and Wright, 1981; Christophersen et al., 1982).

In addition to the physical processes involved in the hydrologic submodel, chemical processes are added, involving sulfate (Christophersen and Wright, 1981). Processes such as biological activity and mineralization of sulphur compounds are not considered quantitatively but are included indirectly in the model, as an input-output budget.

It is proposed that all sulfate of atmospheric origin accumulating in the upper zone remains water-soluble. The concentration in upper reservoir $C_a(mgl^{-1})$ is a function only of the total amount of sulfate on the solid phase, $F_a(mgm^{-2})$. Direct proportionality is assumed:

$$C_a = F_a K_a = (F_a' - AC_a)K_a \tag{6}$$

implying

$$C_a = (F_a' K_a)/(1 + A\,K_a) \tag{7}$$

K_a = proportionality constant (m^2l^{-1})
A = total amount of water in upper reservoir (mm)
F_a' = amount of water soluble SO_4 in solution and on the solid phase (mgm^{-2})

The proportionality constant represents a linear equilibrium sulfate adsorption. The mass balance equation for the upper reservoir is then:

$$\frac{dF_a}{dt} = PC_i + D_r - Q_a C_a \qquad (8)$$

P = daily precipitation (mmd^{-1})

C_i = sulfate concentration in precipitation (mgl^{-1})

D_r = daily dry deposition ($mgm^{-2}d^{-1}$)

Q_a = runoff from the upper reservoir (mmd^{-1})

C_a = sulfate concentration in the upper reservoir (mgl^{-1})

In the lower reservoir, adsorption or desorption is the only process assumed to occur involving sulfate. The amount of sulfate in solution $S_b(mgm^{-2})$ is determined by inputs from the upper reservoir and outputs with the runoff Q_b together with changes in the amount of sulfate on the solid phase $F_b(mgm^{-2})$:

$$\frac{dS_b}{dt} = C_a (Q_a A_{sig} - Q_{over}) - Q_b C_b - \frac{dF_b}{dt} \qquad (9)$$

S_b = amount of SO_4 in solution (mgm^{-2})

A_{sig} = routing parameter (Figure 1)

Q_{over} = overflow (mmd^{-1})

Q_b = runoff from the lower reservoir (mmd^{-1})

C_b = concentration of SO_4 in runoff (mgl^{-1})

F_b = amount of SO_4 in solid phase (mgm^{-2})

In the absence of inputs the concentration of sulfate is assumed to reach a fixed equilibrium value. Evaporation is assumed to cause transfer of sulfate into solid phase, so that unrealistically high concentrations will not be simulated during very dry periods:

$$\frac{dF_b}{dt} = k_b B(C_k - C_{eg}) + E_b C_b \qquad (10)$$

k_b = adsorption rate constant (d^{-1})
C_{eg} = equilibrium concentration (mg l^{-1})
E_b = evapotranspiration (mmd^{-1})
B = the amount of water in the lower reservoir(mm).

MODEL FOR STREAMWATER CHEMISTRY

The task of modeling streamwater chemistry has been approached by making several simplifying assumptions (Christophersen et al., 1982). The anion Cl^- is assumed to be accompanied by the cation Na^+ and essentially to follow water through the catchment. These ions have thus only a minor influence on the concentrations of the other ions in streamwater, and they are henceforth ignored. The ions K^+, NH_4^+, NO_3^-, HCO_3^-, and organic anions can be ignored because they generally account for no more than a few percent of the ionic sum of the streamwater.

The cations Ca^{2+} and Mg^{2+} behave similarly in many respects. Therefore in the model Ca^{2+} and Mg^{2+} are merged together into a new parameter, M^{2+}, which represents the sum of those two divalent cations. Thus only positively charged species H^+, M^{2+}, and Al^{3+} are left with the anion SO_4^{2-}. The concentration of sulfate is assumed to balance the charge of

the sum of cation concentrations:

$$[H^+] + 2[M^{2+}] + 3[Al^{3+}] = 2[SO_4^{2-}] \qquad (11)$$

Gibbsite ($Al(OH)_3$) is assumed largely to control the equilibrium concentration of aluminium ion (Al^{3+}) and mononuclear hydroxy species in freshwaters. The solubilities of different types of gibbsite have great variability. Therefore only concentrations of Al^{3+} computed from gibbsite solubility, have been included in Christophersen's model :

$$[Al^{3+}] + [H^+] = {}^*K_{so}, \qquad K_{so} = 10^{8.1} \qquad (12)$$

For the upper reservoir Christophersen et al., (1982) assumed the relationship between H^+ and M^{2+} concentrations to be controlled by ion exchange. The Gapon equation has been used:

$$\frac{[H^+]}{[M^{2+}]^{1/2}} = k\,\frac{H_a^+}{M_a^{2+}} = Kg \qquad (13)$$

H_a^+ and M_a^{2+} = amounts adsorbed on the exchange complex
k = selectivity coefficient
Kg = $10^{-2.2}$

During periods with little or no rain, the upper reservoir 'dries up' due to evapotranspiration. The drying effect has been included in the model by assuming that a pool of water soluble M^{2+} is incremented by a fixed amount for every day the upper reservoir is dry. The initial value

for H^+ concentration in the upper reservoir is derived from equations (11), (12) and (13):

$$3K_{so}[H^+]^3 + \frac{2[H^+]^2}{Kg} + [H^+] = 2[SO_4^{2-}] \qquad (14)$$

The final H^+ concentration after correcting the value for drying effect is computed from:

$$3K_{so}[H^+]^3 + [H^+] = 2[SO_4^{2-}] - 2[M^{2+}]^* \qquad (15)$$

$[M^{2+}]^*$ = corrected M^{2+} – concentration
$[SO_4^{2-}]$ = sulfate concentration supplied by the sulfate submodel

The solution of this equation $[H^+]^*$, is then used to compute aluminum ion concentration in the upper reservoir:

$$[Al^{3+}]^* = {}^*K_{so}([H^+]^*)^3 \qquad (16)$$

For the lower reservoir, processes considered are (Christophersen et al., 1982): (1) Inputs of ions from the upper reservoir, (2) ideal mixing and output of ions through runoff, (3) evapotranspiration which causes adsorption of cations and sulfate, but leaves the concentrations unchanged, (4) adsorption/desorption of cations in proportion to exponential sulfate adsorption/desorption, (5) weathering, and (6) equilibrium with gibbsite. Differential equations are needed to compute the

unknowns $[H^+]$, $[M^{2+}]$ and $[Al^{3+}]$.

PREDICTING WITH BIRKENES MODEL

The model of Christophersen and Wright (1981) and Christophersen et al., (1982) can be used to treat possible long-term trends in streamwater composition even though the models were not constructed for this purpose (Christophersen, 1983). The models were designed for quantifying the effect of different processes on freshwater quality. The two major aspects that have to be considered in the long horizon projections are the anthropogenic emissions of sulphur and the base saturation of the cation exchange buffer range in the soil.

Christophersen (1983) did not quantify the response of the base saturation to acid deposition; the model was simply run with four different hypothetical situations (Table 3). The composition and runoff volume from each reservoir depend on the hydrologic regime. Therefore results for half-year periods with both wet and dry summers are given.

3.1.2. Empirical Models

Empirical models for lake acidification derive from the observation that acidification is analogous to a large scale titration in which a bicarbonate solution is titrated with a strong acid. Biological activity and chemical weathering provide the bicarbonate and acid precipitation provides the strong acid. The models merely use empirical relationships between various chemical components to describe observed regional patterns in lake acidificaton. The empirical model by Henriksen (1980) is a static model. However, it forms the basis for predicting the chemical

Table 3: Simulated volume-weighted averages from the complete Birkenes model (Christophersen *et al.* 1982) for two summer half years with different hydrologic regimes (1974:dry and 1978:wet). All concentrations are in μeql^{-1} (from Christophersen, 1983)

Situation	Hydrologic regime as in 1974					Hydrologic regime as in 1978				
	$[SO_4]$	$[H^+]$	(pH)	$[M^{2+}]$	$[Al^{3+}]$	$[SO_4]$	$[H^+]$	(pH)	$[M^{2+}]$	$[Al^{3+}]$
A Current situation	140	33	(4.48)	92	15	135	25	(4.60)	101	9
B Present BS, deposition down 50%	71	22	(4.66)	45	5	69	16	(4.80)	50	2
C Doubled BS, deposition down 50%	71	12	(4.92)	59	1	69	9	(5.05)	59	0
D BS down 50%, present deposition	140	43	(4.37)	60	38	135	36	(4.44)	75	24

composition of lakes resulting from a change in loading of strong acids from the atmosphere (Wright, 1983).

The empirical model is simply a consequence of the ionic balance (Wright, 1983):

$$H^+ + Al^{3+} + Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+ = Cl^- + NO_3^- + SO_4^{2-} + HCO_3^- + \text{org.anions} \quad (17)$$

A fraction of the dissolved constituents is marine seaspray. This fraction is subtracted under the assumptions that all Cl^- is of seawater origin and other ions are proportional to the ionic composition of seawater. Minor ions (NH_4^+, NO_3^-, K^+, Na^+ and organic anions) are neglected. Equation (17) is simplified:

$$H^+ + Al^{3+} + f(Ca^* + Mg^*) = \text{net } SO_4^* + HCO_3^- \quad (18)$$

f = empirical function of $C_a^* + Mg^*$
net SO_4^* = SO_4^* above background
(asterisks denote non–marine fraction)

In reference areas net SO_4^*, H^+ and Al^{3+} are negligible:

$$f(Ca^* + Mg^*) = HCO_3^- \quad (19)$$

The function f is obtained from the empirical relationships between $Ca^* + Mg^*$ and HCO_3^- in reference areas (Henriksen, 1980). Original alkalinity is given by:

$$alk = 0.91(Ca^{*} + Mg^{*}) \quad (20)$$

In acidified areas the equation (18) can be simplified in three ways depending upon pH-level. At pH > 5.5 bicarbonate is present in significant concentrations, and H^{+} and Al^{3+} can be neglected (21). At pH about 5.0 - 5.5 H^{+}, Al^{3+} and HCO_3^{-} can be neglected (22). At low pH, below 5.0, HCO_3^{-} can be neglected (23) (Wright, 1983):

$$pH > 5.5: \; 0.91(Ca^{*} + Mg^{*}) = \text{net } SO_4^{*} + HCO_3^{-} \quad (21)$$

$$pH\ 5.0 - 5.5: \; 0.91(Ca^{*} + Mg^{*}) = \text{net } SO_4^{*} \quad (22)$$

$$pH < 5.0: \; 0.91(Ca^{*} + Mg^{*}) + H^{+} + Al^{3+} = \text{net } SO_4^{*} \quad (23)$$

The acidification diagram of Henriksen (1980) separates lakes into three similar classes (Figure 2).

The division of the lake groups is obtained from the regression lines for $(Ca^{*}+Mg^{*})$ on SO_4^{*} for lakes in the pH range 5.2 - 5.4 and for lakes in the pH range 4.6 - 4.8. The nomograph provides a simple model for lake acidification and relates the stages of acidification to levels of precipitation pH in sensitive regions.

The equation for lake acidification by Wright (1983) (18) links these three stages (21), (22), (23) and the reference area case (19). An increase in acid deposition leads to an increase in SO_4^{*} concentrations in lake water which is compensated by either a corresponding decrease in bicar-

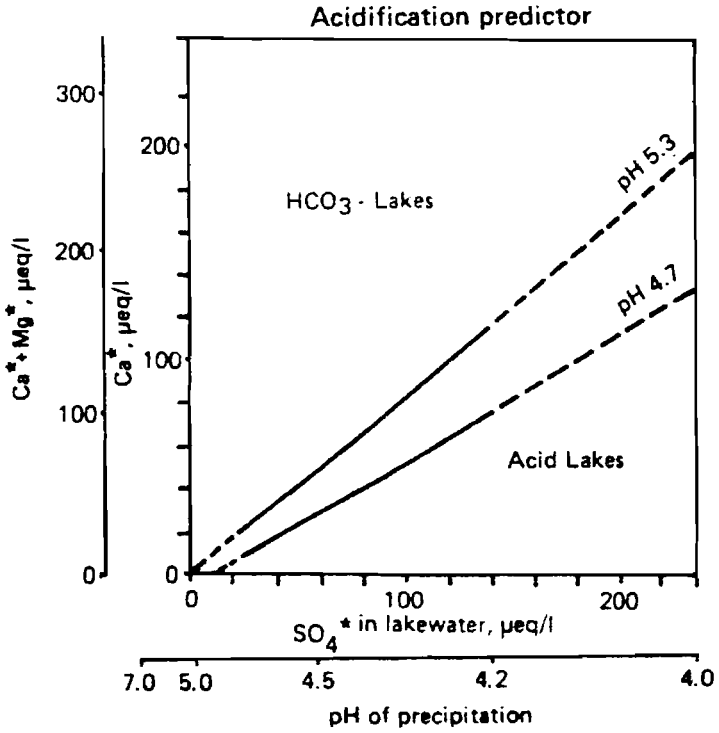

Figure 2. Henriksen's (1980) predictor nomograph to specify the pH of lakes given $Ca^* + Mg^*$ or Ca^* and SO_4^* in lakewater or weighted-average pH of precipitation.

bonate (HCO_3^-) or a corresponding increase in cations (Ca^*+Mg^*) or a fraction of both.

The empirical model provides two quantitative measures of acidification (Henriksen, 1980; Wright, 1983). Loss of alkalinity is defined as original alkalinity minus present day alkalinity:

$$\Delta alk = 0.91(Ca^* + Mg^*) - HCO_3^- + H^+ + Al^{3+} \quad (24)$$

The second measure is simply the amount of non-marine sulphate above background, net SO_4^* (18). If the assumptions behind the empirical model are correct then these two measures of acidification (18) and (24), should be equal.

PREDICTING WITH THE EMPIRICAL MODEL

The empirical relationships provide the basis for predicting future trends in lake acidification given the time pattern of the precipitation chemistry. A major question is whether acidification of lakes entails a change in base cation concentrations in addition to a loss of alkalinity (Henriksen, 1980). An increase of Ca^{2+} and Mg^{2+} - concentrations mainly reflect the depletion of base cations in the soil, in addition to changes in the chemical weathering rate.

To assess changes in base cation concentrations in response to increases in SO_4^*, different methods have been used (Henriksen, 1982a). It is concluded that for lakes still containing bicarbonate, the increase has been mainly compensated by a decrease in alkalinity. For acidifying

or acidified lakes, the data sets yield a clear increase in base cations (Henriksen, 1982a). The ratio of change in $Ca^* + Mg^*$ to change in SO_4^* is defined as:

$$F = \Delta(CA^* + Mg^*) / \Delta SO_4^* \quad (25)$$

Base cation increases due to acidification can be estimated to be a maximum of about 0.4 μeq (Ca^*+Mg^*) per $\mu eqSO_4^*$ as an average for groups of lakes (Henriksen, 1982a, Wright, 1983). The increase factors for individual lakes may deviate widely from these average values. For prediction purposes, increase factors in the range of 0 - 0.4 probably give reasonable estimates (Wright, 1983).

For prediction of the chemical composition of lakes in response to a change in deposition of strong acids the acidification equation (18) can be written as (Wright, 1983):

$$\Delta (H^+ + Al^{3+} - HCO_3^-) + \Delta\, 0.91(Ca^* + Mg^*) = \Delta\, SO_4^* \quad (26)$$

Applying the fraction F:

$$(1 - F)\Delta (H^+ + Al^{3+} - HCO_3^-) + F\Delta\, 0.91\, (Ca^* + Mg^*) = \Delta\, SO_4^* \quad (27)$$

According to equation (31), the predicted level of base cations $(Ca^*+Mg^*)p$ is given by:

$$(Ca^* + Mg^*)p = (Ca^* + Mg^*) + F\,\Delta\,SO_4^* \qquad (28)$$

Similarly

$$(H^+ + Al^{3+} - HCO_3^-)p = (H^+ + Al^{3+} - HCO_3^-) + (1 - F)\Delta SO_4^* \qquad (29)$$

The following conditions can be used to simplify equation (29):

$$\text{If } (H^+ + Al^{3+} - HCO_3^-) > 0, \qquad \text{then } HCO_3^- = 0 \qquad (30)$$

and H^+ and Al^{3+} can be calculated from empirical relationships between Al^{3+} and H^+.

$$\text{If } (H^+ + Al^{3+} - HCO_3^-) < 0, \qquad \text{then } Al^{3+} + H^+ = 0 \qquad (31)$$

and predicted pH can be calculated from the empirical relationship between pH and HCO_3^-.

As an example of use of the predictive model, the response of the high elevation lakes in the Adirondack mountains to different loadings is shown in Figure 3 (Wright, 1983). The pH frequency distributions following a 50% increase and a 50% decrease in net SO_4^* in the lakes have been calculated. Also the preacidification situation has been estimated.

The calculated preacidification pH-levels using F = 0.4 have agreed well with historical pH measurements. In Norwegian data the preacidification pH-levels derived from the model have agreed best with historical

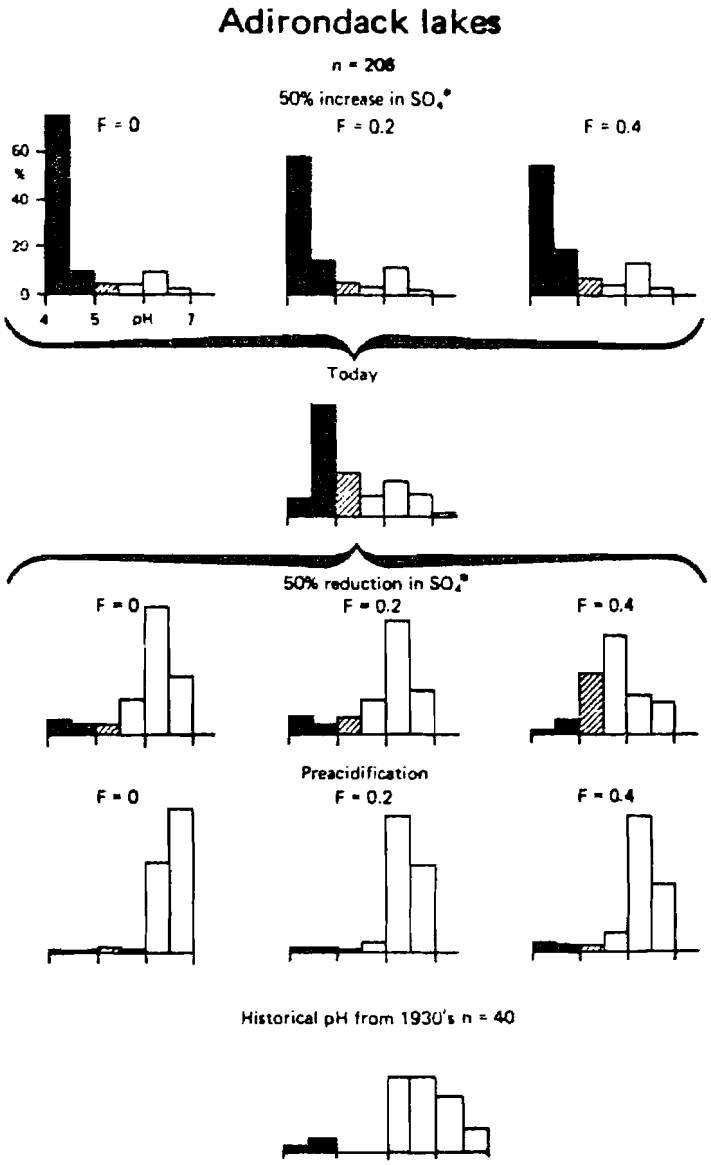

Figure 3. Measured and predicted pH frequency distributions with the empirical model (from Wright, 1983). Four SO_4 - loadings and three F-factors are used. The historical pH frequency distribution has been sampled in the 1930s (from Schofield, 1976).

pH measurements when F = 0.2 was used (Henriksen, 1982b).

3.1.3. Cation Denudation Model

Thompson (1982) has proposed a cation denudation model of acidification. The objective of the model is to relate the Cation Denudation Rate (CDR) of the watershed, the atmospheric load of excess SO_4^{2-}, and the pH of the river. The Cation Denudation Rate as used in the model, is the rate at which a watershed contributes cations to runoff as products of chemical weathering. The base cations (Ca^{2+},Mg^{2+},K^{+},Na^{+}) are considered to have been brought into solution during chemical silicate weathering by reactions with either H_2CO_3 or H_2SO_4. The discussion is restricted to areas underlaid by resistant rocks.

$$\text{Ca–Silicate} + H_2CO_3 = Ca^{2+} + HCO_3^- + H_2\,\text{Silicate} \qquad (32)$$

$$\text{Ca–Silicate} + H_2SO_4 = Ca^{2+} + SO_4^{2-} + H_2\,\text{Silicate} \qquad (33)$$

The cation denudation rate for each river was calculated using sea salt - corrected and discharge-weighted sums of cations times mean sample - date discharge, divided by drainage area. Sulfate is assumed to originate from atmospheric deposition and no correction for background sulfate is applied. The model in concentration form is described by equations (34) and (35):

$$\text{sum of cations} = HCO_3^- + SO_4^{2-} \qquad (34)$$

$$pH = 10.3 - p\,HCO_3^- \qquad (35)$$

Thompson's plot shown in Figure 4 is very similar to the Henriksen model, except that the sum of cations replaces the sum of calcium and magnesium, and pH is predicted theoretically rather than empirically (35). As a rate model, it is a predictor of the mean pH to be expected for a given CDR, runoff, and excess SO_4^{2-}-load.

The Thompson model assumes the base cations to have been brought into solution during chemical weathering. All base cations originate from the weathering of parent material in the long run. A specific amount of cations is, however, stored in the soil on the negatively charged soil particles. As the atmospheric deposition rate increases and the H^+ ion load exceeds the buffer rate by silicate weathering, the system switches over to the cation exchange buffer system (Matzner and Ulrich, 1981). The cation exchange leads to a liberation of base cations by displacement of Ca, Mg, K, and Na, and finally results in an almost complete loss of exchangeable base cations in the soil. This process, the leachout of exchangeable cations from soil under the influence of acid rain, is not considered in Thompson's rate model. At this situation, the cation denudation rate is not proportional to the weathering rate. Therefore, the total buffer capacity of the watershed will be overestimated. The cation exchange capacity of the soil is usually limited and after it is exhausted, the excess SO_4^{2-} is no longer balanced by base cations, but by H^+ and Al^{3+} ions. Acidification of surface waters occur.

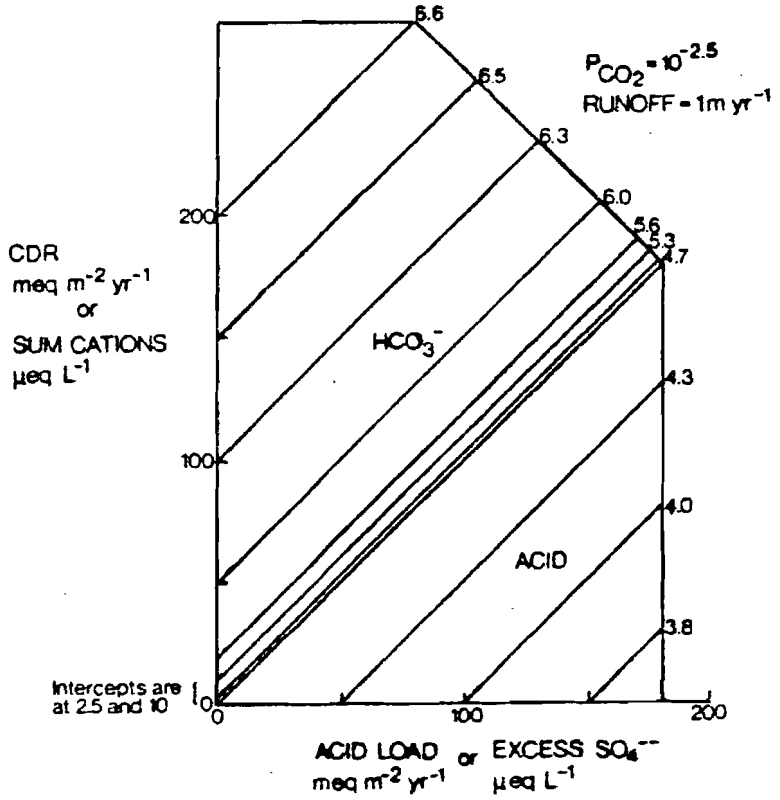

Figure 4. A plot of the Thompson model relating pH and sum of cations to excess SO_4^{2-} in concentration units, or pH and CDR to rate of excess SO_4^{2-} - loadings in rate units (from Thompson, 1982).

The applicability of the predictive cation denudation rate model is thus restricted to watersheds where the cation exchange does not currently play any significant role in neutralizing acidic inputs.

The application of the concentration model by Haines and Akielaszek (1983) gave fair results. Lower pH lakes generally fit the model better than higher pH lakes. The static concentration model assumes that cations are mobilized by sulfate and therefore the accuracy of the model does not depend on stable cation concentrations.

3.2. AEA

The following two acidification models have been developed at a series of workshops drawing on the expertise and experience of a variety of specialists and decision makers. These workshops were based on a methodology known as Adaptive Environmental Assessment (AEA) which was developed by system analysts at the University of British Columbia and the International Institute for Applied Systems Analysis (IIASA). This methodology deals with inter-disciplinary ecological problems (Holling, 1978). Workshops are structured around the construction of a quantitative simulation model of the resource system under study.

3.2.1. Model for Individual Watersheds

The first model (U.S. Fish and Wildlife Service, 1982) is focused on local areas, where empirical monitoring data was available for determining correlations between stream flows and chemical concentrations. Stream water quality parameters are computed by an empirical concentration-discharge relationship. This component of the model structure forms the watershed system, which receives input from the

atmosphere and yields chemically altered surface and ground waters. The other three investigated systems were: changes in the chemistry of aquatic environments; food chain components; and key fishery populations.

The chemical composition of the stream and lake systems is computed in a water chemistry submodel (Figure 5) based on electroneutrality. Water quality parameters (Ca^{2+},Mg^{2+},Na^{+},K^{+},SO_4^{2-},NO_3^{-},andCl^{-}) enter the aquatic environment from the watershed system. Inorganic carbon and aluminum are calculated from thermodynamic equilibrium relationships with atmospheric CO_2 and solid phase aluminum ($Al(OH)_3$) (cf. Christophersen et al., 1982) respectively.

The total fluoride F_T is calculated based on aluminum concentrations.

$$F_T = [F] + [AlF] + [AlF_2] \tag{36}$$

The free fluoride [F] is iterated until the calculated F_T is within acceptable limits compared to the input total fluoride value.

Electroneutrality calculation for the solution is performed after all thermodynamic calculations have been made. If there is a cation excess, the pH is incremented to a higher value, and correspondingly to a lower value in the case of anion excess value. The iteration proceeds until the electroneutrality balance is reached.

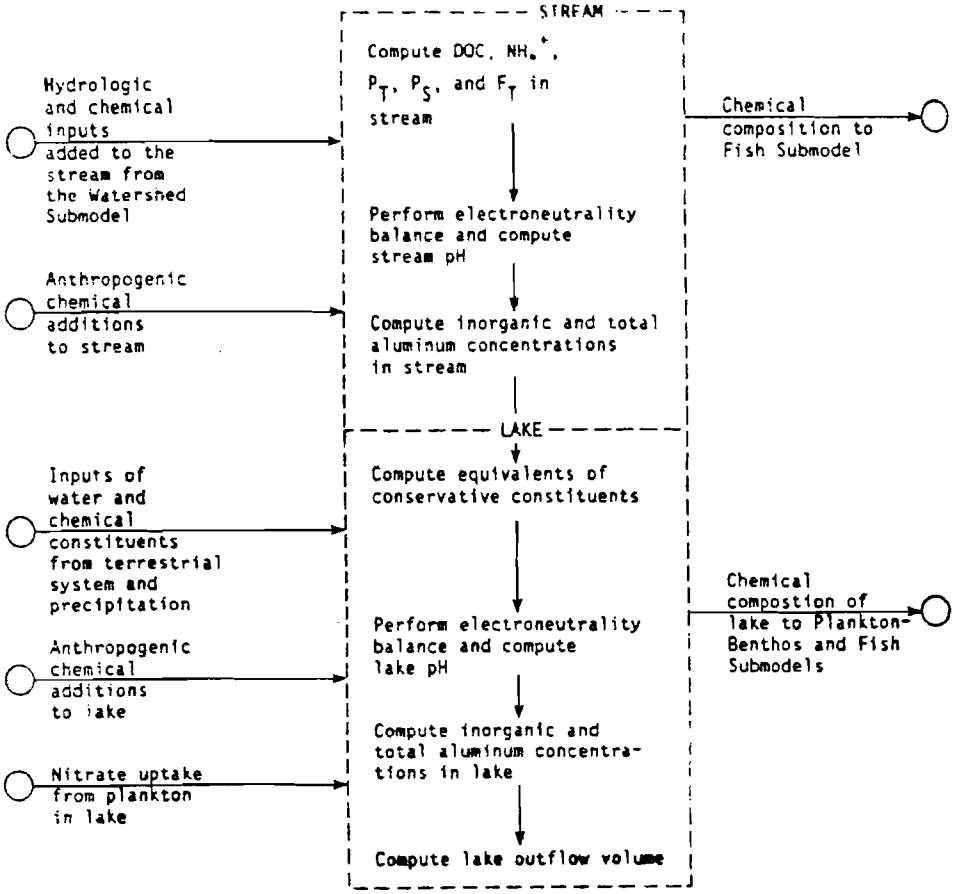

Figure 5. Calculation sequence for the water chemistry submodel (from U.S. Fish and Wildlife Service, 1982).

The simulation model was not intended to be a predictive management tool. At its current level of refinement, use of the model for predictive purposes is inappropriate. However the model does provide a framework for identifying further research needs and develops a more holistic understanding of the acidification process.

3.2.2. Regional Model

The principal purpose of the other survey (Jones et al., 1982) has been to provide a basis for the prediction of potential future impacts of acid rain. The objective of the modeling and analysis were to develop a preliminary model of regional scale impacts and to provide guidance for the future activities.

This regional model has two distinct levels. The first level, called the 'site model' makes predictions about changes over time in fish and chemistry for an individual lake or river. The site model can be run on any known system for which relevant lake and watershed information is available. For regional predictions the site model is used to make predictions for a range of lake types and then the 'scaled model' aggregates these predictions to the regional level.

SITE MODEL

The chemistry submodel computes changes over time in precipitation, acid deposition, and in the lake or river alkalinity, pH, and aluminum concentrations. Each year the chemistry submodel performs a series of operations which are summarized in Figure 6.

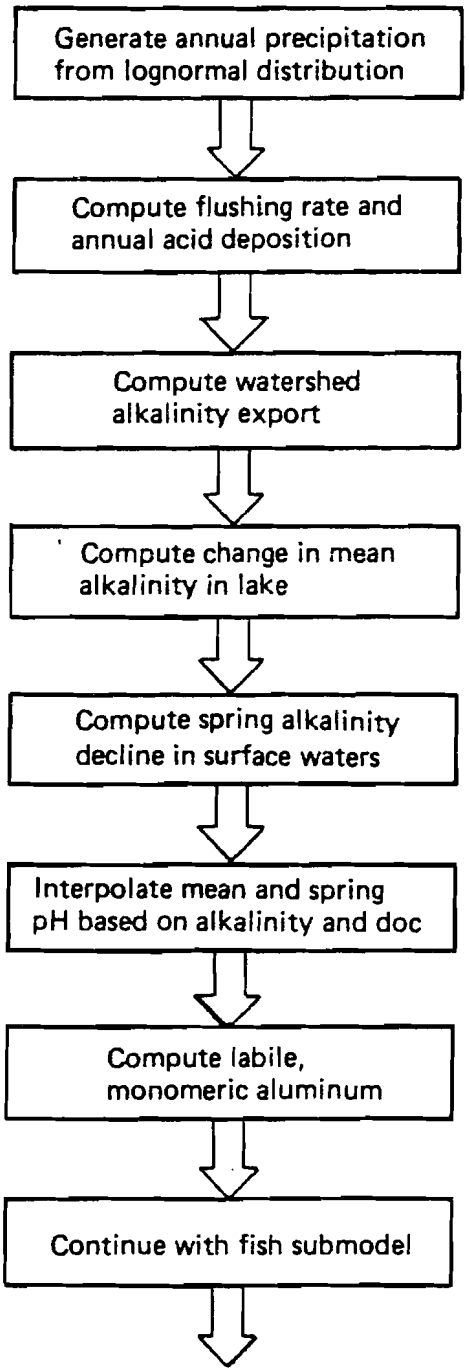

Figure 6. Flow of annual operations in the chemistry submodel (site model) from Jones et al.,(1982).

The chemistry submodel is based on the capability of a lake or river basin to neutralize atmospheric deposition. The term *alkalinity generation* refers to the overall buffering potential of the watershed. Therefore, the alkalinity generation minus the annual acid deposition gives the net export of alkalinity from the basin. If deposition and alkalinity generation are assumed to remain constant, the steady state lake or river alkalinity can be calculated:

$$Alk_{ss} = \frac{[(A_o \cdot D) + A_w(AAG + D)]}{Q} \qquad (37)$$

AAG = alkalinity generation ($meqm^{-2}\ yr^{-1}$)
D = −1. annual deposition ($meqm^{-2}\ yr^{-1}$)
A_w = land area of lake basin (ha)
A_o = lake area (ha)
Q = annual outflow ($m^3\ yr^{-1}$)

The flushing rate is estimated by:

$$R = \frac{Q}{V} = \frac{P \cdot WR \cdot (A_w + A_o)}{Z \cdot A_o} \qquad (38)$$

V = lake volume (m^3)
P = annual precipitation (m)
WR = ratio of outflow to precipitation
Z = mean depth (m)

After replacing Q in equation (37) by $(A_o+A_w)\cdot P\cdot WR$ and rearranging terms, steady state alkalinity can be computed

$$Alk_{ss} = \frac{D + \left[\frac{Aw}{A_w + A_o}\right] \cdot AAG}{P \cdot WR} \qquad (39)$$

The final step is to compute the annual change in mean alkalinity by the difference of equation (40):

$$\Delta Alk = \frac{D + (A_w / A_o) \cdot (AAG + D)}{Z} R \cdot Alk_t + Alk_{int} \qquad (40)$$

ΔAlk = change in mean alkalinity over one year

Alk_t = previous year's mean alkalinity

Alk_{int} = net internal generation of alkalinity per year

The episodic alkalinity declines are estimated by converting equation (46) to a monthly time step. To perform this conversion new parameters are specified for the month in which the lake or river shows maximum alkalinity declines.

FD = the fraction of annual deposition D in that month

FG = the fraction of AAG in that month

FQ = the fraction of Q in that month

ZS = the mean mixing depth.

In the model, the titration curves are used to compute the mean and episodic pH-values from their respective alkalinities, dissolved organic carbon (DOC) concentrations and assumed saturation of atmospheric CO_2.

Labile monomeric aluminum (Al^{3+}) is computed by:

$$Al_{free} = Al_{total} - Al_{org} - Al_{coll} \qquad (41)$$

Total aluminum is assumed to depend only on pH, and is estimated from a regression equation:

$$Al_{total} = 10^{(5.54 - 0.68\ pH)} \tag{42}$$

Organic aluminum was estimated from DOC according to a regression equation

$$Al_{org} = 54.9 \cdot DOC - 88 \tag{43}$$

The concentration of colloidal aluminum was assumed to equal 20 ppb.

SCALED MODEL

The final stage of the regional model development is to embed the site model into a larger structure which would scale the predictions for individual systems up to a regional level. The inputs necessary to run the site model are classified to define each lake or river type. A single input value represents each class. The total number of lake or river types is given by the product of the number of classes defined for each criterion. If criteria are closely correlated with another (e.g. mean depth with lake area), the value of one determines the value of the other.

Given the distribution of lake types within a region, the scale model can be run to provide regional level estimates over time. The overall structure of the scaled model is depicted in Figure 7.

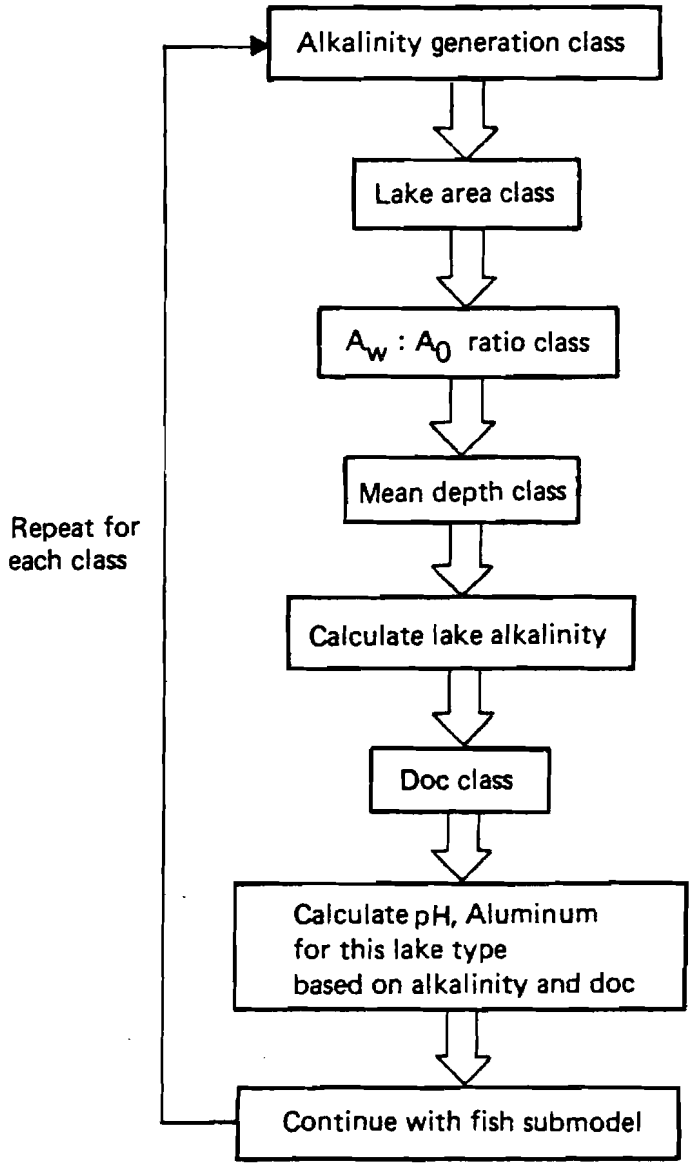

Figure 7. Schematic representation of the scaled model structure (from Jones et al., 1982).

This model treats all waters as headwaters. It is known that headwaters are far more sensitive to acidification than downstream (higher order) lakes and rivers. Thus this regional model gives estimates of the overall effects of acid precipitation and of the geographic extent of the impacts on sensitive ecosystems.

3.3. ILWAS

The basic concept of the Integrated Lake-Watershed Acidification Study (ILWAS) has been described by Goldstein et al., (1980). The study has been initiated to provide a scientific link between acid deposition and lake acidification. The study includes field investigations, laboratory experiments and mathematical modeling. The model simulates the physical and chemical transformations occurring in watersheds and lakes, as induced by acid deposition and internal acid generation. The ILWAS model includes hydrologic, canopy chemistry, snowmelt chemistry, soil chemistry, and stream and lake water quality modules. The role of the model system is to organize the lake-watershed acidification processes into an integrated theoretical framework.

The hydrologic module (Chen et al., 1982) provides a method for simulating the routing of internal flows so that all the chemical characteristics can be properly predicted.

For modeling purposes, a drainage basin is divided into several terrestrial subcatchments, stream segments, and a lake. Vertically, each subcatchment is further segmented into canopy, snow pack, and litter, organic, and mineral soil layers. Also the lake is vertically layered. Flows are routed through these physical compartments to the lake outlet.

A schematic outline of the model is shown in Figure 8. The inputs that drive the model are precipitation quantity and quality, and ambient

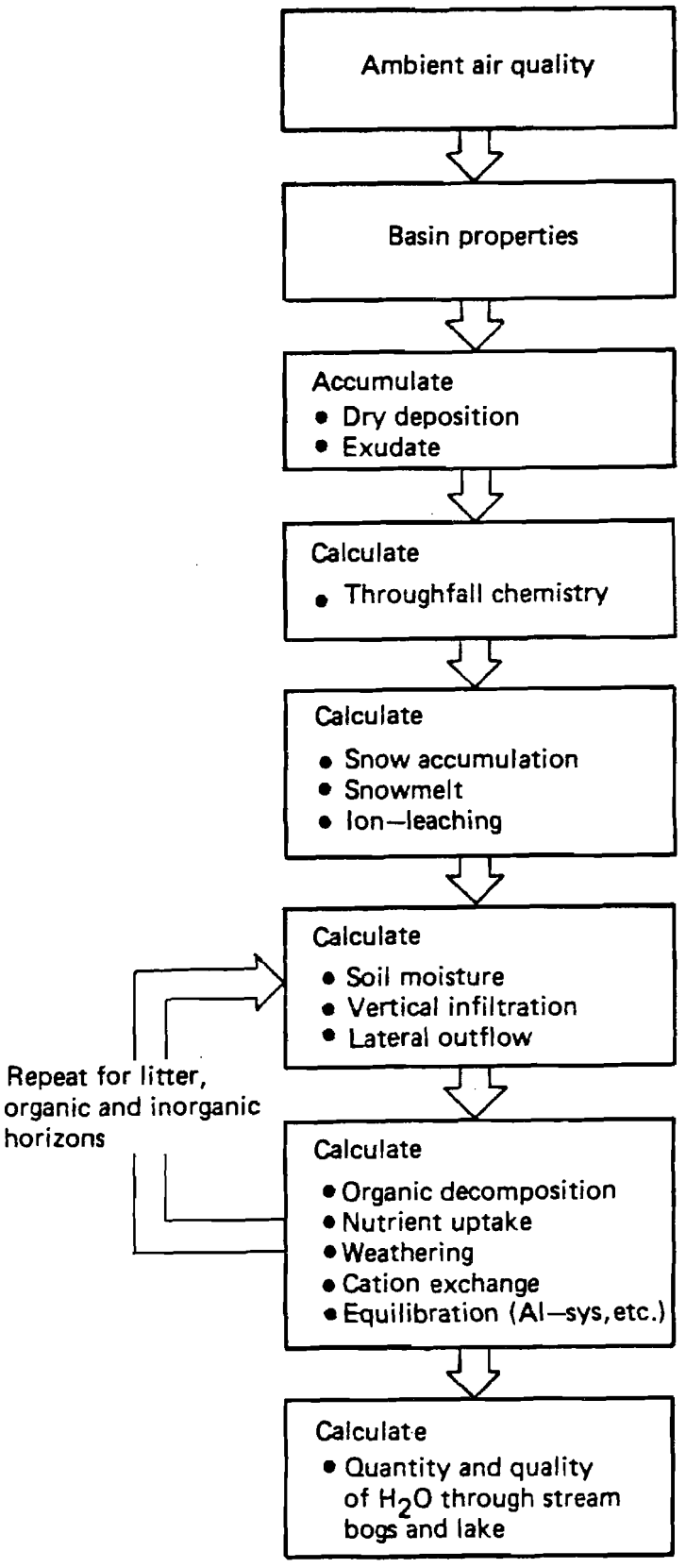

Figure 8. ILWAS model flowchart (from Chen et al., 1982)

air quality. On days when precipitation does not occur, the model calculates dry deposition onto the canopy. On days with precipitation, the model simulates throughfall chemistry. On all days, the model simulates the snow pack behaviour and the chemical behaviour of the soil solution. The chemistry modules take into account organic matter decomposition, plant nutrient uptake, mineral weathering, cation exchange and aqueous chemical equilibria. The equilibria of the carbonate and aluminum systems and the effect of organic acid ligands on acid buffering are considered.

The canopy module (Chen et al., 1983) calculates the quantity of the throughfall reaching the forest flow. The canopy module considers the following processes: (1) interception of precipitation; (2) dry deposition of particulates; (3) dry deposition of SO_2 and NO_x; (4) SO_2 and NO_x uptake by plants; (5) leaf exudation; (6) SO_2 and NO_x oxidation; (7) nitrification, and (8) wash-off (Chen et al., 1983). Other modules of the ILWAS model have not been published.

4. SUMMARY

Previous research on the impacts of acid precipitation on surface waters has been based on a qualitative determination of the acidification process.

Recently the need to provide predictions of potential future impacts of acid rain has been recognized. Scientific information can assist in making policies for emission control by describing quantitative consequences of alternative scenarios. For that purpose, methods for simulating acidification of surface waters have been developed. Many of these approaches have been organized into a computerized form in order to make the description of the processes easy to handle and demonstrate. A summary of these approaches is presented in Table 4.

Table 4. Summary of the approaches used to predict impacts of acid deposition on surface waters.

Predicting Impacts on Individual Water Bodies		Predicting Impacts on a Regional Basis	
Predictions based on		Predictions based on	
Observed water quality (Chap. 3.1.2 & 3.1.3)*	Processes in the watershed (Chap.3.1.1,3.2.1 & 3.3)*	Receptor Sensitivity (Chapter 2)*	Scaling up Watershed Model (Chapter 3.2.2)*
Henriksen, 1980 Thompson, 1982 Wright, 1983	Goldstein *et al.*, 1982 Chen *et al.*, 1982 Chen *et al.*, 1983 Christophersen & Wright, 1981 Christophersen *et al.*, 1982 Christophersen, 1983 U.S. Fish & Wildlife Service, 1982	Norton, 1979 Hendrey *et al.*, 1980 a,b; Omernik & Powers, 1982 Zimmerman, 1982 Kämäri, 1983	Jones *et al.*,1982

* Chapters refer to this paper.

To a certain degree these approaches can be adapted by IIASA for a regional scale assessment of acid rain impacts in Europe. Moreover, this paper is a starting point for collaboration of IIASA analysts with the scientists who developed these approaches.

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