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Sensitivity analysis of a watershed acidification model

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A computer model is developed and calibrated for simulating the movement of water and H ion through a forested watershed. The model is appropriate to a small (1 km^2) non-calcareous basin. The model is run on a daily time step with meteorological and pH of precipitation inputs. The model incorporates acid neutralizing capacity (a.n.c.) for various soil horizons. Changes in field capacity on the short and long term (weeks and months) and change in the hydraulic conductivity of the saturated zone on the long term affect basin outflow; a.n.c. and depth of the soil affect the pH of water on the long term. Reasonable changes in snow leaching, canopy enrichment, a.n.c., soil depth and total soil thickness have no effect on pH in the short term.

1. Introduction

The interaction of acidic precipitation and soils and rocks and the flow path of the resulting solution is considered a most important process affecting the chemistry of lakes and streams. There are presently a number of models that attempt to simulate this process and, or, predict changes over time. These models can be divided into two groups: (i) static models based upon ion balance and constant weathering rate assumption, and (ii) dynamic models. In the former case, the ion balance equation is derived from classical concepts of silicate mineral dissolution or cation exchange, and the acidic input is incorporated in the proton balance equation (Kramer & Tessier 1982). Normally the assumption of constant weathering rate (Thompson 1982; Henriksen 1980) is used to obtain a temporal aspect to the calculation. The second group of models (Chen *et al.* 1982; Christopherson *et al.* 1982; Fish & Wildlife Service 1982; Stumm *et al.* 1983) typically use various weathering–soil exchange reactions and a hydrological flow system. These models are driven by hydrometeorological parameters. At present, most of the models are site specific, for small watersheds of about 1 km^2, covering short periods of time (days and months), and may be generalized by statistical grouping and fitting of some of the parameters (Stumm *et al.* 1983).

Modelling of watershed (catchment) response in a non-calcareous environment is in an early stage of development. The purpose of this study is to incorporate current concepts into a simulation model to carry out a sensitivity analysis. The emphasis then is on defining the more sensitive processes for further research. Sensitivity is assessed by using different functions, different empirical coefficients from the literature, and modifying the input parameters by reasonable amounts.

It should be noted that this simulation and other simulations do not consider the oxidation reduction–proton reactions involving C, N and S that would commonly be important in soil microbiological processes, although Chen *et al.* (1982) consider denitrification.

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2. Model design

Figure 1 portrays the overall structure of the model. A summary of the processes associated with each compartment is presented in table 1. Details of the model are described elsewhere (Booty 1983). The watershed is divided into homogeneous sub-basins. The sub-basins are defined by surface area, ground slope, percentage open, forested and exposed bedrock areas as well as vegetation-type areas. For each sub-basin a 'typical' soil profile is defined by horizon thickness, porosity, field capacity, saturated hydraulic conductivity, soil and soil water chemistry. Owing to the absence of a thick, continuous overburden, which is typical of most headwater basins, regional groundwater flow is not considered.

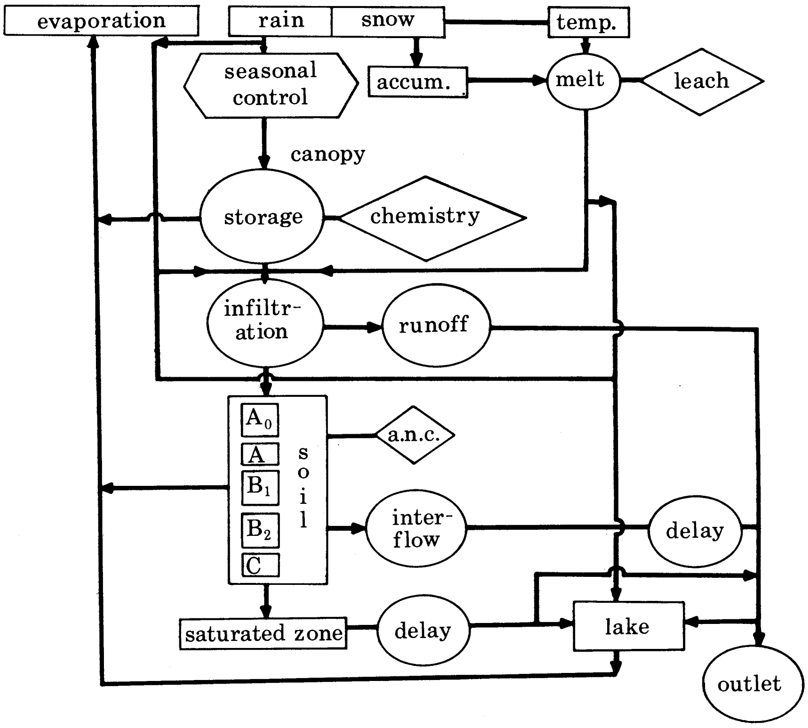

Figure 1. Schematic of computer simulation model. See table 1 for details. The a.n.c. is the acid neutralizing capacity of soil horizon.

The model operates on a daily time step. The processes that operate within the model are also controlled by the season of the year. Consequently, controls are used in the model to regulate the influence of the various processes during the year.

During the spring mode, all of the pathways may be operational. If there is a snowpack present or if the ground is frozen, then evapotranspiration is assumed to be negligible. The influence of the canopy is restricted to the coniferous tree influence on throughfall moisture volume and chemistry. In the spring mode, the most significant process is snowpack melting. Snowpack meltwater normally generates a major portion of the annual watershed outflow and causes the spring lakewater pH depression.

In the summer mode, all of the pathways in figure 1 are operational except for the snowpack accumulation, snowmelt, snow leaching and surface runoff over the soil.

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TABLE 1. WATERSHED ACIDIFICATION MODEL SUMMARY

hydrology	processes	sources
canopy interception	moisture balance between precipitation, evapotranspiration and canopy storage capacity	Fleming 1975
snow accumulation	evenly distributed and measured as equivalents	—
snowmelt	temperature and rain induced for forested and open areas	U.S.C.E. 1960; Lee 1980
surface runoff	only considered to be significant over exposed bedrock or over frozen soil during the spring melt	—
streamflow	based on the continuity equation for low order streams	Fleming 1975
infiltration	all moisture in excess of interception storage is assumed to go directly to infiltration	—
	snowmelt will infiltrate the soil if the ground is not frozen which is determined by the degree-day method	Fleming 1975
soil moisture	water balance between storage, interflow, evapotranspiration and percolation for each soil horizon	Nash & Sutcliffe 1970; Chen *et al.* 1978
evapotranspiration	empirical formulae using air temperature and relative humidity	Hargreaves 1974
percolation	moisture in excess of field capacity which increases linearly to the saturated hydraulic conductivity of the soil horizon at saturation	—
groundwater flow	linear flow based on the Darcy equation	—
lake	water balance between precipitation, streamwater and groundwater inflows, evaporation and lake outflows single or multi-layer	—
time interval	daily time step	—
input–output	input daily precipitation depth, mean daily temperature and vapour pressure output canopy moisture content, soil horizon moisture contents, streamflow groundwater flow, lake and basin outflow volumes	

chemistry	processes	sources
canopy modification	determined by the use of attenuation–enrichment coefficients for specific tree species	Fleming 1975; Booty 1983
snowpack and snowmelt	snowpack water and snowmelt are treated as aqueous carbonate systems	Stumm & Morgan 1981
	exponential function is used to determine ion enrichment of early snowmelt	Johannessen & Henricksen 1978
streamwater	mass balance of conservative ions at a control point (aqueous carbonate system)	Stumm & Morgan 1981
soil water	acid neutralization capacity functions determined analytically for each soil horizon	Kramer *et al.* 1981
	functions incorporate cation exchange and mineral dissolution over specific pH ranges	
lake	aqueous carbonate system modified by biological reactions	Stumm & Morgan 1981

input: daily precipitation pH and alkalinity.
output: pH of soil horizon waters,
pH of streamwater,
pH of groundwater,
pH of lakewater.

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During the autumn mode all of the pathways may be operational except for the influence of the deciduous forest canopy, which is assumed to be negligible.

In the winter mode, evapotranspiration is assumed to be negligible if the ground is frozen or if a snowpack is present. If the ground is frozen, then most of the snowmelt will generate surface runoff. A portion of the snowmelt may infiltrate the soil. This portion is determined as a function of the soil moisture content of the upper soil horizons and the value of the degree day. This is also the case for the spring mode.

3. Model calibration

The model has been applied to Batchawana Lake Basin, which is the headwater basin of the Turkey Lakes Watershed. The Turkey Lakes Watershed is a calibrated research watershed located approximately 50 km north of Sault Ste Marie, Ontario. Batchawana Lake Basin has a total surface area of approximately 1 km^2. Batchawana Lake actually consists of two distinct lake basins. The north and south lakes have surface areas of approximately 0.06 km^2 each.

Batchawana Lake Basin is underlain by basic to intermediate Archaean meta-volcanics and to a lesser extent by Archaean granite. The overburden consists of a thin (1 m) and discontinuous ground moraine that has been locally derived. The soil consists of an organic layer (10 cm) and a brown podzol (30 cm). The vegetation consists of mature red maple (60 %), yellow birch (40 %) with spruce near lakeshores.

The average lake and streamwater pH value is 6.0 and the average alkalinity is 0.06 meq l^{-1}. The weighted mean precipitation pH is 4.7 and the annual precipitation is 1120 mm. An evapotranspiration value of 500 mm a^{-1} has been determined for the Batchawana Lake Basin (Booty 1983).

The saturated hydraulic conductivities of the soil horizons range from 0.001 to 0.1 cm s^{-1}. The soil horizon porosities range from 0.36 to 0.61 and the field capacities range from 0.22 to 0.37.

3.1. *Hydrology*

Parameters not based on measurements (attenuated winter groundwater flow factor, attenuated lower soil horizon evapotranspiration coefficient, unsaturated zone physical parameters) must be optimized to achieve minimum variation in model output values from measured values. Also, some measured parameters that exhibit a range of values owing to inhomogeneities may be optimized to fine tune the model. Calibration of this model is achieved by adjusting model parameters using a trial and error method. The criterion of accuracy used in the calibration is the minimum value of the sum of the squares of the differences between the observed and simulated values.

An example of the daily outflow volumes from Batchawana Lake Basin, as predicted by the model, is presented in figure 2 for the period 17 September 1980 to 14 July 1981. Also shown are the measured outflow volume data that were collected for this period. Continuously measured flow data are not available. Consequently, a comparison of measured and model calculated cumulative outflow volumes is not presented.

The calculated daily flow volumes match the measured flows with little deviation for both the high and low periods of flow. The deviation for the 24 measured against calculated flow values range from 0.07 to 100 % with a mean value of ±21 %.

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3.2. *Chemistry*

Model chemical parameters which are not based on measurement or measured parameters and which exhibit a range of values (snow leach coefficient, net algal proton uptake coefficient) are optimized to calibrate the chemical portion of the model.

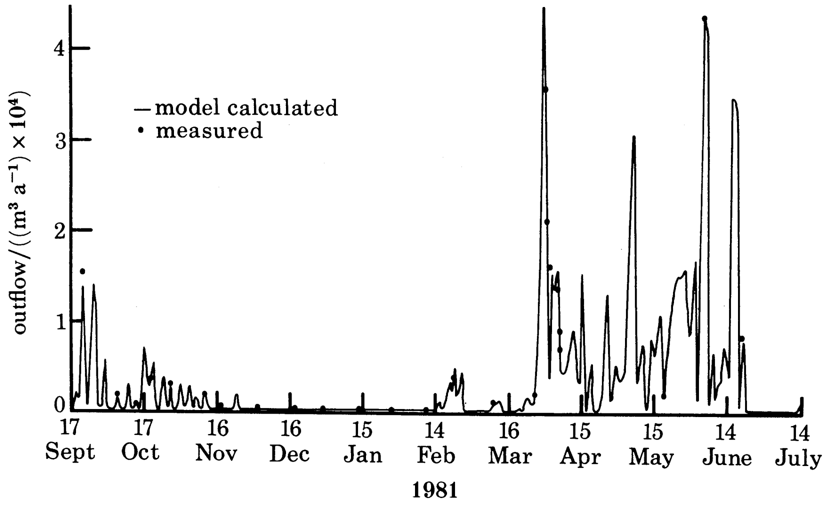

FIGURE 2. Comparison of measured and simulated streamflow values for Batchawana Lake outflow.

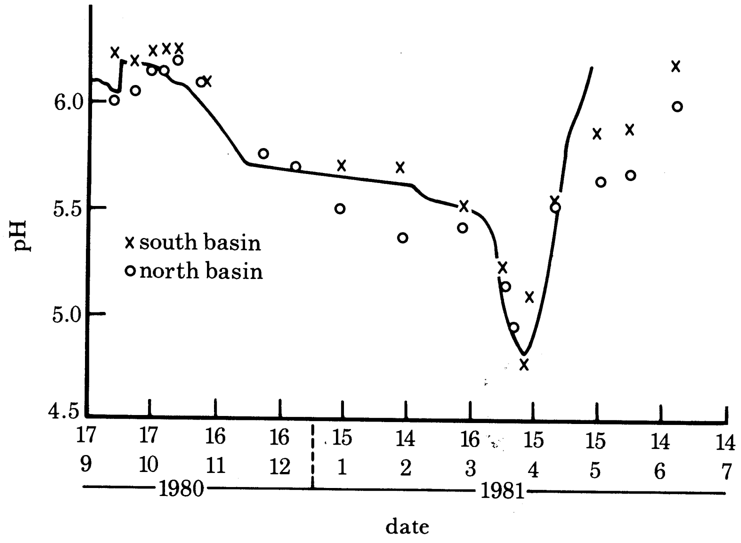

FIGURE 3. Simulated compared to measured (north and south basin) pH values. The model predicts the spring pH decline.

An example of the daily model calculated lakewater pH data is presented in figure 3 for the period 17 September 1980 to 15 June 1981. Measured lakewater pH data for the north and south basins of Batchawana Lake are also presented. The calculated lakewater pH values closely simulate the measured lakewater pH values until 1 May. The lakewater pH plateau for both of the lake basins during the period 1 May to 4 June is not predicted by the model. This may be owing to a reduction in the rate of photosynthesis in the lake or to flow from the A horizon, which can be a source of protons during the final stages of snowmelt.

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4. SENSITIVITY ANALYSIS

The sensitivity of the model outputs to changes in model parameter values have been determined. This allows one to emphasize the key parameters which control the rate of acidification of a watershed. Once these parameters are known precisely, they may be used to predict the susceptibility of other watersheds to acidification.

4.1. *Hydrology*

The sensitivity of the cumulative outflows from Batchawana Lake Basin ($\Sigma L_0(T)$) to changes in model parameter values are determined for a short period (one week) and a longer period (two months). The results are summarized in tables 2 and 3. All of the parameters have been changed over ranges.

TABLE 2. HYDROLOGY PARAMETER SENSITIVITY ANALYSES EFFECT ON BASIN OUTFLOW ($\Sigma L_0(T)$). SHORT TERM (ONE WEEK)

K, hydraulic conductivities; F, field capacity moisture content; Z, saturated moisture content; R, evapotranspiration attenuation factor.

parameter	change	$\Sigma L_0(T)$	change	$\Sigma L_0(T)$	change	$\Sigma L_0 T)$
K_1	×10	1.0	×0.1	1.0	×0.001	1.0
K_2	×10	1.0	×0.1	1.0	×0.001	1.0
K_3	×10	1.0	×0.1	1.0	×0.001	1.0
K_4	×10	1.0	×0.1	1.0	×0.001	1.0
K_5	×10	1.0	×0.1	1.0	×0.001	1.0
F_1	×1.1	0.687	×1.3	0.181	×0.8	1.77
F_2	×1.1	0.653	×1.3	0.182	×0.8	1.68
F_3	×1.1	0.655	×1.3	0.182	×0.8	1.68
F_4	×1.1	1.0	×1.3	1.0	×0.8	1.63
F_5	×1.1	1.0	×1.3	1.0	×0.8	2.48
Z_1	×1.1	1.0	×1.3	1.0	×0.8	1.0
Z_2	×1.1	1.0	×1.3	1.0	×0.8	1.0
Z_3	×1.1	1.0	×1.3	1.0	×0.8	1.0
Z_4	×1.1	1.0	×1.3	1.0	×0.8	1.0
Z_5	×1.1	1.0	×1.3	1.0	×0.8	1.0
R	×0.3	1.0	×0.5	1.0	×0.7	1.0

The sensitivity of basin outflows to changes in the saturated hydraulic conductivities for the soil horizons (K_1–K_5) are considered first. The values have been varied over four orders of magnitude, all of which are within the natural field of variation for a glacial till. It can be seen that varying the values of K_1–K_4 for both time periods has no significant effect on the cumulative outflows. However, the output flows are sensitive to significant decreases in the value of K_5, the C horizon saturated hydraulic conductivity, over the two month period. The value of K_5 is important in the model since it has a large control on the amount of water that is retained as groundwater storage.

The field capacity moisture content values F_1–F_5, for the five soil horizons (A_0, A, B_1, B_2 and C), are considered next. Field capacity values typically range from 0.1 for gravel to 0.4 for clay. Increasing the values of F_1–F_3 by 10% (×1:1) results in the outflow being decreased by approximately 33% for the short term while it remains unchanged over the longer term. Increasing the values of F_4 and F_5 by 10% results in the outflow remaining unchanged for the

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short term while increasing it slightly for the long term analyses. Decreasing the values of F_1–F_3 by 30 % (× 1.3) results in a large decrease (80 %) in the cumulative outflow for the one week period, whereas the two month outflow values are increased. Increasing the value of K_4 or K_5 by 30 % over the one week period has no effect on the cumulative outflows. Over the two month period the outflow is doubled when the value of K_5 is increased by 30 %. A 10 % decrease in the F_1–F_4 values results in an average increase in the outflow volumes of 0.75 % for the long term analyses. The outflow volumes are most sensitive to changes in the value of F_5, particularly over the long term.

TABLE 3. HYDROLOGY PARAMETER SENSITIVITY ANALYSES EFFECT ON BASIN OUTFLOW ($\Sigma L_0(T)$). LONG TERM (TWO MONTHS)

K, hydraulic conductivities; F, field capacity moisture content; Z, saturated soil moisture content; R, evapotranspiration attenuation factor.

parameter	change	$\Sigma L_0(T)$	change	$\Sigma L_0(T)$	change	$\Sigma L_0(T)$
K_1	× 10	1.0	× 0.1	1.0	× 0.001	1.0
K_2	× 10	1.0	× 0.1	1.0	× 0.001	1.0
K_3	× 10	1.0	× 0.1	1.0	× 0.001	1.0
K_4	× 10	1.0	× 0.1	1.0	× 0.001	1.0
K_5	× 10	1.0	× 0.1	0.997	× 0.001	0.173
F_1	× 1.1	1.0	× 1.3	1.026	× 0.9	1.003
F_2	× 1.1	1.0	× 1.3	1.003	× 0.9	1.007
F_3	× 1.1	1.0	× 1.3	1.003	× 0.9	1.005
F_4	× 1.1	1.03	× 1.3	1.091	× 0.9	1.015
F_5	× 1.1	1.34	× 1.3	2.084	× 0.9	1.34
Z_1	× 1.1	1.0	× 1.3	1.0	× 0.9	1.0
Z_2	× 1.1	1.0	× 1.3	1.0	× 0.9	1.0
Z_3	× 1.1	1.0	× 1.3	1.0	× 0.9	1.0
Z_4	× 1.1	1.0	× 1.3	1.0	× 0.9	1.0
Z_5	× 1.1	1.0	× 1.3	1.0	× 0.9	1.0
R	× 0.3	1.0	× 0.5	1.0	× 0.7	1.0

The saturated soil moisture content values, Z_1–Z_5, have been increased and decreased by 10–30 % for both the short and long term analyses. No changes in the values of the outflow volumes are observed. The basin outflow volumes are completely insensitive to the value of R, the evapotranspiration attenuation factor for the lower soil horizons over the period of study.

4.2. *Chemistry*

The sensitivity of the model outputs to changes in a number of the chemical parameters is summarized in table 4. The sensitivity factors represent the mean values of 10 daily calculations.

Increasing the value of K_L (snow leaching fraction coefficient) by 20 % results in an average increase in the value of the snowmelt [H$^+$] ($C_S(T)$) of 0.1 %, the average streamwater [H$^+$] ($C_Q(T)$) of 0.07 % and has no effect on the average lakewater [H$^+$] ($L_P(T)$).

Increasing the value of any of the three canopy attenuation-enrichment coefficients (K_Y, K_R, K_S) by a factor of 10 has no effect on the [H$^+$] of the A_0 horizon soilwater ($P_{\emptyset}(T)$, on $C_Q(T)$, or on $L_P(T)$).

The sensitivities of the soil horizon soilwater values of [H$^+$] ($P_{\emptyset}(T)$–$P_D(T)$) to doubling the slope of the a.n.c. function are shown in table 4. Since the a.n.c. functions are determined per unit mass of soil, doubling the thickness of the soil horizons (D_i) is similar to doubling the a.n.c.

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function slopes. In both cases, the absolute changes in the values of $[H^+]$ for the soil horizons and for the lakewater are extremely small.

The long term effects on the soilwater pH levels owing to acidic precipitation may be evaluated by studying the sensitivity of the soilwater pH values to depressed precipitation pH levels. In table 5, the results of running the model for the period 17 September to 17 October 1980, using measured precipitation values, and precipitation pH values of 3.0 and 2.0 are presented. During this period, all the precipitation is in the form of rain and the soil is not frozen. The average measured precipitation pH value for this period is approximately 5.0. Only the A_0 horizon soilwater pH ($P_{\emptyset}(T)$) is significantly affected by the depressed precipitation levels over the one month period.

TABLE 4. CHEMISTRY SENSITIVITY ANALYSES

parameter	changed by factor	output parameter affected	by factor
K_L (snowmelt leaching coefficient)	× 1.2	$C_S(T)$ (snowmelt $[H^+]$)	1.001
K_L (snowmelt leaching coefficient)	× 1.2	$C_Q(T)$ (average streamwater $[H^+]$)	1.0007
K_L (snowmelt leaching coefficient)	× 1.2	$L_P(T)$ (average lakewater $[H^+]$)	negligible
K_Y (yellow birch canopy enrichment coefficient)	× 10	$P_{\emptyset}(T)$ (A_0 horizon soilwater $[H^+]$)	negligible
K_R (red maple canopy enrichment coefficient)	× 10	$P_{\emptyset}(T)$ (A_0 horizon soilwater $[H^+]$)	negligible
K_S (spruce canopy enrichment coefficient)	× 10	$P_{\emptyset}(T)$ (A_0 horizon soilwater $[H^+]$)	negligible
K_Y (yellow birch canopy enrichment coefficient)	× 10	$C_Q(T)$ (average streamwater $[H^+]$)	negligible
K_R (red maple canopy enrichment coefficient)	× 10	$C_Q(T)$ (average streamwater $[H^+]$)	negligible
K_S (spruce canopy enrichment coefficient)	× 10	$C_Q(T)$ (average streamwater $[H^+]$)	negligible
a.n.c.1 (A_0 horizon a.n.c. function slope)	× 2	$P_{\emptyset}(T)$ (A_0 horizon soilwater $[H^+]$)	negligible
a.n.c.2 (A horizon a.n.c. function slope)	× 2	$P_A(T)$ (A horizon soilwater $[H^+]$)	negligible
a.n.c.3 (B_1 horizon a.n.c. function slope)	× 2	$P_B(T)$ (B_1 horizon soilwater $[H^+]$)	negligible
a.n.c.4 (B_2 horizon a.n.c. function slope)	× 2	$P_C(T)$ (B_2 horizon soilwater $[H^+]$)	negligible
a.n.c.5 (C horizon a.n.c. function slope)	× 2	$P_D(T)$ (C horizon soilwater $[H^+]$)	negligible
(A_0–C horizon a.n.c. function slopes)	× 2	$L_P(T)$ (average lakewater $[H^+]$)	negligible
D_1 (A_0 horizon depth)	× 2	$P_{\emptyset}(T)$ (A_0 horizon soilwater $[H^+]$)	negligible
D_2 (A horizon depth)	× 2	$P_A(T)$ (A horizon soilwater $[H^+]$)	negligible
D_3 (B_1 horizon depth)	× 2	$P_B(T)$ (B_1 horizon soilwater $[H^+]$)	negligible
D_4 (B_2 horizon depth)	× 2	$P_C(T)$ (B_2 horizon soilwater $[H^+]$)	negligible
D_5 (C horizon depth)	× 2	$P_D(T)$ (C horizon soilwater $[H^+]$)	negligible
(A_0–C horizon depth)	× 2	$L_P(T)$ (average lakewater $[H^+]$)	negligible

TABLE 5. EFFECTS ON SOILWATER pH VALUES OWING TO DEPRESSED pH OF PRECIPITATION

($P_{\emptyset}$ to P_D are A_0 to C soil horizon water pHs.)

precipitation pH	$P_{\emptyset}(T)$ ΔpH	$P_A(T)$ ΔpH	$P_B(T)$ ΔpH	$P_C(T)$ ΔpH	$P_D(T)$ ΔpH
measured	-5×10^{-6}	-2×10^{-4}	-4×10^{-6}	-3×10^{-6}	-2×10^{-7}
3.0	-4×10^{-3}	-2×10^{-4}	-1×10^{-5}	-3×10^{-6}	-2×10^{-7}
2.0	-4×10^{-2}	-3×10^{-4}	-6×10^{-5}	-9×10^{-6}	-2×10^{-7}

If one extrapolates the 1980–81 season model results, the pH of the water of the A_0 soil would decrease by about one unit in 100 years.

The possible effects on Batchawana Lake Basin of reductions in H^+ loadings of 50% can be estimated for the period 17 September 1980 to 14 July 1981. The lakewater pH increased by 0.4 pH units (whole lake average) compared to the actual measured values. The soilwater pH values would show no significant changes over the period. However, the bulk snowpack

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and snowmelt pH values would be increased by an average of 0.3 pH units as compared to the values calculated using the measured precipitation data.

5. Conclusions

The model indicates that watersheds such as the Batchawana Lake Basin, which are covered by coarse, glacial till, should not have significant lateral flows through the upper soil horizons.

The key parameters identified in this research, which control the rate of acidification of a watershed, besides the actual acid loading rates are: (i) infiltration – percolation rates; (ii) soil depth (iii) soil horizon a.n.c.s. Both (i) and (ii) control the 'degrees of interaction' of H^+ and soil materials.

Long term acidification can be estimated from the slope of the a.n.c.–pH function for a soil, and the average soil depth affected.

Short term fluctuations in the soilwater pH values owing to biological oxidation–reduction reactions involving C, N and S are not calculated in the model. These biological reactions may be as significant as or more significant than proton uptake and release in the short term.

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