

**Direct/Delayed Response Project:
Future Effects of Long-Term Sulfur Deposition
on Surface Water Chemistry
in the Northeast and Southern Blue Ridge Province**

Volume IV: Appendices

by

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APPENDIX A.1-1
ENHANCED TRICKLE-DOWN (ETD)

Technical Report No. CEE-ARRG-86.03

Modeling Short and Long Term Impacts
of Acid Precipitation Using the
Enhanced Trickle-Down Model:
Lake Woods Case Study

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MODELING SHORT AND LONG TERM IMPACTS OF ACID PRECIPITATION USING THE ENHANCED TRICKLE-DOWN MODEL: LAKE WOODS CASE STUDY

INTRODUCTION

Public awareness of the effect of acid deposition on the terrestrial and aquatic environment has imposed pressure on the governments of European and North American countries to control the emissions of sulfur and nitrogen oxides. However, before any threshold limit be established a critical question concerning the response of aquatic ecosystems to acidification should be answered. The case is whether further decreases in alkalinity of surface waters will occur if present emission loadings remain constant. It is the purpose of this research to aid in answering the above question by application of a mathematical model to lakes in the Adirondack Mountains of New York, where most of the effects of acid rain in the United States have been documented.

In order to examine the behavior of aquatic responses to acid rain, let us define those waters whose alkalinity changes further with time as "direct response" systems. Figure 1 is from a 1984 National Research Council Panel on "Processes of Lake Acidification", which discussed direct response and delayed response systems. A direct response system is expected to respond to changes in acid deposition over a relatively short period of time, depending on the hydraulic detention time of the lake. In this case, the rate of neutralization in the watershed is a kinetically-controlled process, and changes in acid deposition may modify the rate of acid neutralization but would not exhaust the capacity of the watershed for neutralization. A delayed response watershed, on the other hand, would gradually lose its capacity for neutralizing acid deposition, and the alkalinity of its waters would gradually decrease over time (decades to centuries). There are two possible causes of a delayed response: (1) a gradual depletion of mineral bases of base cations from soil exchange sites, and/or (2) a gradual exhaustion of sulfate adsorption sites in the soil. The two processes are related to the ordinate and abscissa of Figure 1. If a watershed has a low ability to supply bases and a low ability to retain sulfate (SO_4^{-2} from H_2SO_4), then it is a direct (quick) response system.

Figure 2 gives a more temporal picture of the difference between direct and delayed response systems. If watersheds are out of the "protected" type of Figure 1, there will be no response to a step function increase in acid deposition (panel B., Figure 2). These watersheds are capable of neutralizing any observed amount of acid deposition. Moderately sensitive lakes may respond with significant decreases in alkalinity. However, they will retain some acid neutralizing capacity (ANC). These lakes are shown in panel C of Figure 2 and are the "direct" response lakes. Depending on their watershed characteristics (water flows only through shallow acidic soil zones, etc.), these lakes may become acidic after 1000 years (delayed-1) or some may have a much faster response (delayed-2), depending on when their soil ANC or sulfate-sorption capacity become exhausted. Extremely sensitive lakes (panel D) have already become acidified due to acid deposition.

Mathematical models can be used to estimate the alkalinity response of lakes over time. The Trickle-Down model has been used to assess resources-at-risk to acid deposition in the Northeast and Upper Midwest. A steady state version of the model was first reported by Stumm and Schnoor (1983), and a time variable version of the model was given by Schnoor, Palmer and Glass (1984) for Omaday Lake and Filson Creek, Minnesota. The time variable model has been applied to two seepage lakes in Wisconsin (Lakes Clara and Vandercook) by Lin (1985). The steady state version has been used to estimate the number of lakes that would become acidic under various acid loading scenarios for approximately 1400 lakes across the depositional gradient (Schnoor, Lee, Nikolaidis and Nair, 1986). Being simple and yet based on the principle of continuity for alkalinity, the model has proven to be useful in acid precipitation assessments. The model, as it is used by Lin (1985) is suitable for seepage lakes only. Several modifications were required to generalize the model for every surface water hydrologic system.

The Enhanced Trickle-Down model (ETD) is a combination of four submodels (Nikolaidis et al., 1986). It simulates the hydrology, alkalinity, sulfate and chloride of a catchment simultaneously. The construction of the hydrologic submodel equations was done in such a way that each flow component

is multiplied by a correction factor that reflects the lumped nature of the model. The alkalinity and sulfate submodels are sets of mass balance equations on each compartment. The mass balance equations for alkalinity and sulfate include the predominant processes of ion exchange, chemical weathering, sulfate sorption, sulfate reduction and iron oxidation as reaction term.

The scope of this report is to calibrate, verify, and perform a sensitivity analysis on the parameters and examine the long term response to various acid loadings of Lake Woods, using the ETD model. Lake Woods is a 2.1 km² forested watershed located in the Adirondack Park region of New York State. Lake Woods is considered acidic, with a mean outlet pH of 4.7 and mean outlet alkalinity of -10 µeq/L. The lake receives an annual precipitation of 1/2 m and the mean annual temperature is 5° C. The vegetation of the watershed is dominated by Sugar Maple, Beech, Yellow Birch and Red Spruce. The watershed is underlain by granitic bedrock. The surficial geology is comprised by thin but variable thickness glacial till. The soils are predominately Becket Spodosols.

MODEL CALIBRATION

PROCEDURE

The calibration of ETD for Lake Woods was achieved by decoupling the hydrologic, sulfate and alkalinity submodels. Since there is a coupling between hydrology and chemistry, the hydrologic parameters were calibrated first. When a good fit between the simulated and the observe outflow was achieved, then the hydrologic parameters were fixed and the sulfate reaction parameters were calibrated. Finally, with fixed hydrologic and sulfate parameters the weathering rates were adjusted so a good fit would be established for alkalinity. The calibration of each submodel was achieved by using a standardized optimization package, IDESIGN (Arora et. al, 1985) and a trial and error procedure. The ranges of parameters for calibration were input to IDESIGN, which was connected with the ETD model. At each iteration (complete two year simulation) the cost function was evaluated. The cost function is of the form:

$$\text{COST} = \sum_{t=1}^m (S_t - O_t)^2$$

where: S_t = simulation value of model output variable at time, t;
 O_t = observed value of model output variable at time, t; and
 m = total number of time steps of observed data.

The model output variables that participated in the cost function were outflow, alkalinity and sulfate. IDESIGN perform minimization of the cost function using Fletcher-Reeves algorithm (gradient method). Bounds known a priori on physical quantities and parameters were included as constraints in the optimization process. However, in all gradient methods when the objective function is of the least-squares type, assume that the residuals are homoscedastic, independent and sufficiently small to assume their normality. When this is the case, the maximum likelihood method justifies the use of the least squares objective functions (Isabel et. al, 1986). In our case the residuals are not homoscedastic, thus the results of the optimization by IDESIGN tend to bias the results towards the extreme values of the residuals. On the other hand, IDESIGN does bring the parameters within a reasonable range from their optimal value. After this point, optimal calibration was based on trial and error method. There were three main guidelines used to establish the optimum value:

- 1) obtain closure of cumulative flow or mass during the whole period,
- 2) capture the seasonal variability of the state variables, and
- 3) capture the peaks and valleys of the daily flows and concentrations.

The calibration of the hydrologic parameters was established in six steps. Model variables symbols were borrowed from Nikolaidis et. al, 1986.

Figure 9 and 10 present the wet and dry daily sulfate and acidity loading time series. An analysis of wet and dry deposition is presented in Table 1. Here, one should notice that dry deposition of acidity is about 32% of the total acidity and dry deposition of sulfate is about 42% of the total sulfate loading. On the average, 12 metric tons of sulfate are deposited on Lake Woods' watershed per year, which roughly corresponds to 4 metric tons of sulfur.

RESULTS

A list of the hydrologic and chemical watershed descriptors that were input to the model are presented in Table 2. The optimum values of the calibrated parameters after following the procedure described previously are presented in Table 3. Time-series input for precipitation, evaporation and temperature for the calibration period (9/78 through 8/80) are shown in Figures 3, 4, and 5. Time series plots for wet and dry sulfate and acidity loadings for both calibration and verification periods are presented in Figures 9 and 10, respectively. Comparisons between lake outflow, chloride, sulfate and alkalinity simulations and field data are presented in Figures 11 through 16.

A complete hydrologic budget for Lake Woods is shown in Table 4. 64% of the total inflow to the lake is from the soil compartment. Direct precipitation and snow contributions are 12% each. Finally, 4% of the total inflow to the lake is from the unsaturated zone. The I/Q ratio (total precipitation input to outflow ratio) for Lake Woods is 1.65. As a final comment, one could say that the watershed of Lake Woods is very flashy, since 75% of the total inflow is due either to direct precipitation or due to flow through soil.

An alkalinity budget of Lake Woods is presented in Table 5. The majority of the acidity input to the lake is coming through soil and total, direct to the lake deposition with 69.2 and 18%, respectively. Wet precipitation contributes 11.5% and snowmelt contributes 12.5% of the total acidity input. According to the simulation results, 63.3% of the neutralization of the total acidity input to the watershed is due to the in-lake processes (weathering, sulfate reduction and iron oxidation).

A sulfate budget is shown in Table 6. The majority of sulfate input is through the soil and total, direct to the lake deposition with 66% and 12.9%, respectively. Wet precipitation and snowmelt contribute about 7.1% each. The net sulfate reduction in the lake sediments is 11.2% of the total input to the lake.

Table 7 presents the MSE evaluation for the calibration period for discharge, cumulative discharge, chloride, alkalinity, and sulfate.

VERIFICATION

The verification simulations of Lake Woods were performed by using one more year of input field data time series not included in the calibration period. The time-series input for precipitation, evaporation and temperature for the verification period (9/80-8/81) are shown in Figures 6, 7, and 8. The wet and dry deposition time-series of sulfate and acidity were part of Figures 9 and 10, respectively. The simulation results between lake outflow, chloride, sulfate and alkalinity for the verification period and field data are presented in Figures 17 through 22. The results are comparable with the calibration results except for the fact that the model underestimates the total cumulative outflow. This is due to the fact that a 25 mm/day flow was measured for a few days the first week of March 1981 where the temperature was about 10°C and there was snowcover. Examining the amount of evaporation during the same period, one can see that it is rather high (~5-7 mm/day). This indicates that instead of melting this water, the model evaporates it. It is obvious that such a condition is not taken under consideration. Since it was observed during the verification period, no changes were made in the model formulation. Table 8 presents the MSE evaluation for the verification period.

SENSITIVITY ANALYSIS

The sensitivity of lake outflow to each of the hydrologic parameters was checked by varying the parameters 10% above and 10% below their optimum values using the calibration period record. The percent change of the mean square error (MSE) of the outflow is presented in Table 9. The most sensitive parameters were: the snow parameters BETA, KAPPA and KPAN2, the lake evaporation correction factor, KPAN5 and the soil lateral and vertical permeability correction coefficients.

The sensitivity of outflow alkalinity to each of the chemical parameters was similarly checked. Table 10 contains the percent change in MSE. The most sensitive parameters were: the lake compartment weathering constants KH5 and KO5 and the lake sulfate reduction reaction rate k. The alkalinity MSE sensitivity results were expected to be low because Lake Woods has a flashy hydrology so the detention time of the water in the watershed is small and there is not enough time for weathering to occur.

LONG TERM SIMULATION

In order to perform long term simulations, the existing 3 year record was input repeatedly for 17 times, which extended the simulation period to 51 years. Three simulation runs were made: one for present loading, one for half loading and one for double loading. In order to establish the half and double loadings both wet and dry sulfate and alkalinity inputs were halved or doubled, respectively. Figures 23 and 24 show the projection of lake alkalinity and sulfate for the next 50 years under three different loading scenarios. The prediction indicates that Lake Woods is a direct response system and that it would only take a few years for the lake to respond to a decrease in acid deposition loading. The lake currently has reached steady state with a mean alkalinity of about $-10 \mu\text{eq/L}$ and a mean sulfate of $130 \mu\text{eq/L}$. If the loading was to be halved, the mean alkalinity would be $25 \mu\text{eq/L}$ and the mean sulfate concentration $65 \mu\text{eq/L}$. On the other hand, if the loading was to be doubled, the mean alkalinity would be $-40 \mu\text{eq/L}$ and the mean sulfate concentration $260 \mu\text{eq/L}$.

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Table 1. Lake Woods analysis of wet and dry deposition

Period:	ACIDITY (eq/ha-yr)		SULFATE (eq/ha-yr)	
	Wet	Dry	Wet	Dry
9/78-8-79	865.6	382.4	820.0	547.6
8/79-8/80	719.4	342.3	617.0	457.4
9/80-8/81	781.0	332.3	671.0	487.0
Average	788.7	352.3	702.7	497.3

Total average Acidity = 1141 eq/ha-yr
 Dry Deposition = 30.9% total Deposition

Total average Sulfate = 1200 eq/ha-yr
 Dry Deposition = 41.5% total Deposition

Sulfate Loading (Average)

Wet = 33.73 kg/ha-yr
 Dry = 23.87 kg/ha-yr
 Total = 57.60 kg/ha-yr

On the average, 12 metric tons of sulfate are deposited on Lake Woods' watershed (or 4 metric tons of Sulfur).

Table 2. List of watershed descriptors used for model calibration

GENERAL WATERSHED CHARACTERISTICS :

AQUATIC AREA =	0.2300E+06 SQUARE METERS
TERRESTRIAL AREA =	0.1840E+07 SQUARE METERS
CHARACTERISTIC DISTANCE =	0.2625E+03 METERS
DEPTH TO BEDROCK =	2.3000 METERS
PARTIAL PRESSURE OF ATM CO ₂ =	0.0003 ATMOSPHERES
SURFACE WATER PCO ₂ IS 1.50 TIMES SATURATED PCO ₂	

SOIL COMPARTMENT CHARACTERISTICS:

POROSITY =	.2700
DEPTH OF SOIL LAYER =	0.3684 METERS
SUM OF BASES =	106.1000 EQUIVALENTS/KILOGRAM
SOIL DENSITY =	1009.0000 KILOGRAMS/CU. METER

UNSATURATED ZONE COMPARTMENT CHARACTERISTICS:

POROSITY =	0.2000
TRANSPIRATION COEFFICIENT =	0.0010 INCHES/DAY
BARE-GROUND FROST COEFFICIENT =	0.1000
REDUCTION IN FROST COEFFICIENT =	0.0800
DAILY THAW RATE =	0.1200 DEGREES C
INITIAL FROST INDEX =	0.0000 DEGREES C
LIMITING FROST INDEX =	-3.0000 DEGREES C
THAW COEFFICIENT =	0.2000
BULK DENSITY =	1620.0000 KILOGRAMS/CU. METER

SURFACE WATER BODIES CHARACTERISTICS:

STREAM BED ELEVATION AT OUTFLOW =	11.9000 METERS
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GROUNDWATER COMPARTMENT CHARACTERISTICS:

POROSITY =	0.2000
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Table 3. List of optimum values of the calibrated parameters

a) Hydrologic Parameters	b) Alkalinity Parameters
-Snow:	RE3 = $6.4\text{E-}8 \text{ m}^3/\text{eq/day}$
BETA = 0.6795	KH4 = $9.0\text{E-}1 \text{ meq/m}^2/\text{day}$
KAPPA = $1.1423 \text{ in/day/ } ^\circ\text{C}$	KH5 = $8.5\text{E-}2 \text{ meq/m}^2/\text{day}$
KPAN2 = 1.0066	KH6 = $1.0\text{E-}2 \text{ meq/m}^2/\text{day}$
-Evaporation:	K04 = $1.1\text{E-}2 \text{ meq/m}^2/\text{day}$
KPAN3 = 1.5471	K05 = $7.9\text{E-}2 \text{ meq/m}^2/\text{day}$
KPAN4 = 1.6381	K06 = $1.1\text{E-}3 \text{ meq/m}^2/\text{day}$
-Lateral and Vertical Flows:	c) Sulfate Parameters
KLAT3 = 242.810	CF = 2.0247
KLAT4 = 14.791	KP3 = $6.0\text{E-}5 \text{ eq/kg/eq/m}^3$
KPERC3 = $1.3117\text{E-}2$	KP4 = $4.90\text{E-}6 \text{ eq/kg/eq/m}^3$
KPERC4 = $1.1741\text{E-}2$	K = $2.033\text{E-}3 \text{ 1/day}$
	KP6 = $4.90\text{E-}7 \text{ eq/kg/eq/m}^3$
-Groundwater:	
D1 = 0.5963	
FRAX = 0.4804	
ALF1 = $6.2375\text{E-}4$	
ALF2 = $4.4043\text{E-}1$	

Table 4. Monthly hydrologic budget of Lake Woods

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Out 2	Out 3	Storage
0.1312E-01	0.0000E+00	0.6574E-01	0.5024E-01	0.3567E-02	0.1290E-02	0.2697E-01	0.1868E-01	0.5042E-01	0.1964E-01
0.1245E-01	0.0000E+00	0.5540E-01	0.4749E-02	0.5060E-04	0.1334E-02	0.2790E-05	0.1887E-01	0.5349E-01	0.1613E-02
0.4204E-02	0.1785E-02	0.2194E-01	0.3560E-02	0.6356E-06	0.1280E-02	0.2678E-05	0.1217E-01	0.2038E-01	0.2147E-03
0.4260E-02	0.1007E-01	0.2822E-01	0.3056E-02	0.1626E-05	0.1325E-02	0.2772E-05	0.2450E-03	0.4772E-01	-0.1041E-02
0.5955E-02	0.2636E-01	0.3538E-01	0.2616E-02	0.2067E-04	0.1323E-02	0.2768E-05	0.0000E+00	0.7069E-01	0.1466E-02
0.4233E-03	0.8484E-02	0.1175E-01	0.2338E-02	0.1486E-08	0.1187E-02	0.2483E-05	0.0000E+00	0.2599E-01	-0.1813E-02
0.1245E-01	0.6891E-01	0.8028E-01	0.4079E-02	0.2332E-03	0.1320E-02	0.2761E-05	0.5098E-03	0.1632E+00	0.3576E-02
0.9793E-02	0.1920E-01	0.6065E-01	0.5253E-02	0.4292E-04	0.1261E-02	0.2637E-05	0.6689E-02	0.9054E-01	-0.2033E-02
0.1230E-01	0.0000E+00	0.5327E-01	0.4714E-02	0.1293E-04	0.1293E-02	0.2704E-05	0.2003E-01	0.5035E-01	0.1208E-02
0.3133E-02	0.0000E+00	0.2286E-01	0.3251E-02	0.3353E-08	0.1242E-02	0.2597E-05	0.2607E-01	0.2122E-01	-0.1681E-01
0.7930E-02	0.0000E+00	0.2104E-01	0.1387E-02	0.1514E-04	0.1278E-02	0.2672E-05	0.2331E-01	0.6428E-02	0.1907E-02
0.1942E-01	0.0000E+00	0.8984E-01	0.3045E-02	0.3829E-03	0.1298E-02	0.2715E-05	0.1703E-01	0.8130E-01	0.1564E-01
0.1600E-01	0.0000E+00	0.8625E-01	0.6190E-02	0.1677E-02	0.1246E-02	0.2607E-05	0.1597E-01	0.1004E+00	-0.5006E-02
0.1324E-01	0.0000E+00	0.6279E-01	0.8018E-02	0.4294E-05	0.1279E-02	0.2674E-05	0.1196E-01	0.7107E-01	0.2294E-02
0.1279E-01	0.1077E-01	0.6037E-01	0.9889E-02	0.1093E-03	0.1234E-02	0.2580E-05	0.6632E-02	0.8525E-01	0.3277E-02
0.3951E-02	0.9904E-02	0.3495E-01	0.1213E-01	0.1898E-05	0.1267E-02	0.2650E-05	0.3115E-02	0.6367E-01	-0.4585E-02
0.5644E-04	0.1083E-01	0.7541E-02	0.1112E-01	0.9677E-09	0.1266E-02	0.2647E-05	0.4548E-03	0.3406E-01	-0.3699E-02
0.0000E+00	0.1703E-02	0.9018E-03	0.8006E-02	0.2984E-11	0.1142E-02	0.2389E-05	0.0000E+00	0.1395E-01	-0.2202E-02
0.5785E-02	0.3500E-01	0.3446E-01	0.7580E-02	0.4382E-05	0.1275E-02	0.2666E-05	0.0000E+00	0.7287E-01	0.1123E-01
0.1154E-01	0.4051E-02	0.6471E-01	0.1039E-01	0.3257E-04	0.1233E-02	0.2578E-05	0.1114E-01	0.8863E-01	-0.7816E-02
0.7845E-02	0.0000E+00	0.2384E-01	0.1005E-01	0.2671E-04	0.1265E-02	0.2646E-05	0.2267E-01	0.2115E-01	-0.8002E-03
0.1061E-01	0.0000E+00	0.5914E-01	0.9609E-02	0.4241E-04	0.1231E-02	0.2575E-05	0.2290E-01	0.6157E-01	-0.3832E-02
0.1781E-01	0.0000E+00	0.7446E-01	0.8473E-03	0.4743E-03	0.1276E-02	0.2668E-05	0.2083E-01	0.7312E-01	0.8532E-02
0.7734E-02	0.0000E+00	0.4004E-01	0.9623E-02	0.1324E-05	0.1274E-02	0.2658E-05	0.1729E-01	0.4671E-01	-0.5341E-02
0.2128E+00	0.2066E+00	0.1096E+01	0.1541E+00	0.6702E-02	0.3042E-01	0.6361E-04	0.2766E+00	0.1414E+01	0.1563E-01

Note: Unit: m of water per month (over the entire watershed-207 ha)

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Out 2: Evaporation from the Lake,

Out 3: Outflow from the Lake,

Storage: Change in Lake storage

Table 5. Monthly alkalinity budget of Lake Woods

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Input 7	Out 2	Reaction	Storage
-0.2422E+04	0.0000E+00	-0.1626E+05	0.4234E+02	-0.6581E+03	0.7914E+02	-0.5304E-01	-0.1371E+04	-0.1080E+04	0.1984E+05	0.3227E+03
-0.1602E+04	0.0000E+00	-0.1552E+05	0.4596E+02	-0.5393E+01	0.8021E+02	-0.4525E-01	-0.5911E+03	-0.8703E+03	0.2049E+05	0.3762E+04
-0.5029E+03	-0.2830E+03	-0.2795E+04	0.1612E+03	-0.6299E-01	0.7643E+02	-0.3153E-01	-0.4533E+03	-0.2404E+03	0.5125E+04	0.1568E+04
-0.5001E+03	-0.2779E+04	-0.3422E+04	0.1323E+03	-0.1952E+00	0.8076E+02	-0.5408E-01	-0.4128E+03	-0.9530E+03	0.6732E+03	-0.5274E+04
-0.1904E+03	-0.1429E+04	-0.3377E+04	0.1256E+03	-0.5271E+00	0.8231E+02	-0.8884E-01	-0.6987E+03	-0.2250E+04	0.5263E+03	-0.2712E+04
-0.2469E+02	-0.1850E+04	-0.6738E+03	0.1589E+03	-0.7992E-04	0.7523E+02	-0.8309E-01	-0.3252E+03	-0.8844E+03	0.3564E+03	-0.1398E+04
-0.1843E+04	-0.1162E+05	-0.1238E+05	0.7297E+02	-0.1585E+04	0.8467E+02	-0.1686E+00	-0.4806E+03	-0.1033E+05	0.3320E+04	-0.1253E+05
-0.8506E+03	-0.2065E+04	-0.1015E+05	0.1294E+03	-0.3699E+01	0.7888E+02	-0.2085E+00	-0.4802E+03	-0.7234E+04	0.2018E+05	0.1409E+05
-0.3054E+04	0.0000E+00	-0.1455E+05	0.1110E+03	-0.3630E+01	0.8070E+02	-0.1648E+00	-0.1032E+04	-0.3092E+04	0.2595E+05	0.1059E+05
-0.6480E+03	0.0000E+00	-0.6523E+04	0.1129E+03	-0.4542E-03	0.7797E+02	-0.1159E+00	-0.9860E+03	-0.1063E+04	0.2398E+05	0.1707E+05
-0.1174E+04	0.0000E+00	-0.5554E+04	0.1412E+03	-0.2490E+01	0.8420E+02	-0.5417E-01	-0.9333E+03	-0.1478E+03	0.2240E+05	0.1511E+05
-0.3076E+04	0.0000E+00	-0.1943E+05	-0.8055E+02	-0.6853E+02	0.8848E+02	-0.2266E-01	-0.1030E+04	-0.6931E+03	0.2094E+05	-0.1966E+04
-0.6549E+03	0.0000E+00	-0.1095E+05	0.1098E+03	-0.2161E+02	0.8317E+02	-0.1647E-01	-0.9784E+03	-0.7725E+03	0.1921E+05	0.7575E+04
-0.1843E+04	0.0000E+00	-0.1168E+05	0.3832E+03	-0.3258E+00	0.8639E+02	-0.1298E-01	-0.6410E+03	0.3590E+03	0.1764E+05	0.3588E+04
-0.1939E+04	-0.1940E+04	-0.1445E+05	0.5203E+03	-0.7882E+01	0.8516E+02	-0.1673E-01	-0.7328E+03	-0.8272E+03	0.4553E+04	-0.1308E+05
-0.4481E+03	-0.1887E+04	-0.5588E+04	0.1037E+04	-0.1115E+00	0.8917E+02	-0.7438E-01	-0.3494E+03	-0.1782E+04	0.1978E+04	-0.3387E+04
-0.1116E+02	-0.9072E+03	-0.9145E+03	0.1700E+04	0.0000E+00	0.9104E+02	-0.8332E-01	-0.2902E+03	-0.1082E+04	0.8470E+03	0.1596E+04
0.0000E+00	-0.7174E+03	-0.8231E+02	0.1847E+04	0.0000E+00	0.8425E+02	-0.7106E-01	-0.3214E+03	-0.4157E+03	0.8340E+02	0.1309E+04
-0.3480E+03	-0.6449E+04	-0.4706E+04	0.1968E+04	-0.1005E+00	0.9669E+02	-0.9005E-01	-0.3130E+03	-0.3051E+04	0.7628E+03	-0.5937E+04
-0.1662E+04	0.0000E+00	-0.1064E+05	0.1300E+04	-0.5098E+01	0.9623E+02	-0.1183E+00	-0.3457E+03	-0.4177E+04	0.1770E+05	0.1062E+05
-0.1507E+04	0.0000E+00	-0.4491E+04	0.1433E+04	-0.5058E+01	0.1026E+03	-0.5775E-01	-0.4720E+03	-0.4856E+03	0.2210E+05	0.1765E+05
-0.1180E+04	0.0000E+00	-0.1282E+05	0.8568E+03	-0.5069E+01	0.1046E+03	-0.2351E-01	-0.7038E+03	-0.6969E+03	0.1986E+05	0.6812E+04
-0.2285E+04	0.0000E+00	-0.1777E+05	0.6407E+03	-0.6183E+02	0.1131E+03	0.6008E-02	-0.1296E+04	0.6133E+02	0.1894E+05	-0.1778E+04
-0.1795E+04	0.0000E+00	-0.1219E+05	0.4229E+03	-0.2357E+00	0.1156E+03	-0.1546E-02	-0.1430E+04	-0.8706E+02	0.1911E+05	0.4312E+04
-0.2956E+05	-0.3192E+05	-0.2169E+06	0.1337E+05	-0.8661E+03	0.2117E+04	-0.1623E+01	-0.1667E+05	-0.4180E+05	0.3066E+06	0.6791E+05

Note: Unit: eq per month

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Out 7: Dry deposition to the Lake,

Out 2: Outflow from the Lake,

Reaction: Internal production in the Lake compartment,

Storage: Change in Lake storage

Table 6. Monthly Sulfate Budget of Lake Woods

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Input 7	Out 2	Reaction	Storage
0.0626E+04	0.0000E+00	0.3149E+05	0.2269E+04	0.1105E+04	0.4540E+04	0.6461E+00	0.1877E+04	0.1223E+05	-0.9570E+04	0.908E+050
0.1246E+04	0.0000E+00	0.1818E+05	0.2255E+04	0.4287E+01	0.5223E+03	0.6991E+00	0.8164E+03	0.1340E+05	-0.1027E+05	-0.6547E+04
0.4671E+03	0.2263E+03	0.3688E+04	0.1385E+04	0.4030E-01	0.5352E+03	0.6820E+00	0.6320E+03	0.5196E+04	0.4221E+04	0.5957E+04
0.4115E+03	0.4055E+04	0.3662E+04	0.8586E+03	0.1654E+00	0.5695E+03	0.7437E+00	0.3551E+03	0.1279E+05	0.9928E+04	0.7750E+04
0.1091E+03	0.1515E+04	0.3998E+04	0.5840E+03	0.2800E+00	0.5760E+03	0.7764E+00	0.5226E+03	0.1969E+05	0.1147E+05	-0.9139E+03
0.5187E+02	0.1251E+04	0.9071E+03	0.3649E+03	0.1679E-03	0.5190E+03	0.7135E+00	0.3001E+0	0.7480E+04	0.1060E+05	0.6514E+04
0.1657E+04	0.1018E+05	0.1242E+05	0.5640E+03	0.1581E+03	0.5769E+03	0.8069E+00	0.8021E+03	0.4789E+05	0.1112E+05	-0.1055E+05
0.7829E+03	0.1601E+04	0.1147E+05	0.9341E+03	0.3747E+01	0.5547E+03	0.7753E+00	0.7569E+03	0.2664E+05	-0.4927E+04	-0.1546E+05
0.2727E+04	0.0000E+00	0.1722E+05	0.1061E+04	0.2768E+01	0.3760E+03	0.7624E+00	0.1391E+04	0.1420E+05	-0.1148E+05	-0.2701E+04
0.7986E+03	0.0000E+00	0.1157E+03	0.1205E+04	0.5058E-03	0.5683E+03	0.7352E+00	0.1760E+04	0.5987E+04	-0.1128E+05	-0.1374E+04
0.1338E+04	0.0000E+00	0.1104E+05	0.9052E+03	0.2930E+01	0.5982E+03	0.7722E+00	0.1750E+04	0.1855E+04	-0.1178E+05	0.1993E+04
0.2953E+04	0.0000E+00	0.2598E+05	0.1573E+04	0.6855E+02	0.6253E+03	0.7705E+00	0.1632E+04	0.2301E+05	-0.1182E+05	-0.2005E+04
0.6886E+03	0.0000E+00	0.1434E+05	0.1968E+04	0.1559E+02	0.6222E+03	0.6859E+00	0.1183E+04	0.2666E+00	-0.1063E+05	-0.1848E+05
0.1594E+04	0.0000E+00	0.1390E+05	0.2146E+04	0.4453E+00	0.6458E+03	0.6559E+00	0.1054E+04	0.1740E+05	-0.1008E+05	-0.8142E+04
0.1397E+04	0.1659E+04	0.1378E+05	0.2599E+04	0.6997E+01	0.6234E+03	0.6364E+00	0.8377E+03	0.2113E+05	0.4135E+04	0.3885E+04
0.3584E+03	0.1507E+04	0.6128E+04	0.2954E+04	0.7853E-01	0.6390E+03	0.6863E+00	0.4492E+03	0.1645E+05	0.9597E+04	0.5185E+04
0.8891E+01	0.8238E+03	0.1209E+04	0.2587E+04	0.0000E+00	0.6366E+03	0.7200E+00	0.3465E+03	0.9255E+04	0.1109E+05	0.7446E+04
0.0000E+00	0.5288E+03	0.1498E+03	0.1845E+04	0.0000E+00	0.5732E+03	0.6558E+00	0.3001E+03	0.4001E+04	-0.1054E+05	0.9932E+04
0.2418E+03	0.5031E+04	0.4267E+04	0.1674E+04	0.9790E-01	0.6378E+03	0.8048E+00	0.3822E+03	0.2215E+05	0.1136E+05	0.1445E+04
0.1151E-04	0.0000E+00	0.9947E+04	0.1947E+04	0.3166E+01	0.6158E+03	0.7512E+00	0.6369E+03	0.2596E+05	-0.4874E+04	-0.1653E+05
0.1693E+04	0.0000E+00	0.7418E+04	0.2015E+04	0.5429E+01	0.6331E+03	0.7378E+00	0.8520E+03	0.5903E+04	-0.1130E+05	-0.4583E+04
0.1298E+04	0.0000E+00	0.1723E+05	0.2461E+04	0.4922E+01	0.6204E+03	0.7007E+00	0.1100E+04	0.1681E+05	-0.1095E+05	-0.5039E+04
0.2308E+04	0.0000E+00	0.2333E+05	0.2708E+04	0.6563E+02	0.6517E+03	0.7206E+00	0.1812E+04	0.1969E+05	0.1123E+05	-0.4112E+02
0.1513E+04	0.0000E+00	0.1415E+05	0.3370E+04	0.2192E+00	0.6600E+03	0.7068E+00	0.1565E+04	0.1243E+05	-0.1103E+05	-0.2198E+04
0.2848E+05	0.2832E+05	0.2782E+06	0.4223E+05	0.1308E+04	0.1423E+05	0.1738E+02	0.2311E+05	0.3882E+06	-0.4716E+05	-0.1949E+05

Note: Unit: m of water per month (over the entire watershed-207 ha)

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Out 2: Evaporation from the Lake,

Out 3: Outflow from the Lake,

Storage: Change in Lake storage

Table 7. MSE Evaluation for the calibration period

Variable	Units	n	MSE	RMSE
Discharge	m ³ /s	730	0.00225	0.0475
Cum. Discharge	m/yr	730	0.00133	0.0364
Chloride	μeq/L	77	3.47	1.86
Alkalinity	μeq/L	77	319.9	17.88
Sulfate	μeq/L	77	129.75	11.4

Table 8. MSE evaluation for the verification period

Variable	Units	n	MSE	RMSE
Discharge	m ³ /s	365	0.00468	0.0684
Cum. Discharge	m/yr	365	0.00144	0.1202
Chloride	μeq/L	45	3.57	1.89
Alkalinity	μeq/L	45	216.25	14.70
Sulfate	μeq/L	45	111.13	10.54

Table 9. Sensitivity analysis of hydrological parameters for outflow

PERCENT MSE OF OUTFLOW CHANGES

Parameter	$\bar{x} + 10\% \bar{x}$	$\bar{x} - 10\% \bar{x}$
BETA	-0.466	-6.335
KAPPA	2.236	-1.180
KPAN2	6.584	-1.863
KPAN3	0.435	-0.497
KPAN5	0.745	-0.839
KLAT3	-2.050	-1.739
KLAT4	-0.186	0.124
KPERC3	0.683	-0.745
KPERC4	0.124	-0.186
D1	0.093	-0.124
FRAX	0.217	0.062
ALF1	0.000	0.000
ALF2	-0.093	0.062

$$* \%MSE \text{ Change} = \left(\frac{MSE_{NEW} - MSE_{opt}}{MSE_{opt}} \right) * 100$$

Table 10. Sensitivity analysis of chemical parameters for alkalinity

PERCENT MSE OF OUTFLOW CHANGES

Parameter	$\bar{x} + 10\% \bar{x}$	$\bar{x} - 10\% \bar{x}$
CF	0.310	-0.207
RE3	-0.035	0.0000
KH4	-0.070	0.070
KH5	2.178	-1.522
KH6	0.000	0.000
K04	0.000	0.000
K05	1.660	-0.830
K06	0.000	0.000
KP3	0.207	-0.207
KP4	0.000	0.000
K	-1.660	2.144
KP6	0.000	0.000

$$* \%MSE \text{ Change} = \left(\frac{MSE_{NEW} - MSE_{opt}}{MSE_{opt}} \right) * 100$$

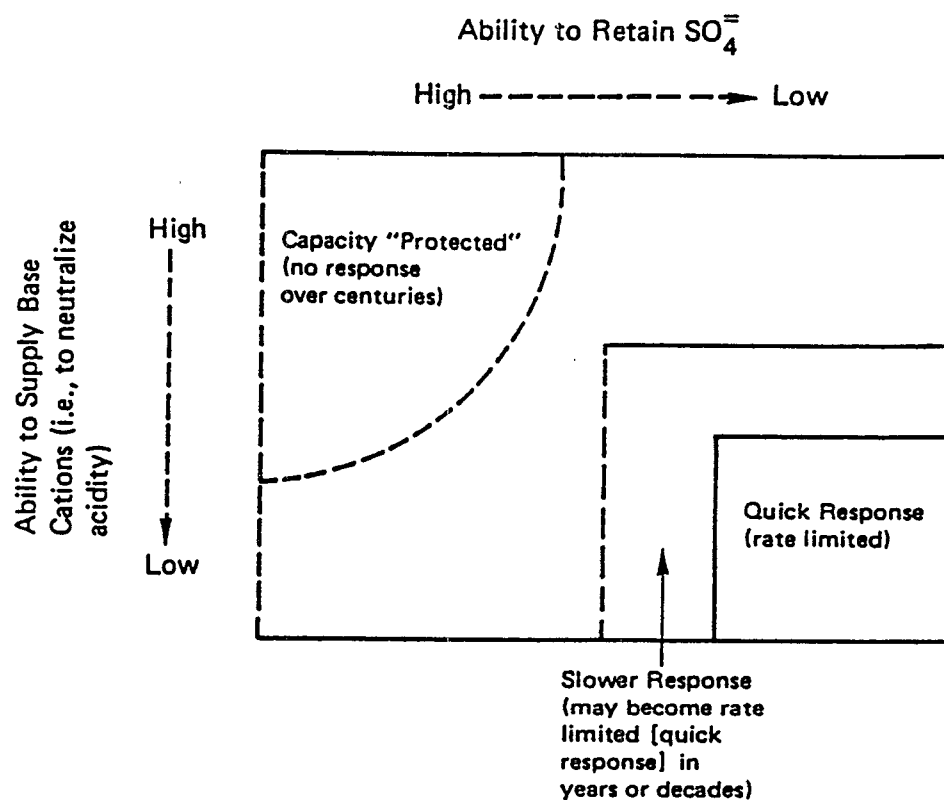


Figure 1. A qualitative presentation of the effect of two major soil properties -- the ability to retain sulfate and the ability to supply base cations -- on the rate at which streams and lakes respond to changes in acid deposition (NRC Panel on Lake Acidification, 1984).

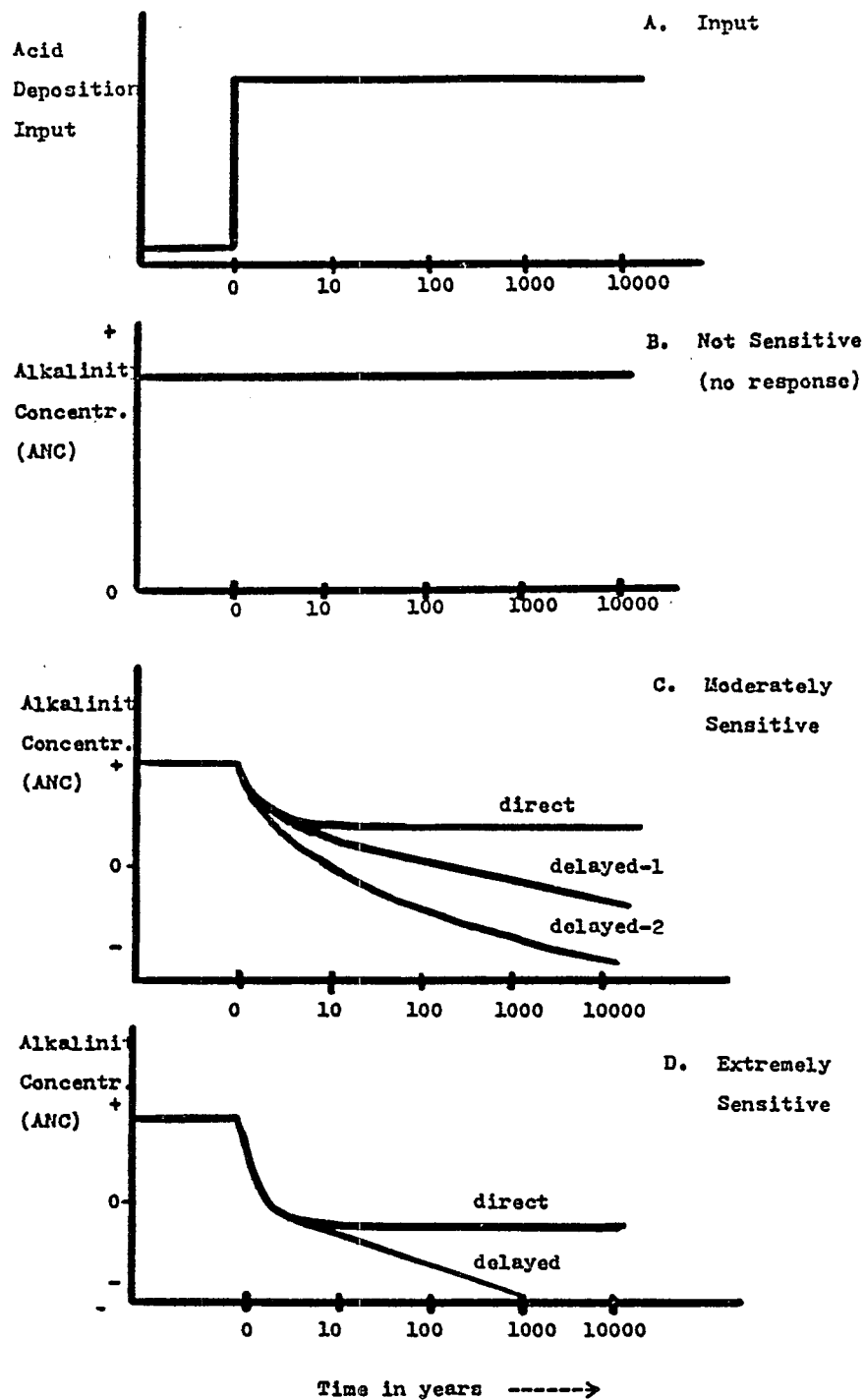


Figure 2. Direct and delayed responses of surface waters to a step-function increase in acid deposition (showing watershed sensitivity classes).

**LAKE WOODS
PERIOD : 9/78 - 8/80**

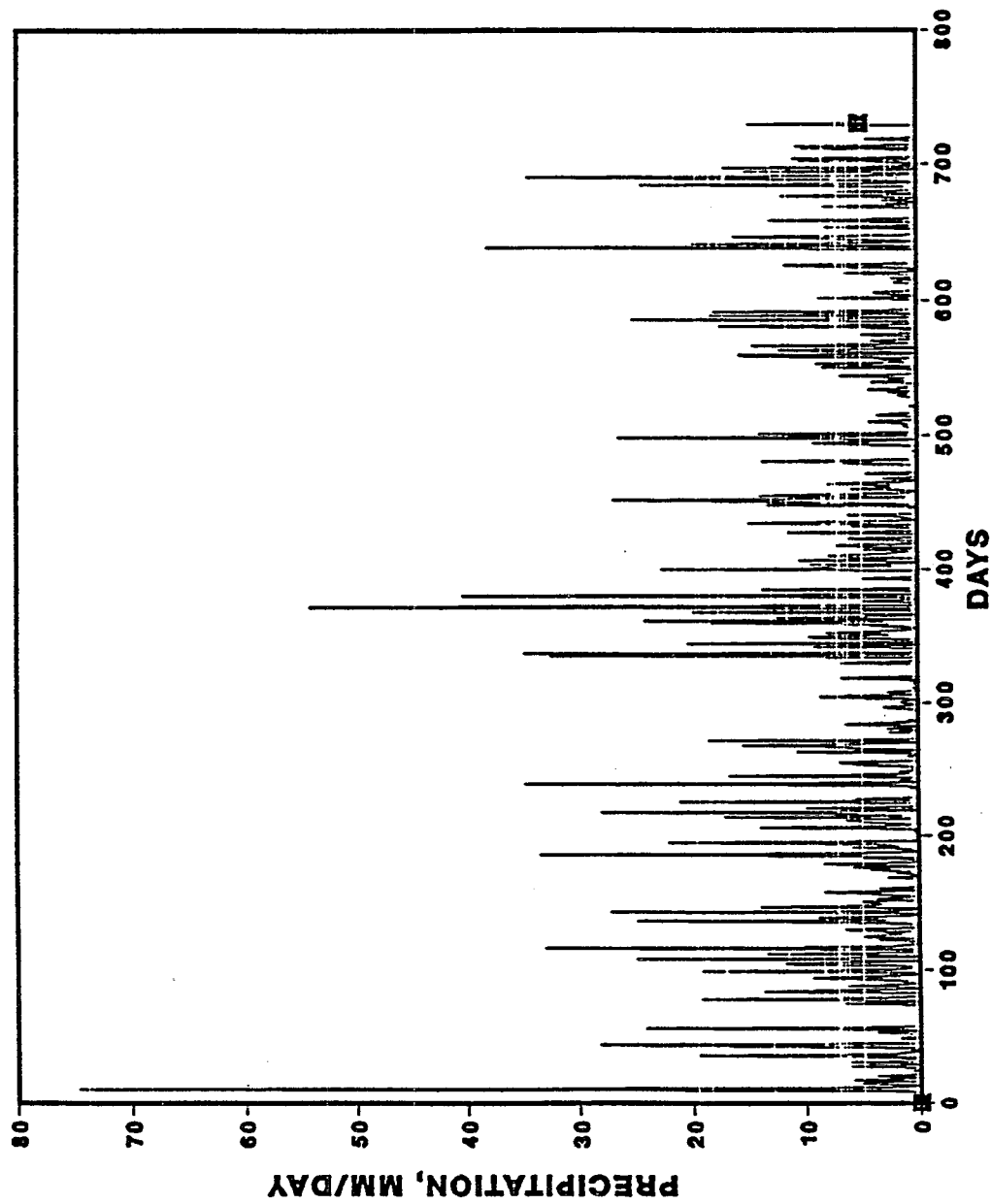


Figure 3. Precipitation data for the calibration period.

**LAKE WOODS
PERIOD : 9/78 - 8/80**

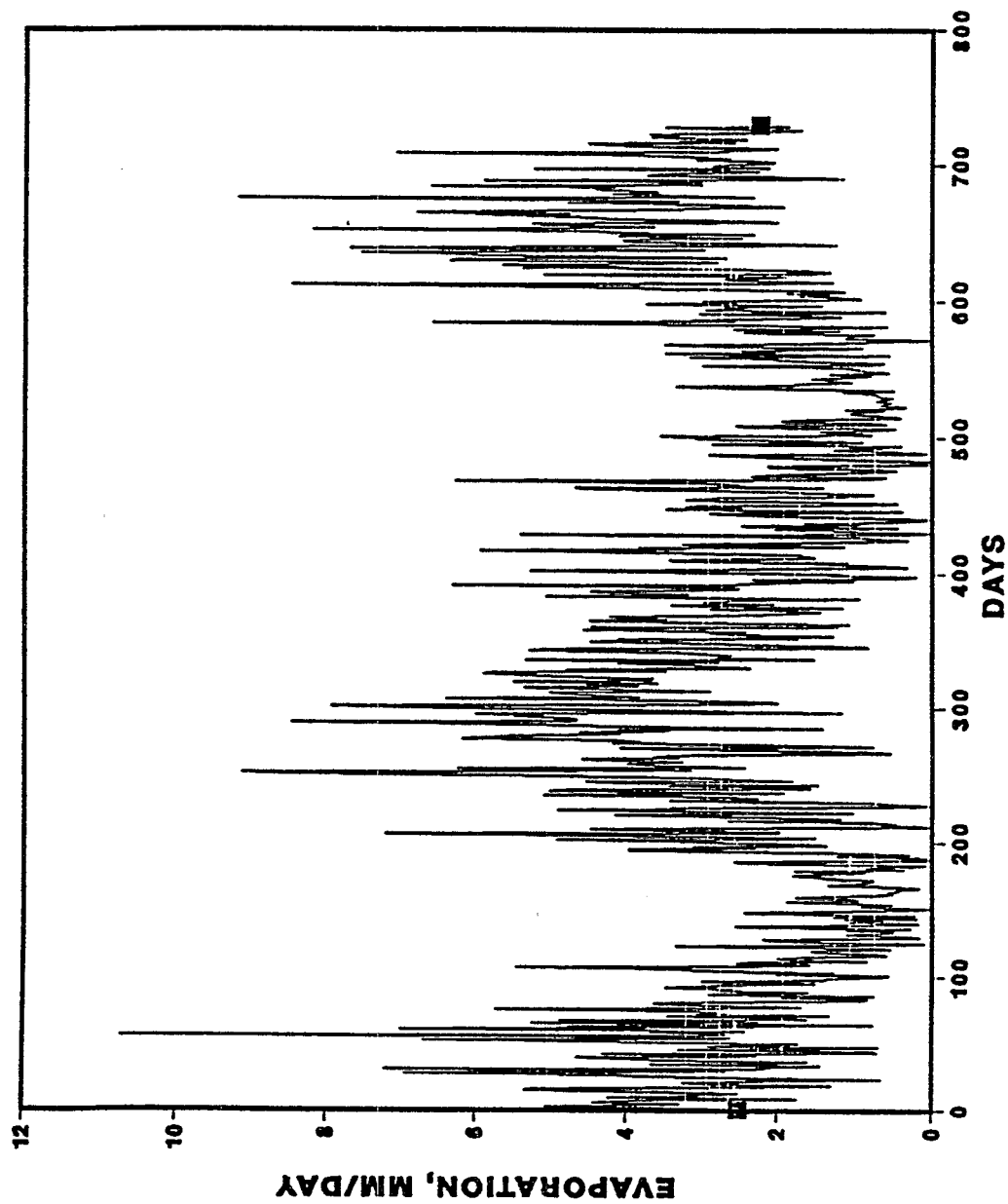


Figure 4. Evaporation data for the calibration period.

LAKE WOODS
PERIOD : 9/78 - 8/80

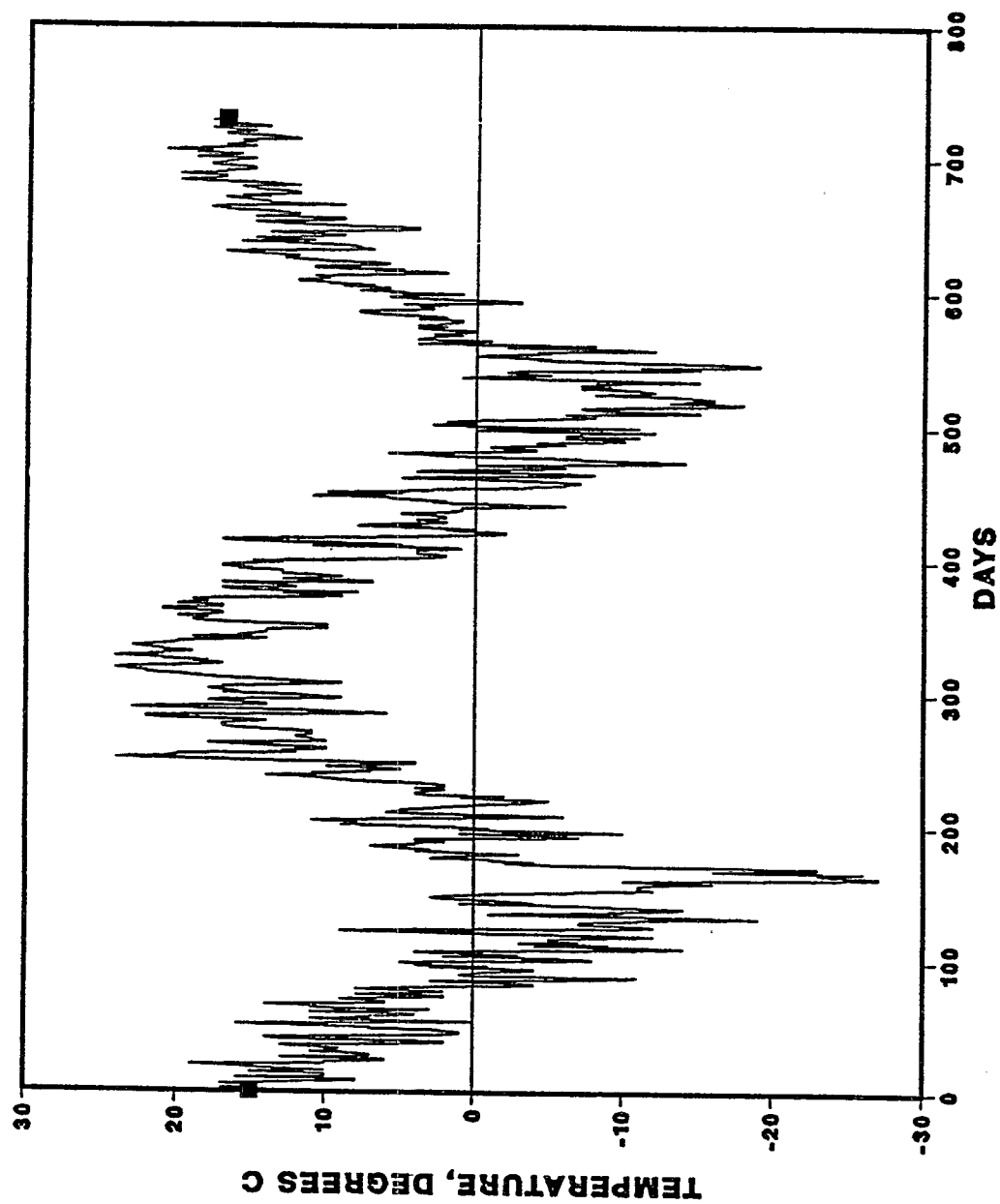


Figure 5. Temperature data for the calibration period.

**LAKE WOODS
PERIOD : 9/80 - 8/81**

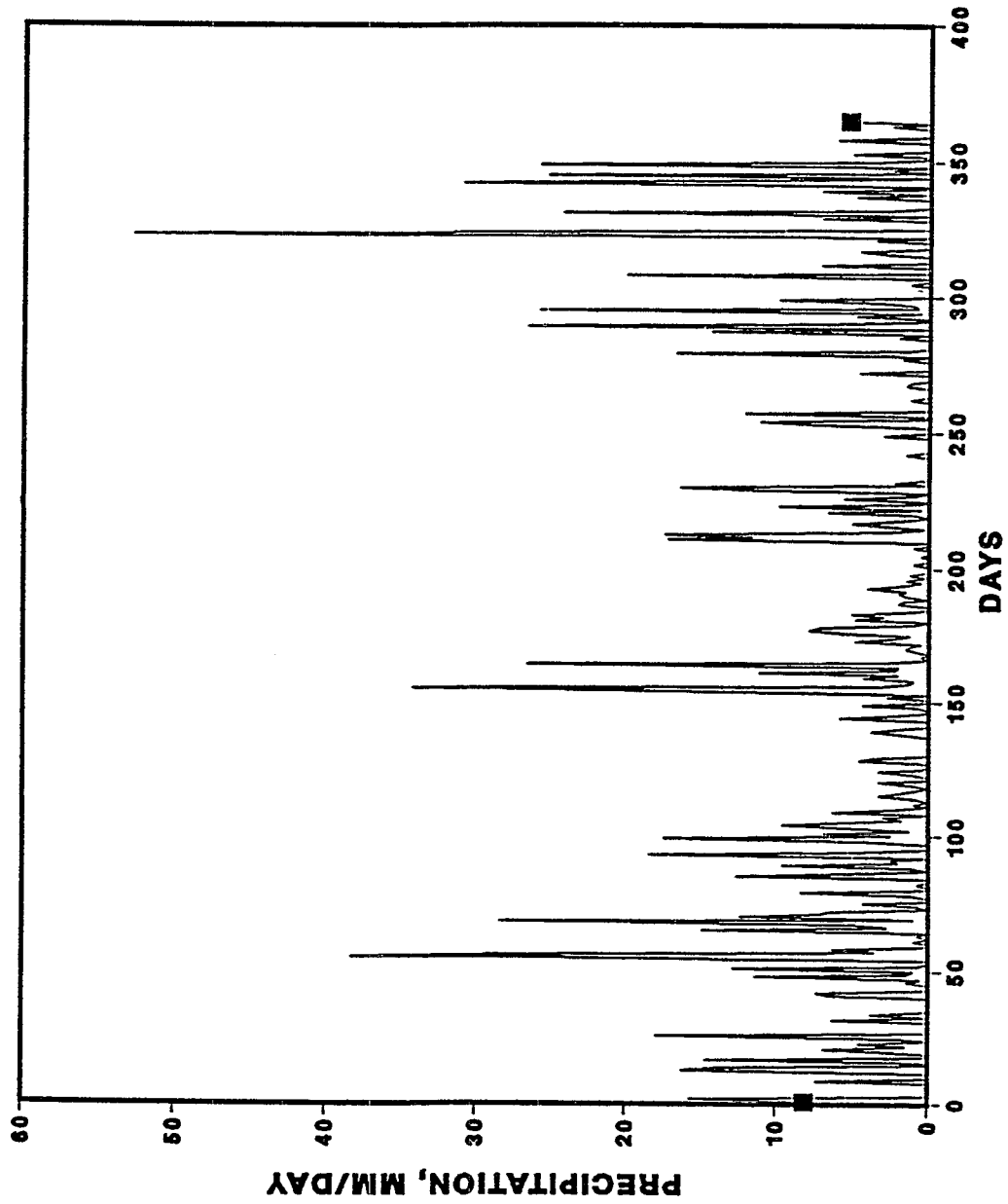


Figure 6. Precipitation data for the verification period.

**LAKE WOODS
PERIOD : 9/80 - 8/81**

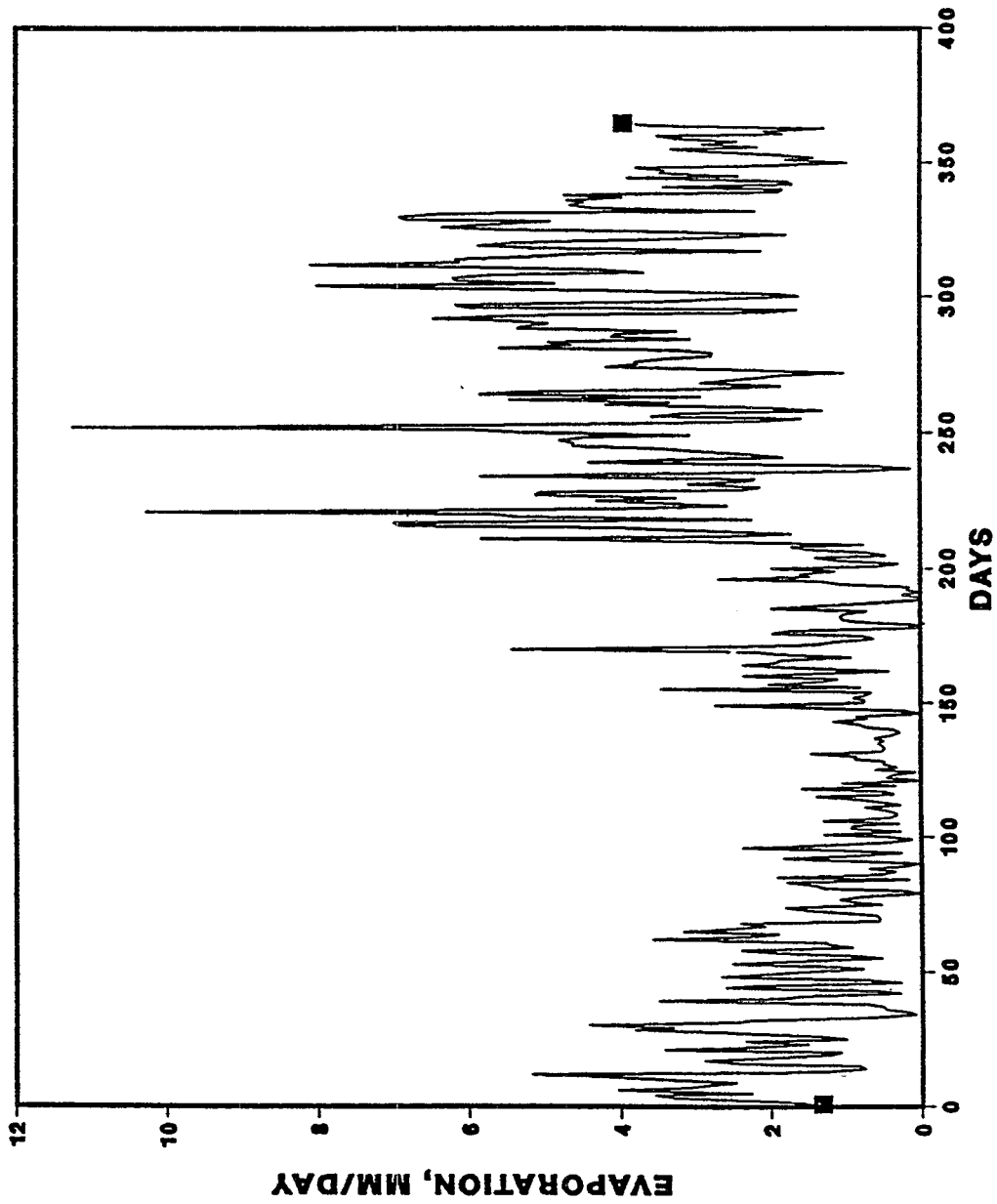


Figure 7. Evaporation data for the verification period.

LAKE WOODS
PERIOD : 9/80 - 8/81

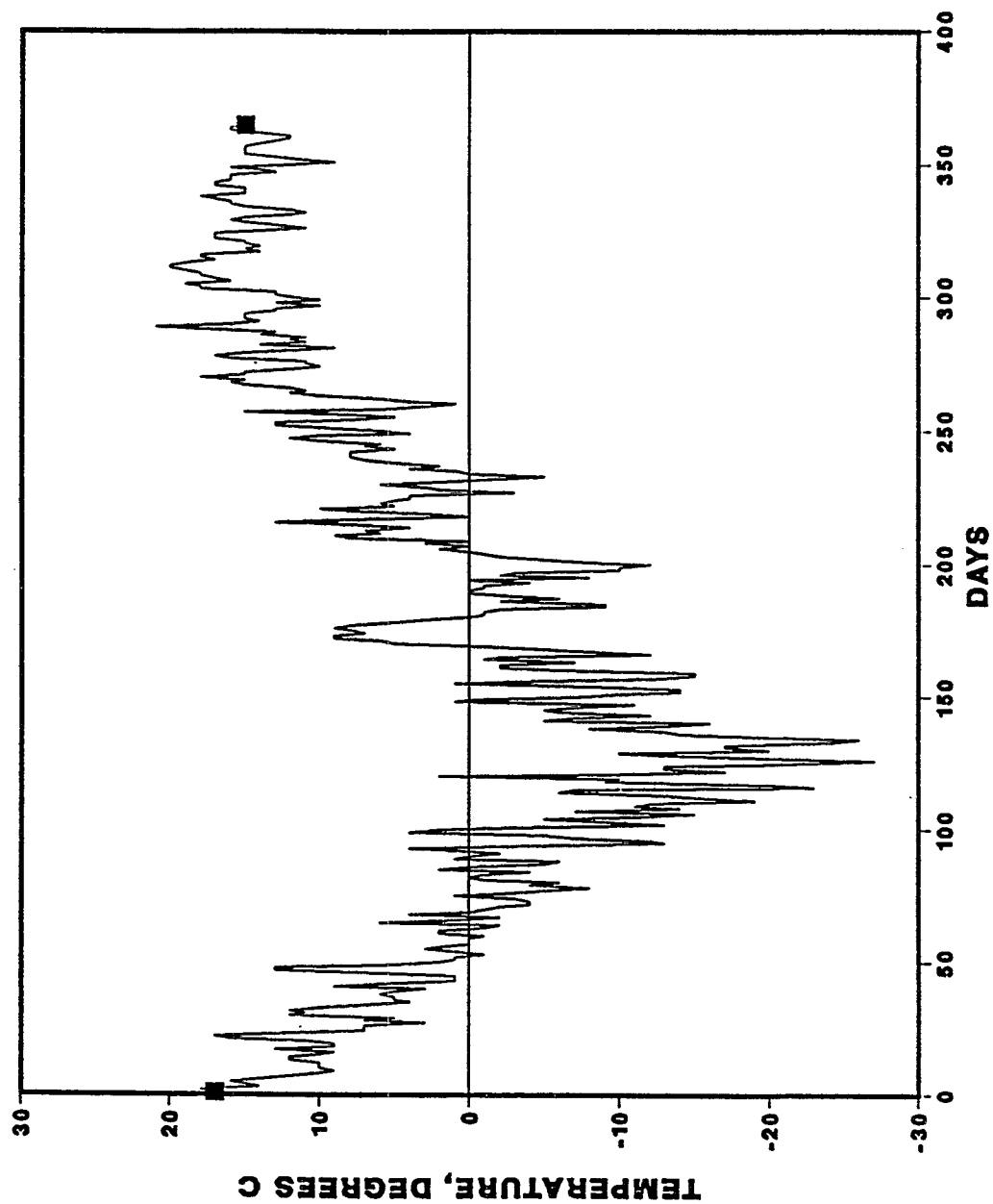


Figure 8. Temperature data for the verification period.

**LAKE WOODS
TIME SERIES OF SULFATE DEPOSITION INPUT
SIMULATION PERIOD: 9/1/78 - 8/31/81**

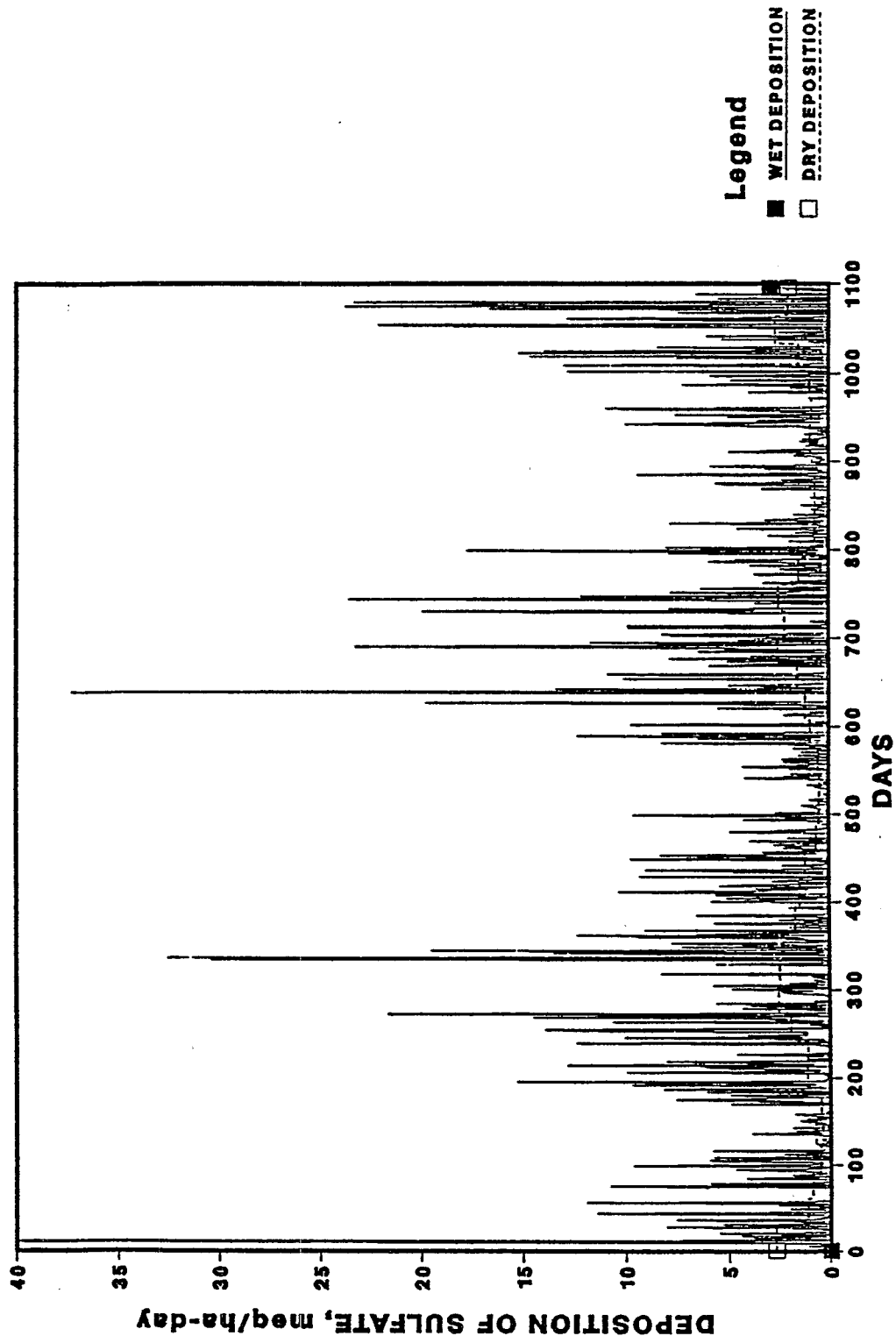


Figure 9. Three years data of wet and dry sulfate loading.

**LAKE WOODS
TIME SERIES OF ACID DEPOSITION
SIMULATION PERIOD: 9/1/78 - 8/31/81**

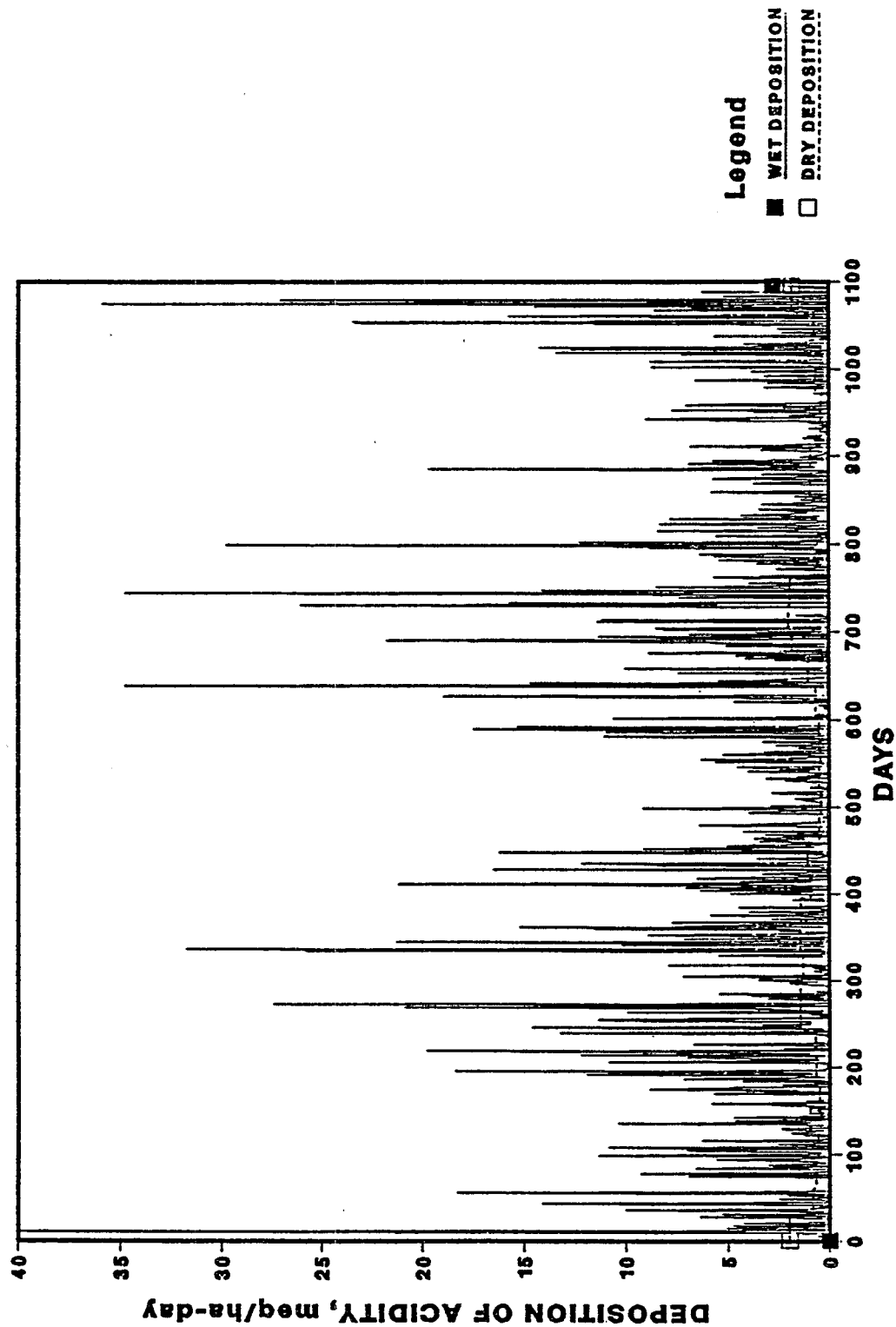


Figure 10. Three years data of wet and dry acidity loading.

LAKE WOODS COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS PERIOD : 9/78 - 8/80

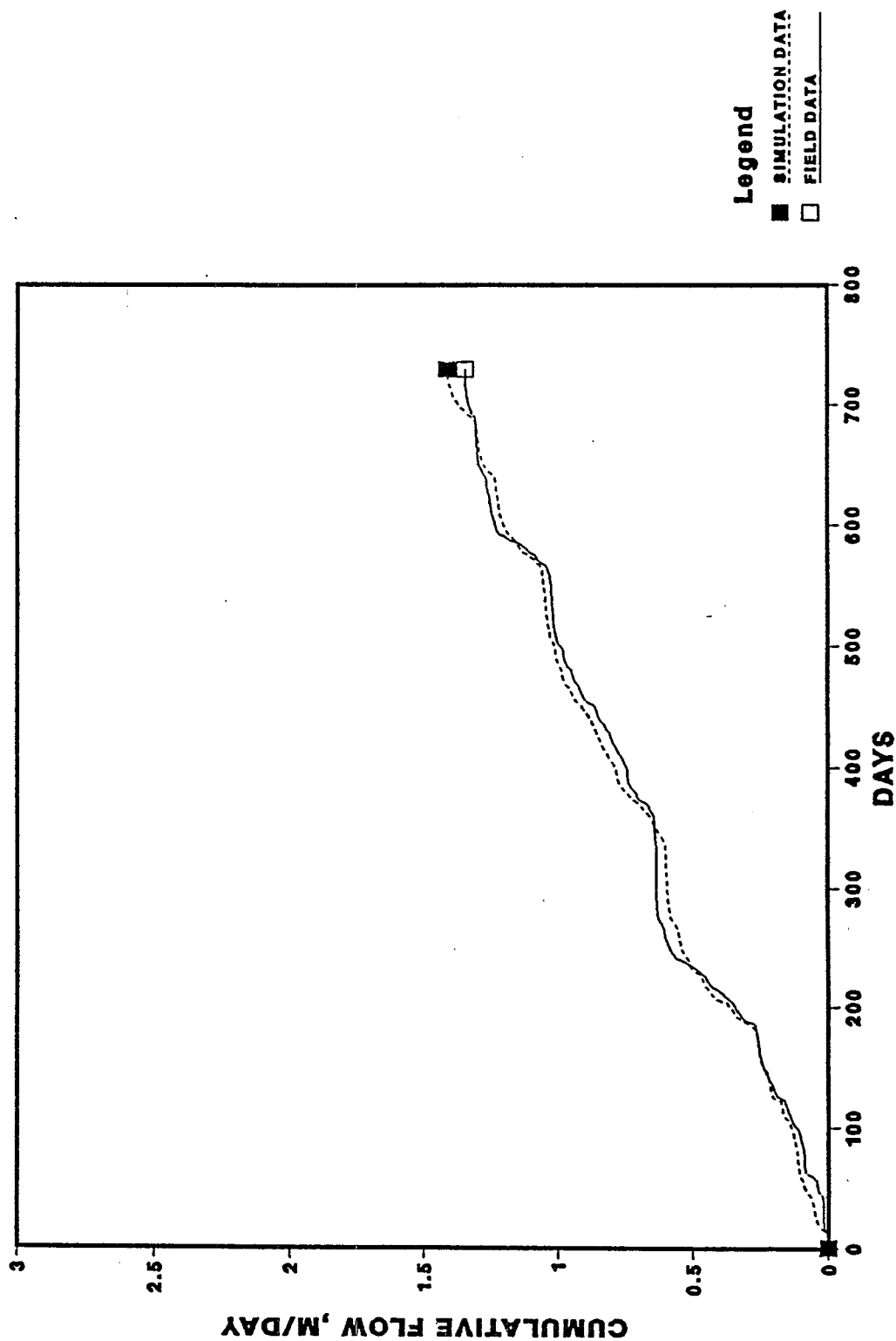


Figure 11. Calibration results of cumulative outflow.

LAKE WOODS **COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS** **PERIOD : 9/78 - 8/80**

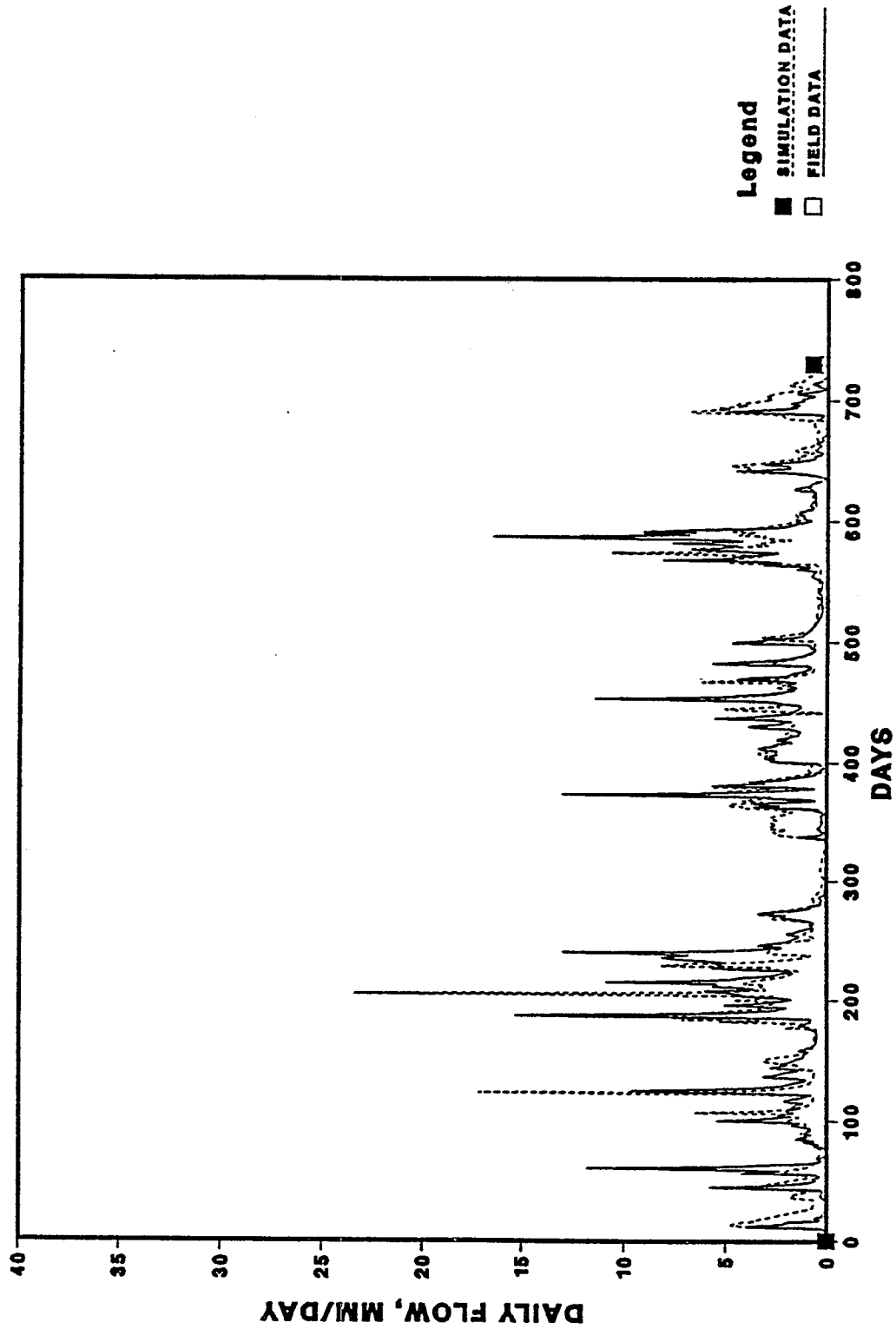


Figure 12. Calibration results of daily outflow.

LAKE WOODS
COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS
PERIOD : 9/78 - 8/80

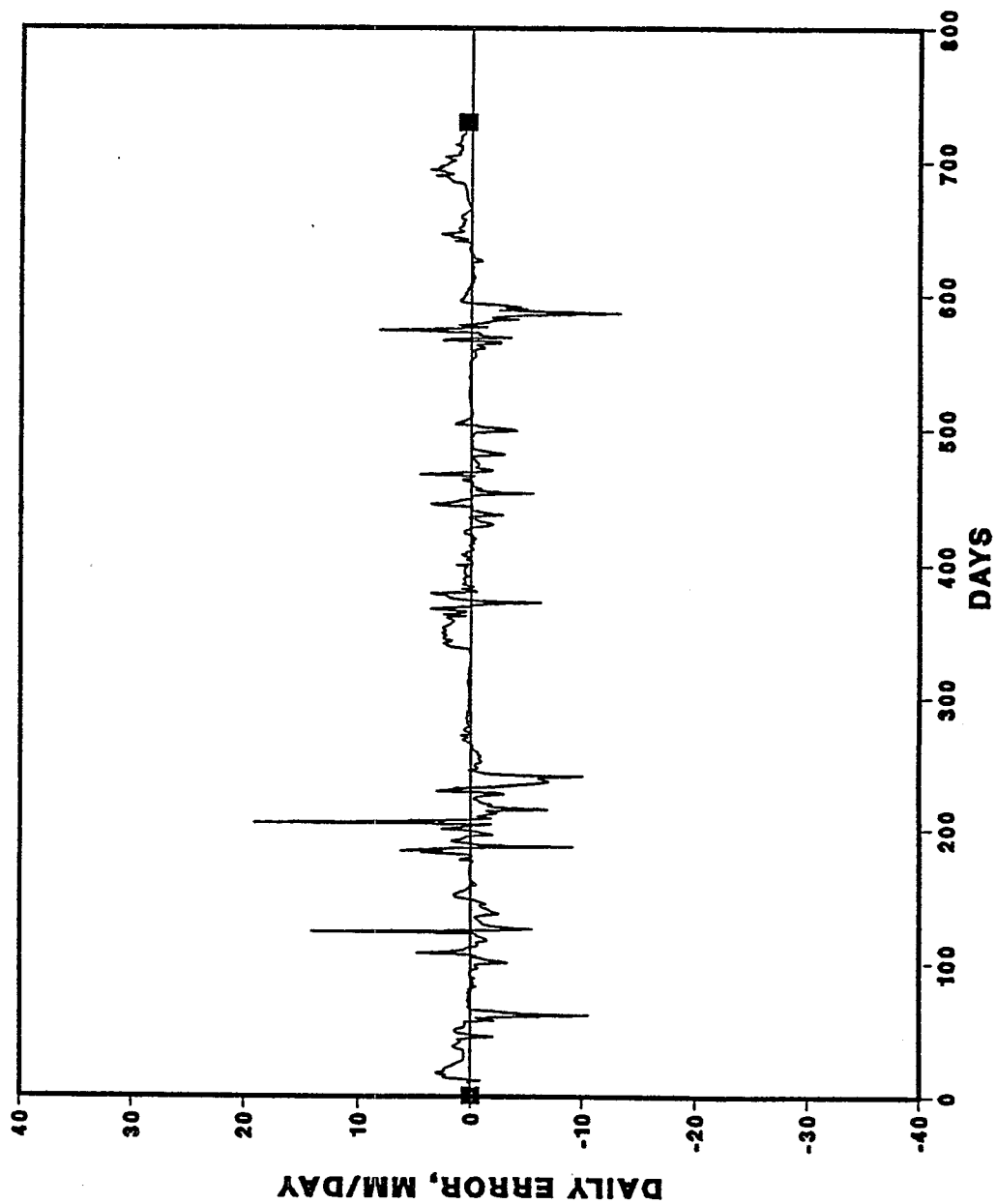


Figure 13. Results of daily outflow error.

LAKE WOODS **COMPARISON OF SIMULATED VERSUS FIELD CONCENTRATIONS** **PERIOD : 9/78 - 8/80**

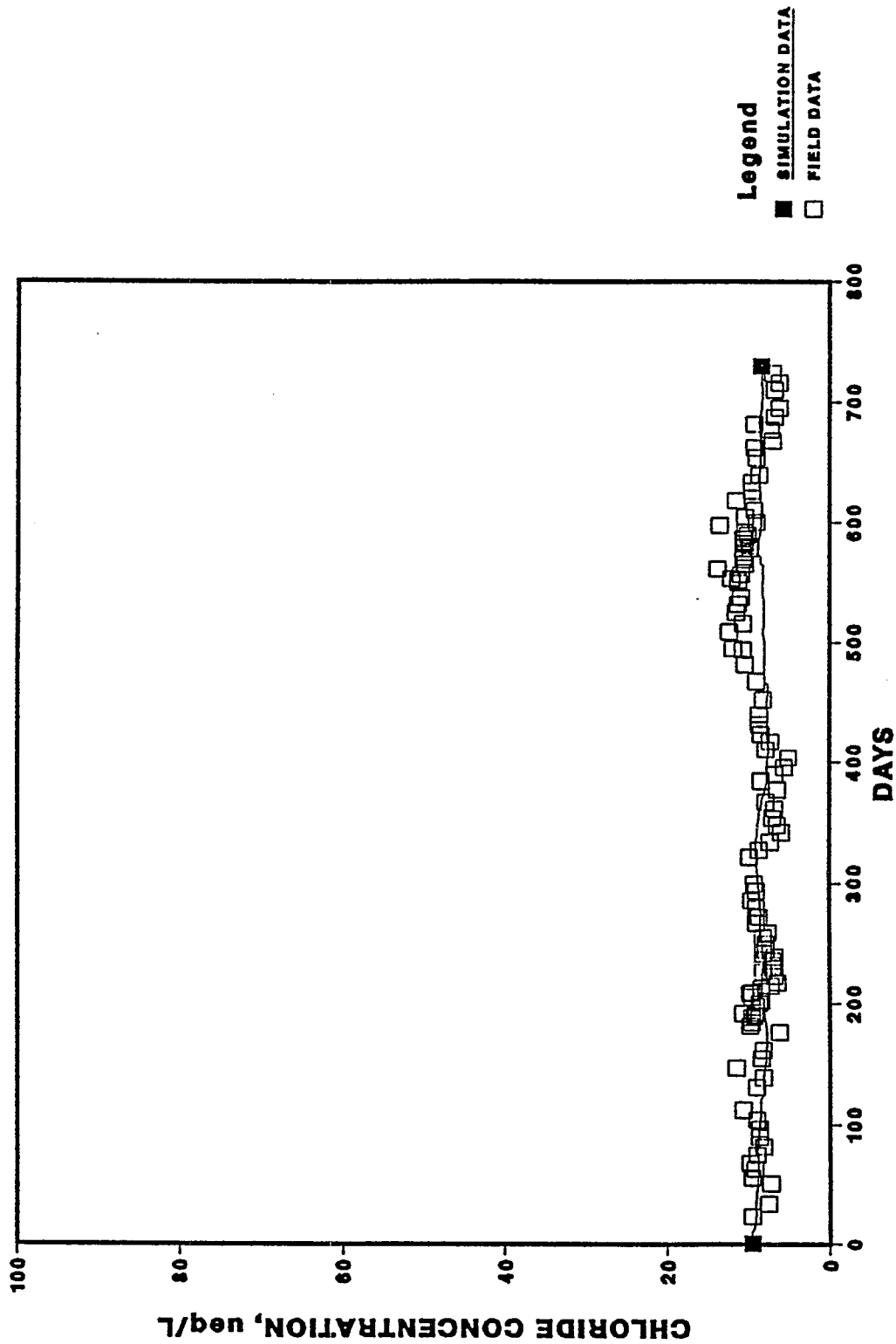


Figure 14. Calibration results of lake chloride.

LAKE WOODS COMPARISON OF SIMULATION AND FIELD SULFATE CALIBRATION PERIOD: 9/1/78 - 8/31/80

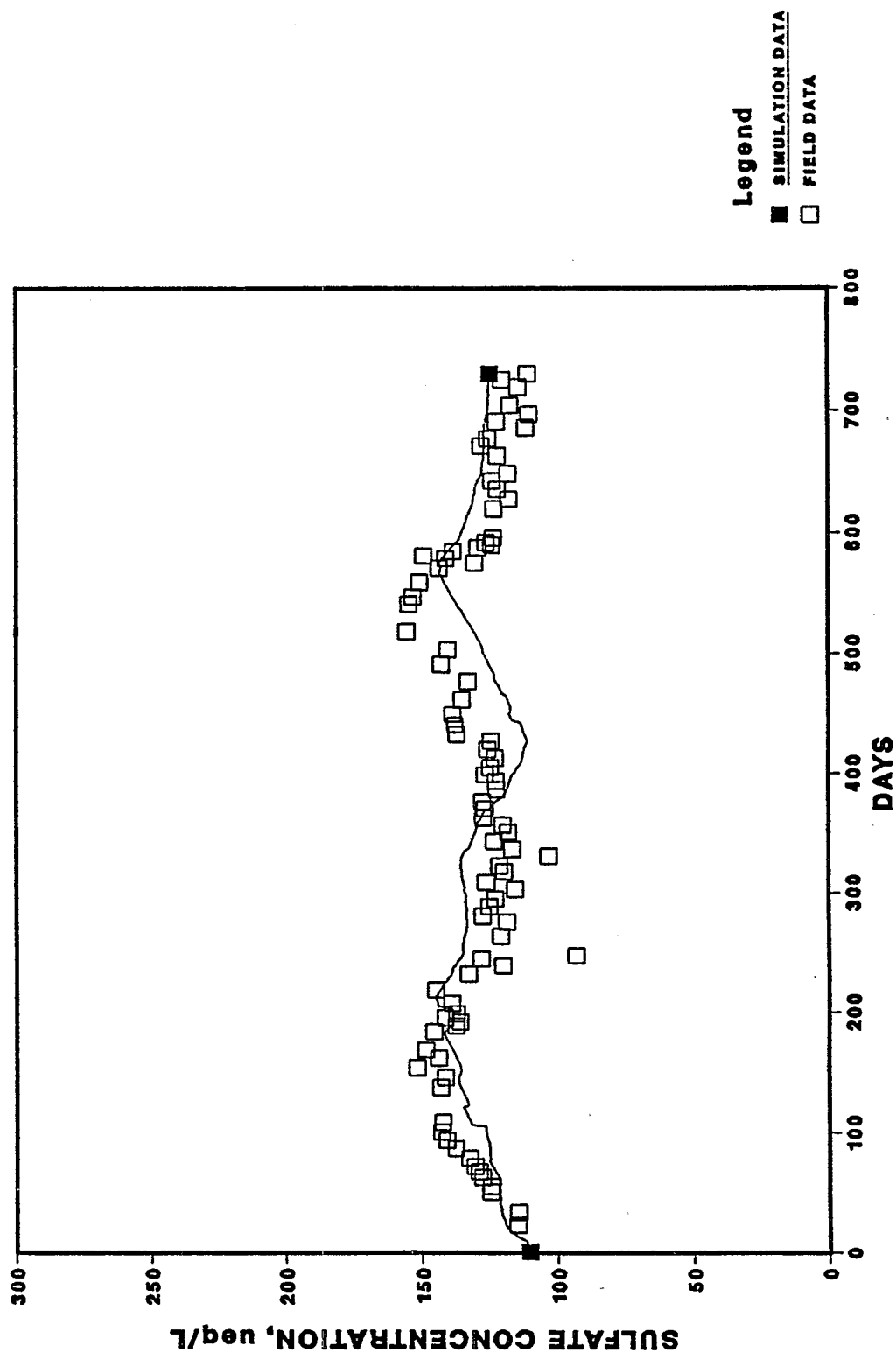


Figure 15. Calibration results of lake sulfate.

LAKE WOODS COMPARISON OF SIMULATION AND FIELD ALKALINITY CALIBRATION PERIOD: 9/1/78 - 8/31/80

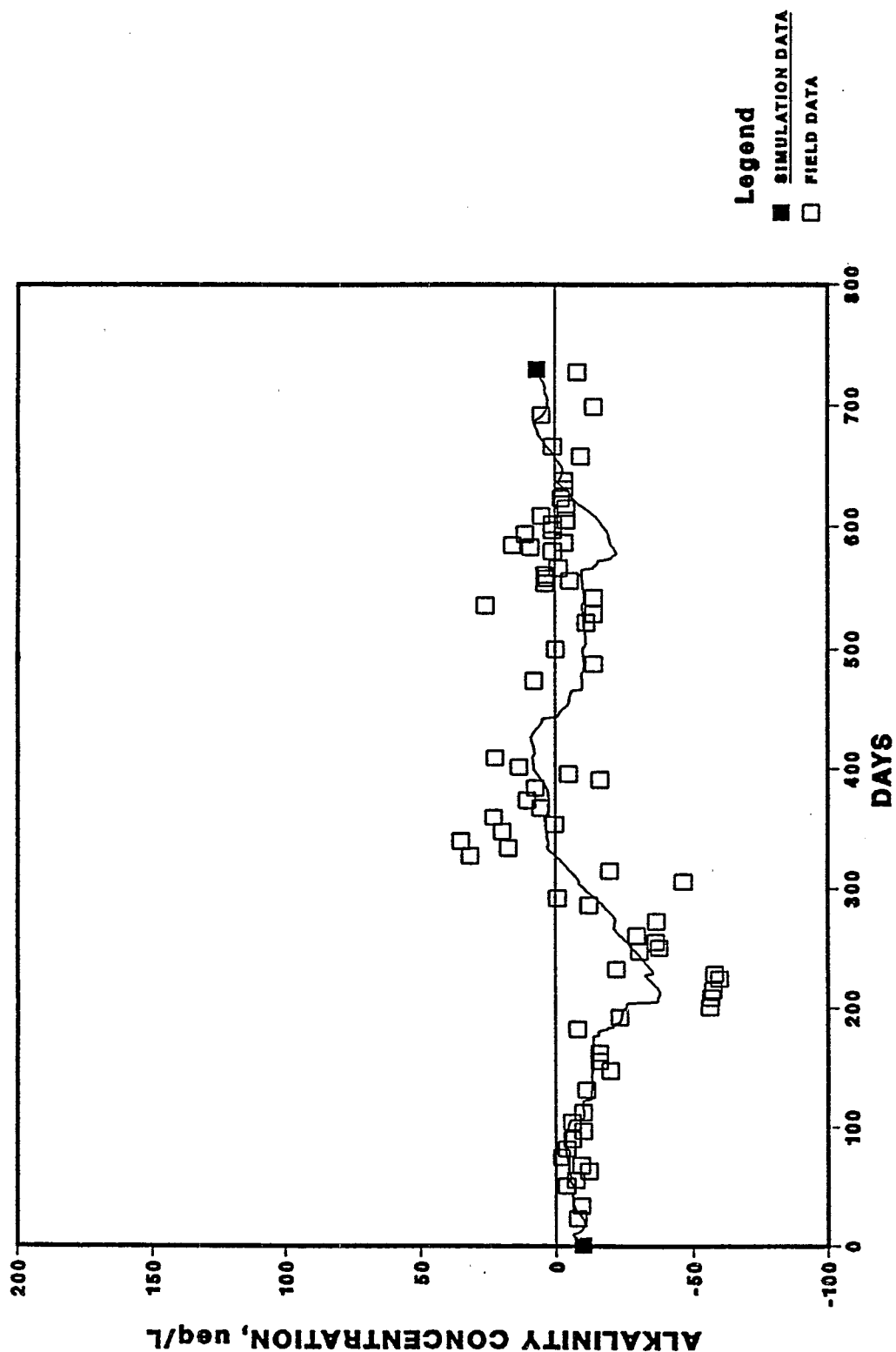


Figure 16. Calibration results of lake alkalinity.

LAKE WOODS COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS PERIOD : 9/80 - 8/81

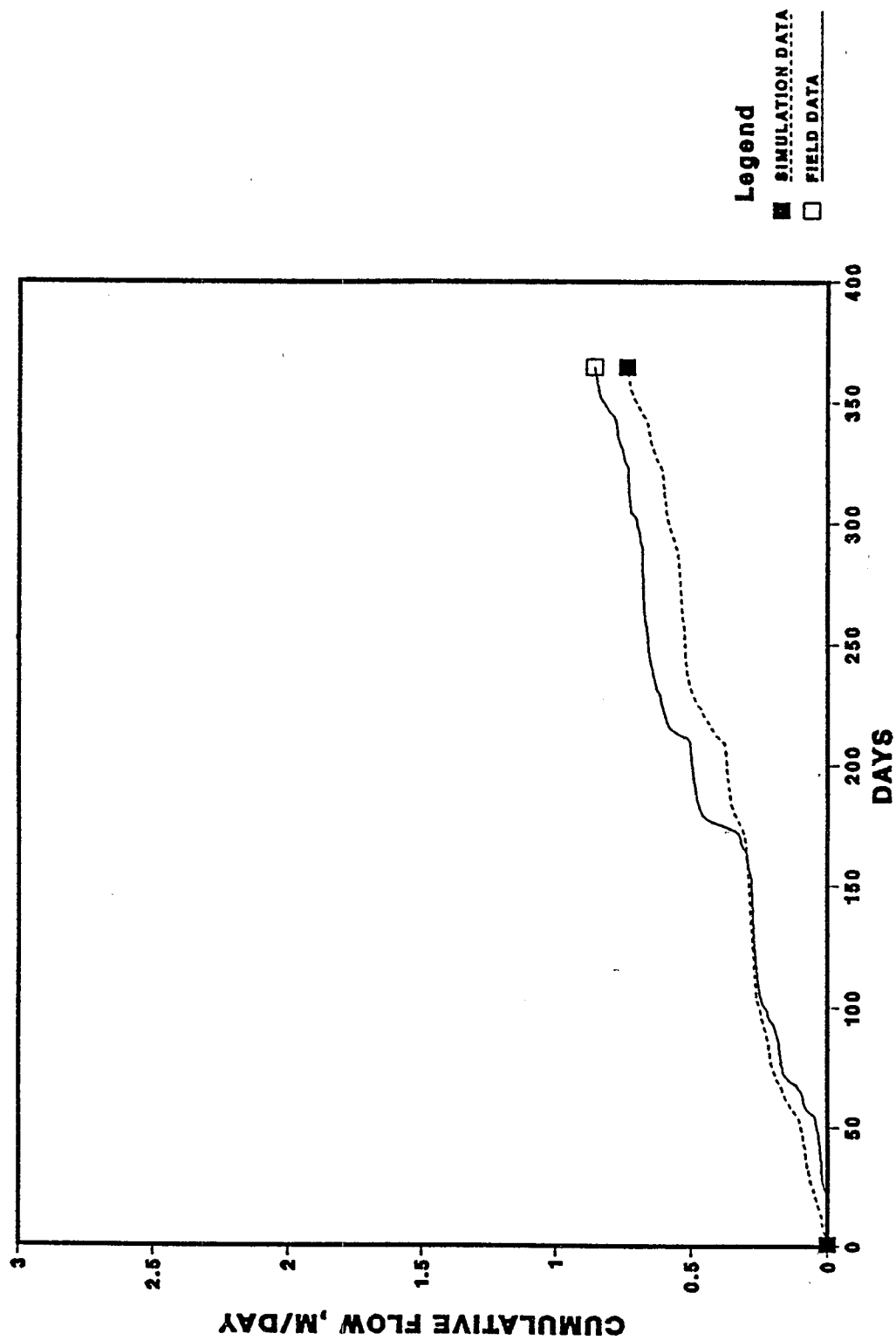


Figure 17. Verification results of cumulative outflow.

LAKE WOODS COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS PERIOD : 9/80 - 8/81

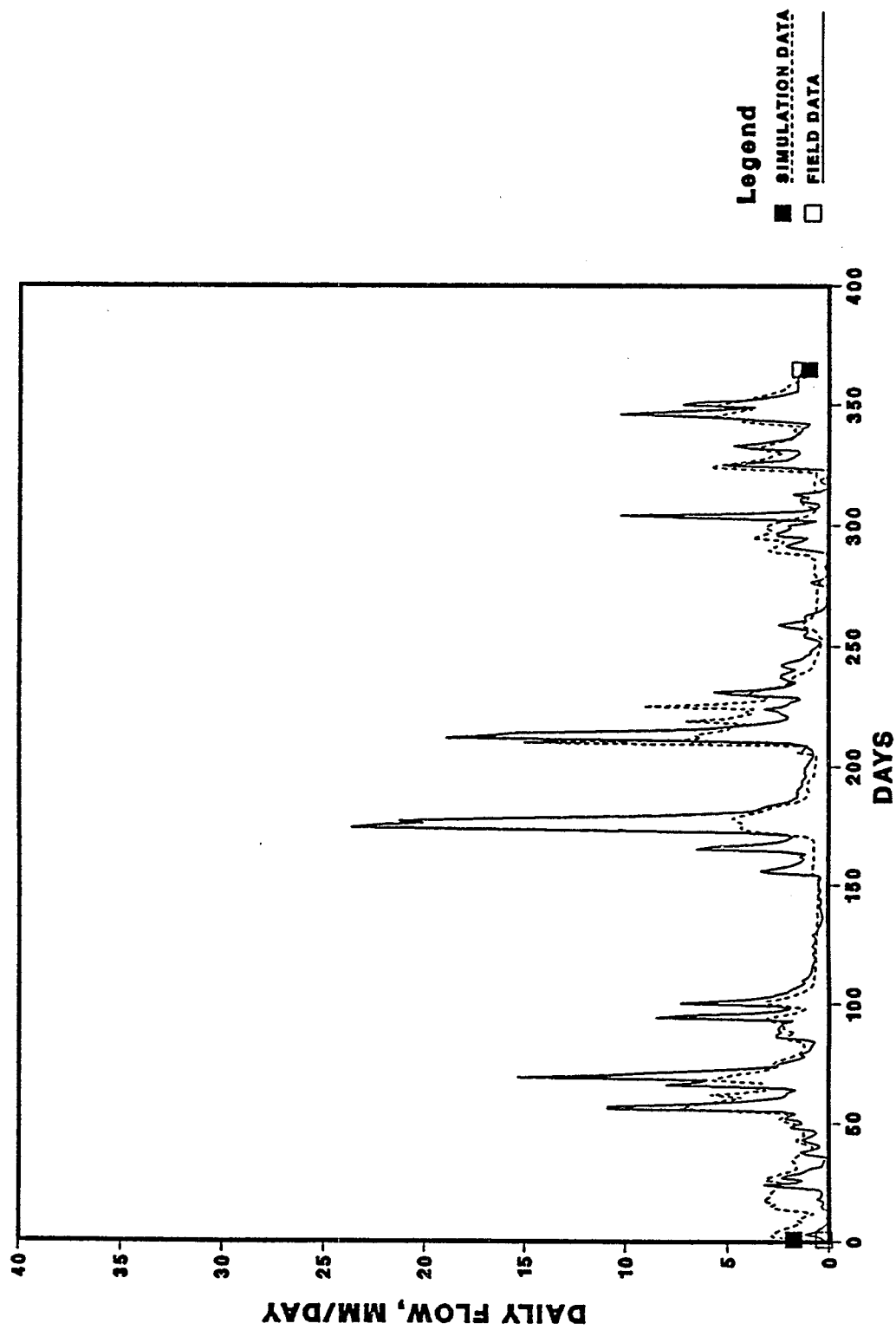


Figure 18. Verification results of daily outflow.

LAKE WOODS
COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS
PERIOD : 9/80 - 8/81

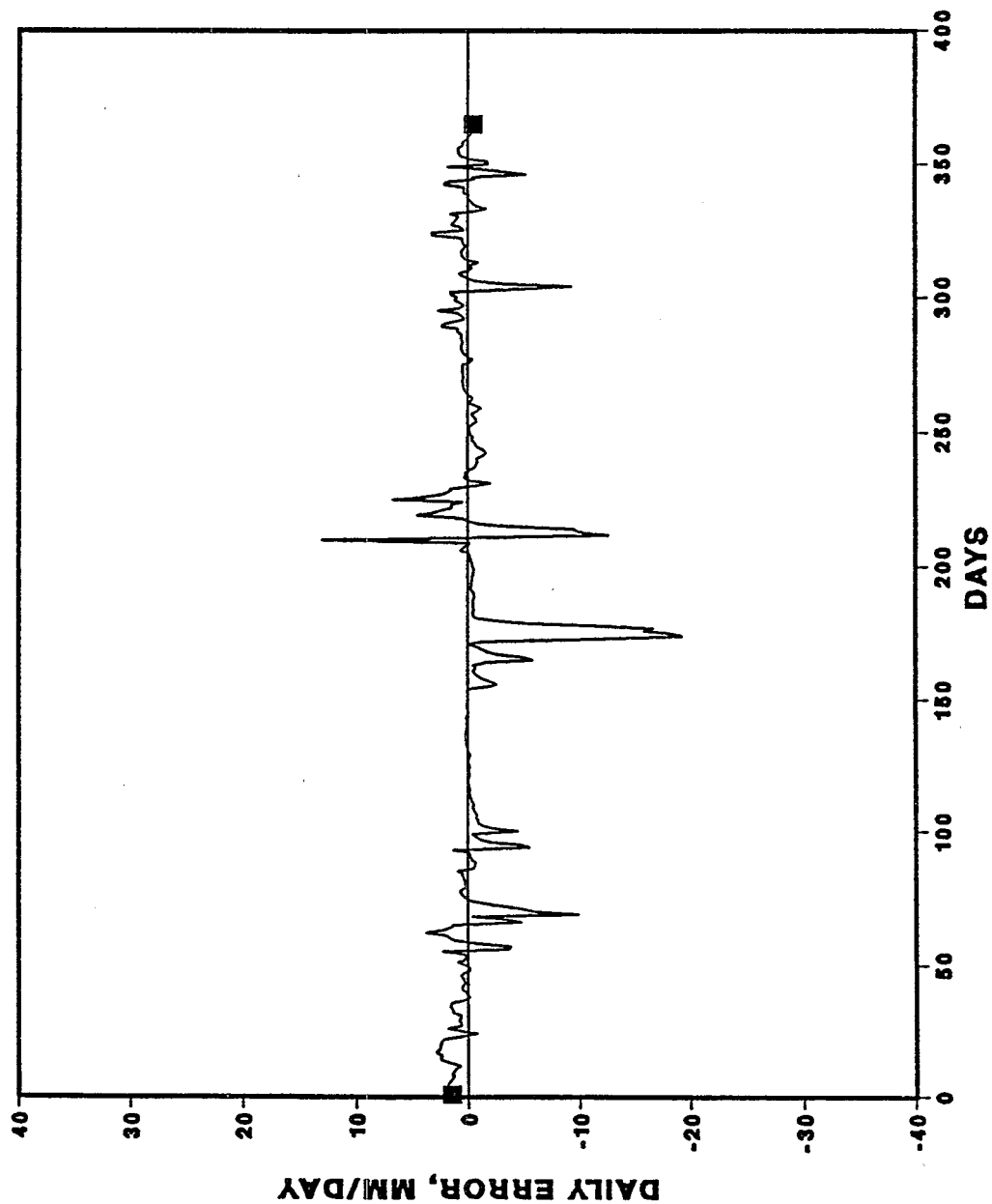


Figure 19. Verification results of daily outflow error.

LAKE WOODS **COMPARISON OF SIMULATED VERSUS FIELD CONCENTRATIONS** **PERIOD : 9/80 - 8/81**

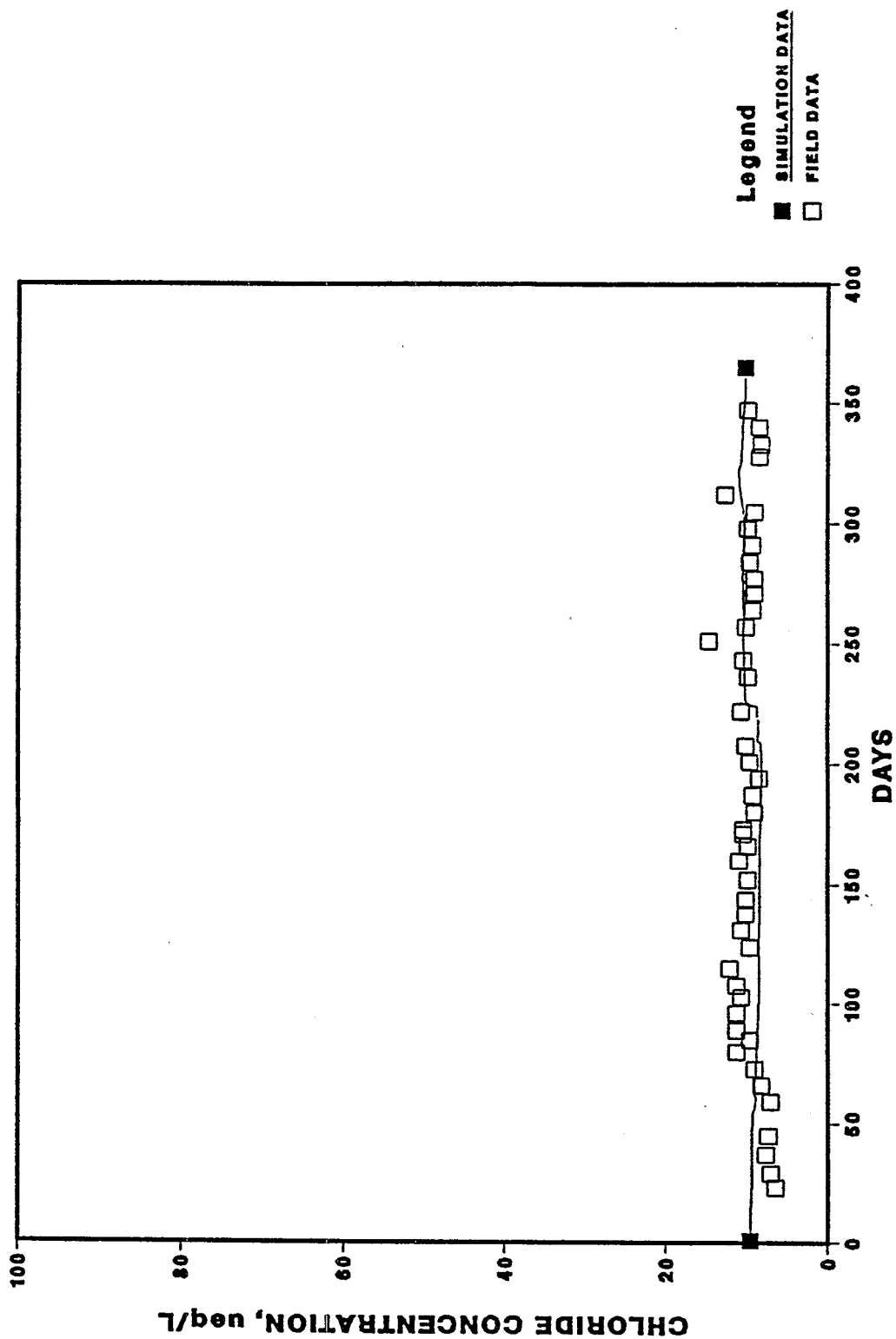


Figure 20. Verification results of lake chloride.

LAKE WOODS COMPARISON OF SIMULATION AND FIELD SULFATE VERIFICATION PERIOD: 9/1/80 - 8/31/81

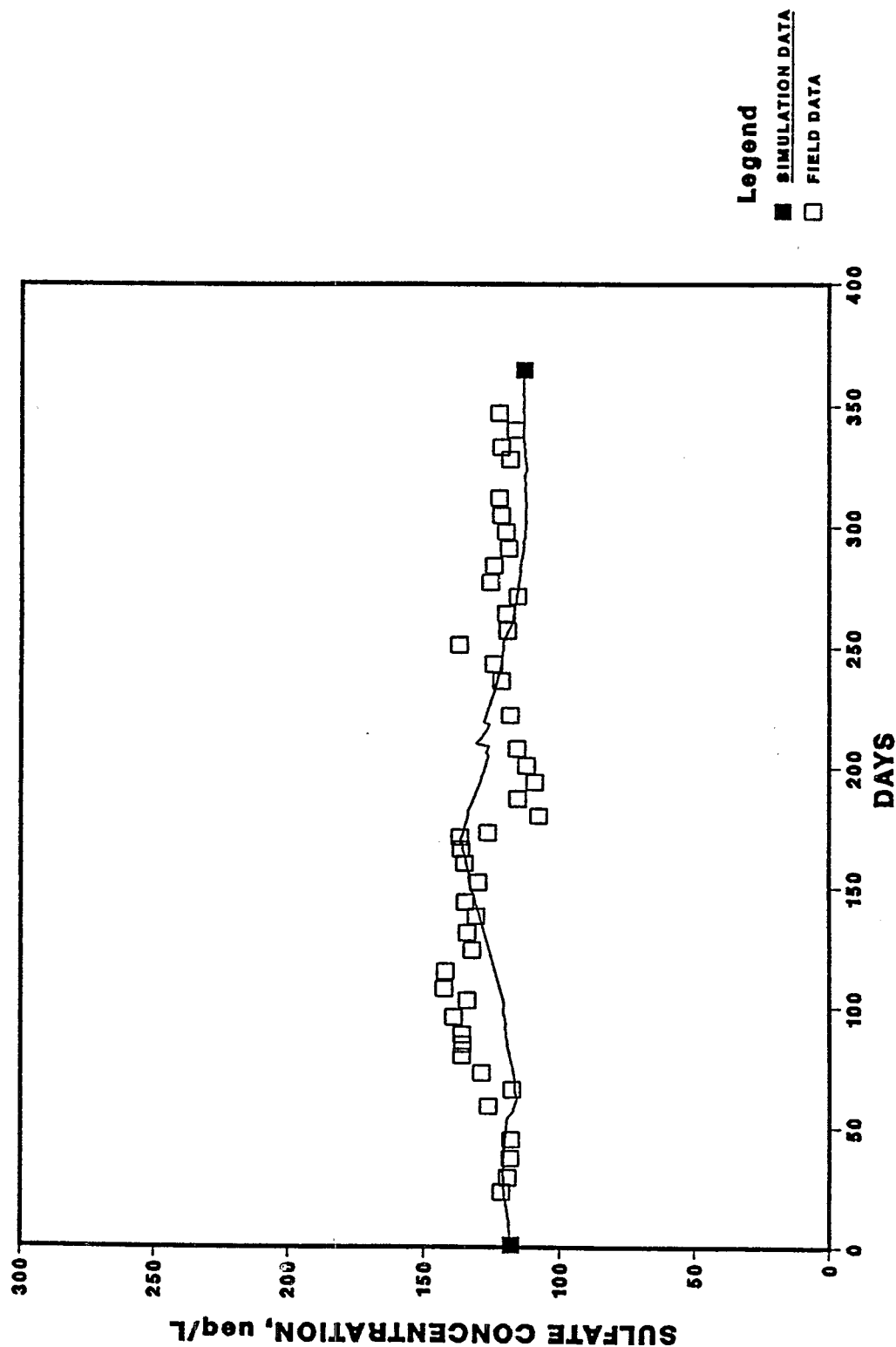


Figure 21. Verification results of lake sulfate.

LAKE WOODS COMPARISON OF SIMULATION AND FIELD ALKALINITY VERIFICATION PERIOD: 9/1/80 - 8/31/81

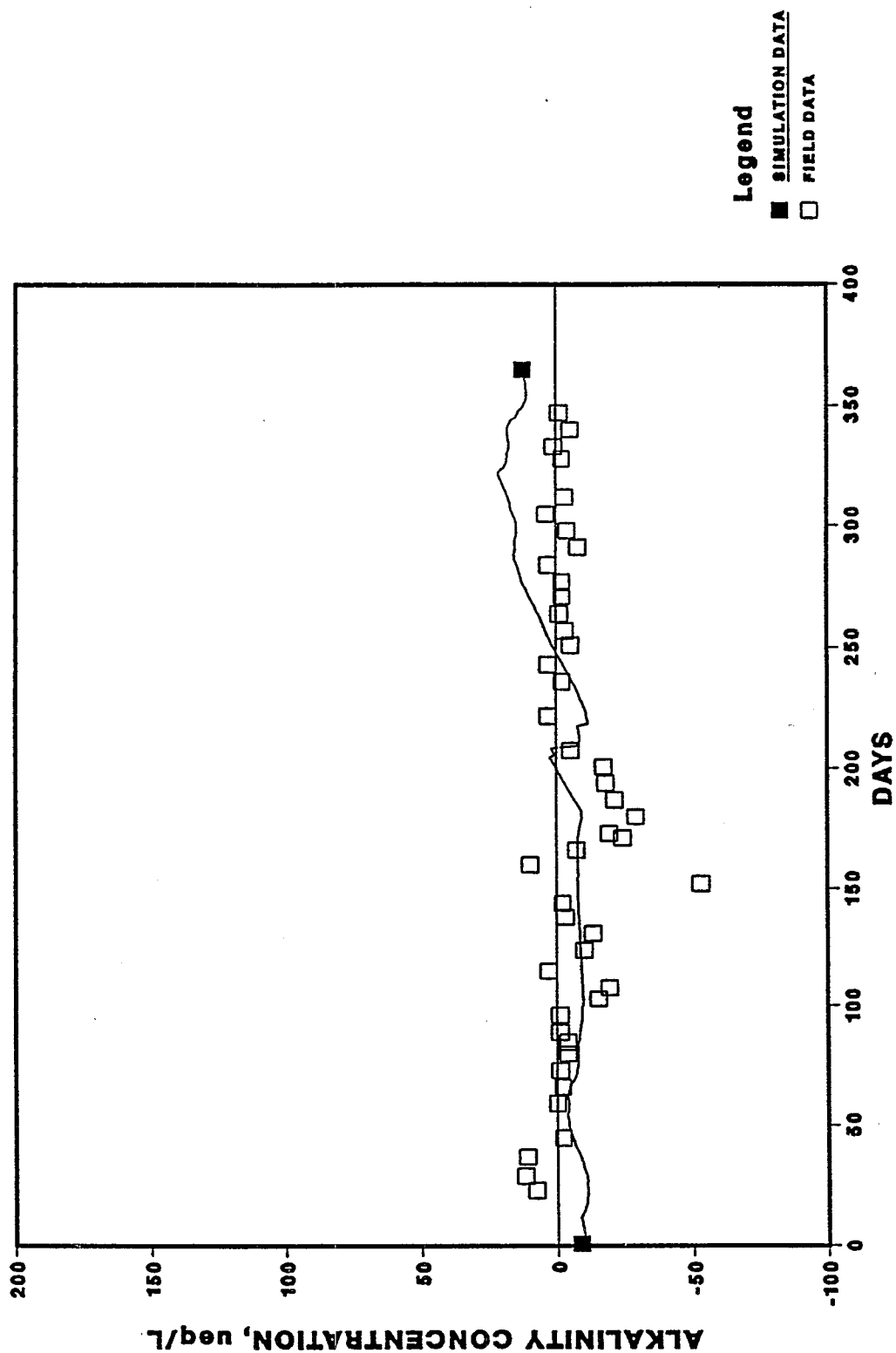


Figure 22. Verification results of lake alkalinity.

LAKE WOODS, NEW YORK STATE **PROJECTION OF LAKE SULFATE UNDER VARIOUS LOADING SCENARIOS**

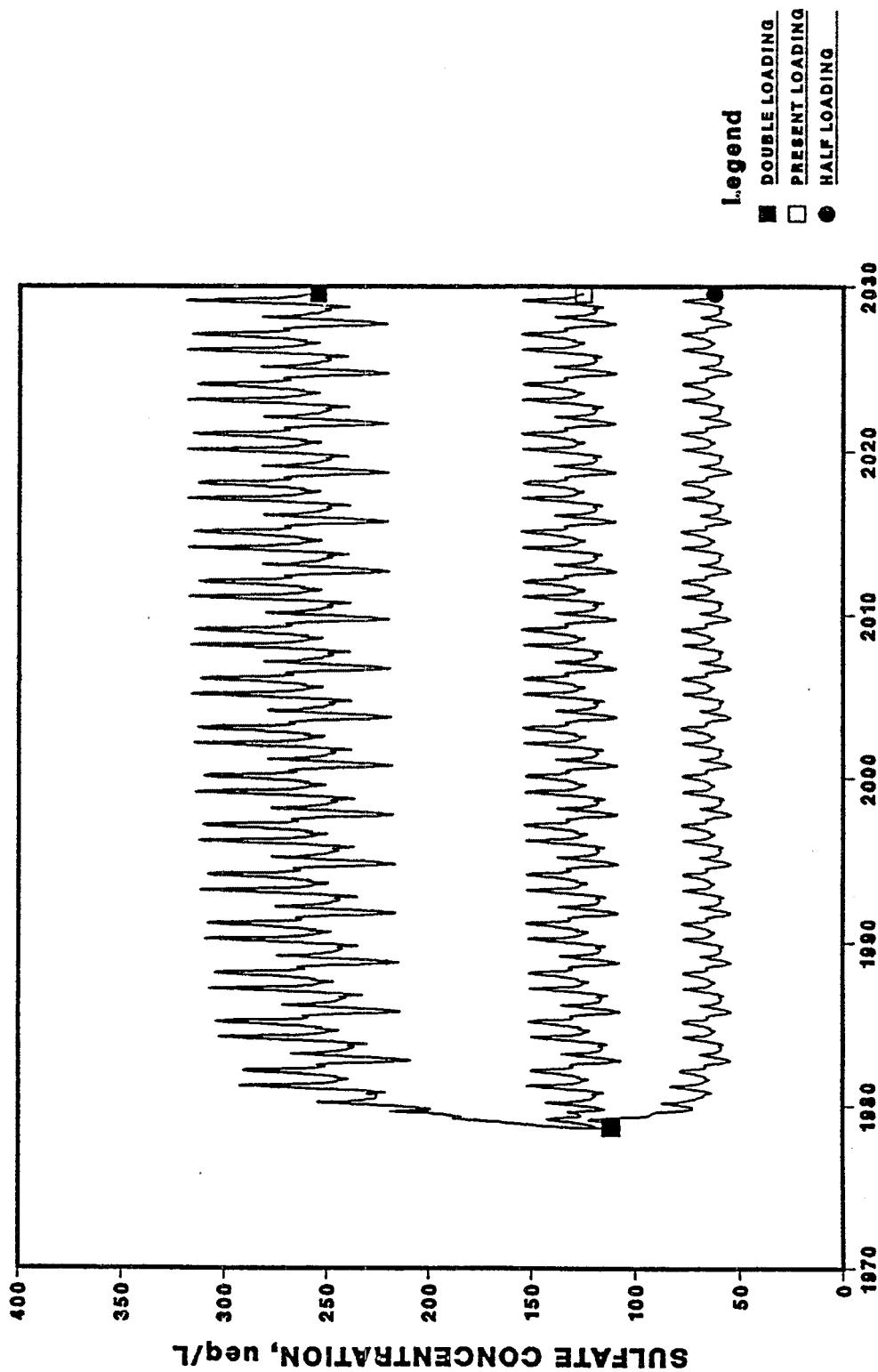


Figure 23. Lake sulfate projection under various loading scenarios.

LAKE WOODS, NEW YORK STATE PROJECTION OF LAKE ALKALINITY UNDER VARIOUS LOADING SCENARIOS

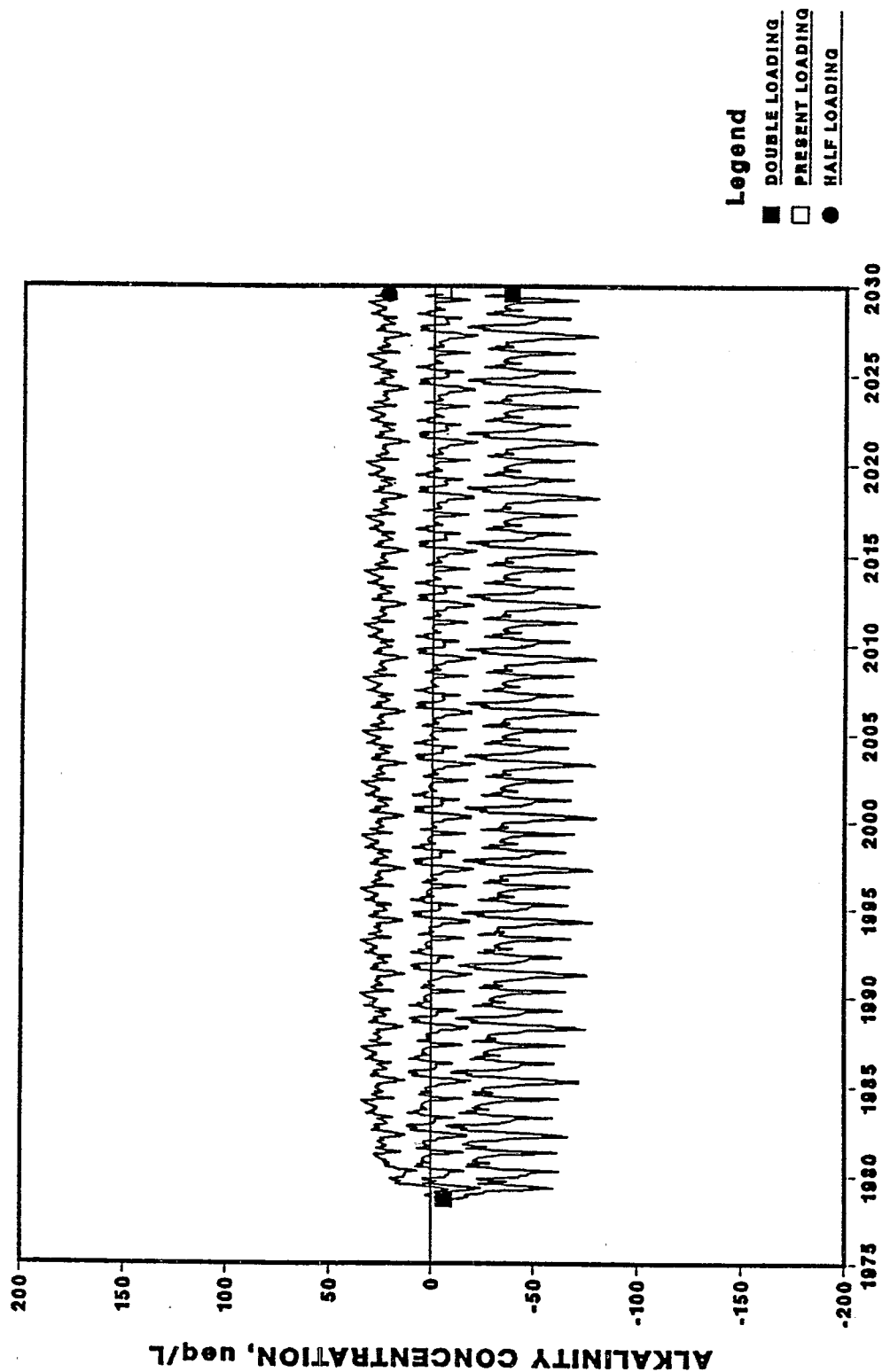


Figure 24. Lake alkalinity projection under various loading scenarios.

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Modeling Short and Long Term Impacts
of Acid Precipitation Using the
Enhanced Trickle-Down Model:
Lake Panther Case Study

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MODELING SHORT AND LONG TERM IMPACTS OF ACID PRECIPITATION USING THE ENHANCED TRICKLE-DOWN MODEL: LAKE PANTHER CASE STUDY

INTRODUCTION

The Enhanced Trickle-Down (ETD) model (Nikolaidis et al. 1986a) is being used to assess the impacts of acid precipitation of Lake Panther's watershed. Lake Panther is a 1.24 km² forested watershed located in the Adirondack Park region of New York State. Lake Panther is considered neutral, with a typical outlet pH of 7. The lake receives an annual precipitation of 1.16 m and the mean annual air temperature is 5°C. The vegetation of the watershed is dominated by Sugar Maple, Beech, Yellow Birch and Red Spruce. The watershed is underlain by hornblende granitic gneiss bedrock. The depth to bedrock is 24.5 m. The basin is covered by thick glacial till. The soils are predominantly spodosols that have been developed on the till and average less than 1 m in depth.

Lake Panther is located 10 km south of Lake Woods (Nikolaidis et al. 1986b). Both watersheds receive the same quality loading, and on the average both have similar vegetation, soils and bedrock type (with the exception of the depth of the till - Panther has 10 times deeper till than Woods), but they have different responses. This was the topic of research that was undertaken by the Integrated Lake-Watershed Acidification Study (ILWAS). The ILWAS project investigated why three lakes (Woods and Panther Lakes were included) that receive similar input of acidity respond differently in neutralizing this acidity. The thesis of the ILWAS project as it was presented by Peters et al. 1985, was that water moves through the acidic upper soil horizons rather than the lower ones and that's why it is more acidic.

The scope of this research is to calibrate, verify, and perform a sensitivity analysis on the parameters and examine the long term response to various acid loadings of Lake Panther, using the ETD model.

MODEL CALIBRATION

PROCEDURE

The calibration of ETD for Lake Panther was obtained by decoupling the hydrologic, sulfate and alkalinity submodels, similar to the calibration of Lake Woods (Nikolaidis et al. 1986b). However, in this case it was not necessary to use the standardized optimization package, IDesign (Arora et al. 1985), since adequate initial estimates for evaporation and snowmelt had already been established after the calibration of Lake Woods. Keeping the same guideline for establishing the optimum value of discharge, by trial and error the lateral and vertical percolation flow parameters were adjusted. These adjustments helped in capturing the seasonal variability as well as the peaks and valleys of the daily discharge. In order to obtain closure of the cumulative flow during the calibration period, the evaporation and snowmelt parameters were adjusted as well. Continuous refinements of the hydrologic parameters were applied until agreement between the simulation and field data was achieved. Trial and error adjustments to sulfate and alkalinity parameters were made starting with the initial values of Lake Woods in a similar manner.

INPUT DATA

The time series data of surface precipitation, evaporation and temperature for the calibration and verification periods are presented in Figures 1, 2 and 3. Precipitation and temperature data were collected at the LMI station of the ILWAS project. Evaporation measurements were obtained by using van Bavel's combination method (Nikolaidis 1986c).

Figures 4 and 5 present the wet and dry daily sulfate and acidity loading time series. An analysis of wet and dry deposition is presented in Table 7. Approximately 37% of the total acidity is dry

deposition and 47% of the total sulfate loading is dry sulfate. The total acidity loading is 1205 eg/ha/yr and the total sulfate loading is 1343 eg/ha/yr.

RESULTS

Table 2 presents a partial list of the hydrologic and chemical watershed descriptors that were input to the model. The optimum values of the calibrated parameters are presented in Table 3. Comparison between lake discharge, chloride, sulfate and alkalinity simulations and field data are presented in Figures 6 through 11. Figures 12 through 15 contain the percent saturation, alkalinity, pH and sulfate plots of the terrestrial compartments.

Table 4 contains a complete hydrologic budget for Lake Panther. Direct precipitation accounts for 14.5% of the total inflow to the lake. The majority of the water is coming through the unsaturated zone (40.5%). Finally, 23% is due to snowmelt and 22% is from the soil compartment.

An alkalinity budget for Lake panther is presented in Table 5. The majority of the acidity input to the lake is coming through soil and unsaturated zone with 23 and 42% respectively. Wet deposition contributes 13% and dry 9.5% of the total acidity input. According to the simulation results, 58% of the neutralization of the total acidity input to the watershed occurs in the terrestrial compartments and the rest is due to the in-lake processes (weathering and sulfate reduction).

A sulfate budget is shown in Table 6. The majority of sulfate input to the lake is coming through the soil and unsaturated zone with 25 and 48.2% respectively. Wet and dry deposition contribute 9% each. The net sulfate reduction in the lake sediments is 9% of the total sulfate deposition. About 25% of the total sulfate deposition is sorbed or stored in the terrestrial compartments.

Table 7 presents the MSE evaluation for the calibration period for discharge, cumulative discharge, chloride, alkalinity and sulfate.

VERIFICATION

The verification simulations of Lake Panther were performed by using one more year of input field data time series not included in the calibration period. The simulation results between lake outflow, chloride, sulfate and alkalinity for the verification period (9/80-8/81) and field data are presented in Figures 12 through 17. The results are comparable with the calibration ones. Table 8 presents the MSE evaluation for the verification period.

SENSITIVITY ANALYSIS

The sensitivity of lake outflow to each of the hydrologic parameters was checked by varying the parameters 10% above and 10% below their optimum values. The percent change of the mean square error (MSE) of the outflow is presented in Table 9. The most sensitive parameters were: the snow parameter BETA, and the soil lateral and vertical permeability correction coefficients.

The sensitivity of outflow alkalinity to each of the chemical parameters was similarly checked. Table 10 contains the percent change in MSE. The most sensitive parameters were: the lake compartment weathering constants KH5 and K05, the lake sulfate reduction reaction rate K, and the unsaturated zone ligand attach rate, K04.

LONG TERM SIMULATION

In order to perform long term simulations, the existing 3 year record was input repeatedly for 17 times, which extended the simulation period to 51 years. Three simulation runs were made: one for present loading, one for half loading and one for double loading. In order to establish the half and

double loadings, both wet and dry sulfate and alkalinity inputs were halved or doubled, respectively. Figure 18 and 19 show the projection of lake alkalinity and sulfate for the next 50 years under three different loading scenarios. The prediction indicates that Lake Panther is a direct response system and that it would only take a few years for the lake to respond to a decrease in acid deposition loading. The lake currently has reached steady state with a mean alkalinity of about 170 $\mu\text{eq/L}$ and a mean sulfate of 140 $\mu\text{eq/L}$. If the loading were to be halved, the mean alkalinity would be 210 $\mu\text{eq/L}$ and the mean sulfate concentration 75 $\mu\text{eq/L}$. On the other hand, if the loading were to be doubled, the mean alkalinity would be 60 $\mu\text{eq/L}$ and the mean sulfate concentration 310 $\mu\text{eq/L}$.

DISCUSSION

An issue that has to be addressed is the importance of the in-lake processes with respect to the neutralization of acidic deposition. One could raise the question why the selection of reducing sulfate in the lake sediments instead of adsorbing it in the terrestrial compartments was made, or, by the same token, why such an amount of alkalinity had to be neutralized in the lake instead of in the soil and unsaturated zone.

In order to answer these questions, the calibration exercise of the terrestrial compartments has to be validated. Figures 20 through 23 present the simulation results of percent saturation, alkalinity, pH and sulfate of the terrestrial compartments. Peters et al. 1985, evaluated the sulfate and alkalinity concentration for summer and winter periods using tension lysimeter for the soil compartment. They found that sulfate concentrations range between 142 to 180 $\mu\text{eq/L}$ (the low values occurred during the winter periods) and alkalinity from -77 to -90 $\mu\text{eq/L}$. The simulation results give a mean sulfate concentration of 130 $\mu\text{eq/L}$ and a mean alkalinity of -60 $\mu\text{eq/L}$. Comparing the simulated and observed values, one could notice that the simulated mean sulfate concentration is less than the observed, which indicates that adequate sulfate is being adsorbed in the calibration exercise. Similarly, simulated mean alkalinity is higher than the measured values, which indicates that sufficient weathering has been applied in the calibration of soil chemistry.

Since the calibration of the terrestrial compartments is in accordance with the limited field data, it is obvious that the validity of the importance of the in-lake processes can be justified.

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Table 1. Lake Panther analysis of wet and dry deposition.

Period:	ACIDITY (eq/ha-yr)		SULFATE (eq/ha-yr)	
	Wet	Dry	Wet	Dry
9/78-8/79	807.4	446.0	791.4	666.3
9/79-8/80	702.6	476.3	697.6	648.7
9/80-8/81	<u>746.0</u>	<u>437.7</u>	<u>647.0</u>	<u>579.0</u>

Total average Acidity = 1205.3 eq/ha .yr
 Dry Deposition = 37.6% total Deposition

Total average Sulfate = 1343.3 eg/ha .yr
 Dry Deposition = 47.0% total Deposition

Sulfate Loading (Average)

Wet = 36.1 kg/ha/yr
 Dry = 30.3 kg/ha/yr
 Total = 66.4 kg/ha/yr

On the average, 8.25 metric tons of sulfate are deposited on Lake Panther watershed (or 2.7 metric tons of sulfur)

Table 2. List of watershed descriptors used for model calibration.

GENERAL WATERSHED CHARACTERISTICS:

AQUATIC AREA = 0.1800E+06 SQUARE METERS
TERRESTRIAL AREA = 0.1060E+07 SQUARE METERS
CHARACTERISTIC DISTANCE = 0.65003+03 METERS
DEPTH TO BEDROCK = 24.5000 METERS
PARTIAL PRESSURE OF ATM CO2 = 0.0003 ATMOSPHERES
SURFACE WATER PCO2 IS 1.50 TIMES SATURATED PCO2

SOIL COMPARTMENT CHARACTERISTICS:

POROSITY = 0.2700
DEPTH OF SOIL LAYER = 0.6300 METERS
SUM OF BASES = 113.1000 EQUIVALENTS/KILOGRAM
SOIL DENSITY = 1283.0000 KILOGRAMS/CU. METER

UNSATURATED ZONE COMPARTMENT CHARACTERISTICS:

POROSITY = 0.2000
TRANSPIRATION COEFFICIENT = 0.0010 INCHES/DAY
BARE-GROUND FROST
COEFFICIENT = 0.1000
REDUCTION IN FROST
COEFFICIENT = 0.0800
DAILY THAW RATE = 0.1200 DEGREES C
INITIAL FROST INDEX = 0.0000 DEGREES C
LIMITING FROST INDEX = -3.0000 DEGREES C
THAW COEFFICIENT = 0.2000
BULK DENSITY = 1549.0000 KILOGRAMS/CU. METER

SURFACE WATER BODIES CHARACTERISTICS:

STREAM BED ELEVATION AT OUTFLOW = 23.5530 METERS

GROUNDWATER COMPARTMENT CHARACTERISTICS:

POROSITY = 0.2000

Table 3. List of optimum values of the calibrated parameters.

a) Hydrologic Parameters

-Snow:

BETA = 0.8095

KAPPA = 1.1423

KPAN2 = 0.1766

-Evaporation:

KPAN3 = 1.5471

KPAN5 = 1.5381

-Lateral and Vertical Flows:

KLAT3 = 4.5281

KLAT4 = 4.9791

KPERC3 = 4.3117E - 3

KPERC4 = 4.1741E - 3

-Groundwater

DI = 0.5963

FRAX = 0.4804

ALFI = 6.2375E - 4

ALF2 = 3.4045E - 2

b) Alkalinity Parameters

RE3 = 8.1 E-8 m³/eq/day

KH4 = 2.0E-2 meq/m²/day

KH5 = 6.5E-1 meq/m²/day

KH6 = 1.0E-2 meq/m²/day

K04 = 1.1E-3 meq/m²/day

K05 = 3.9E-1 meq/m²/day

K06 = 1.1E-3 meq/m²/day

c) Sulfate Parameters

CF = 2.0247

KP3 = 4.3E-5 eq/kg/eq/m³

KP4 = 8.5E-6 eq/kg/eq/m³

K = 2.033E-3 1/day

KP6 = 4.7E-7 eq/kg/eg/m³

Table 4. Monthly Hydrologic Budget of Lake Panther

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Out 2	Out 3	Storage
0.1906E-01	0.0000E+00	0.2536E-01	0.2789E-01	0.2141E-03	0.2314E-03	0.6261E-05	0.2301E-01	0.4406E-01	0.3889E-02
0.1648E-01	0.0000E+00	0.2149E-01	0.2518E-01	0.3043E-05	0.2253E-03	0.6095E-05	0.2327E-01	0.4003E-01	0.6603E-04
0.6342E-02	0.1346E-03	0.1092E-01	0.1673E-01	0.1055E-06	0.2035E-03	0.5055E-05	0.1564E-01	0.2220E-01	0.3503E-02
0.4129E-02	0.2312E-01	0.8611E-02	0.1347E-01	0.1539E-07	0.2087E-03	0.5646E-05	0.0000E+00	0.4914E-01	0.3887E-03
0.6638E-02	0.5344E-02	0.9723E-02	0.9178E-02	0.9840E-07	0.1992E-03	0.5390E-05	0.0000E+00	0.2697E-01	0.4105E-02
0.2434E-02	0.2255E-02	0.4147E-02	0.8195E-02	0.1604E-08	0.1739E-03	0.4706E-05	0.0000E+00	0.2325E-01	-0.6054E-02
0.1515E-01	0.3087E-01	0.2373E-01	0.2421E-01	0.2641E-05	0.1890E-03	0.5113E-05	0.0000E+00	0.9350E+00	0.1015E-01
0.1235E-01	0.1998E+00	0.2773E-01	0.2922E-01	0.6120E-05	0.1755E-03	0.4749E-05	0.0000E+00	0.2690E+00	0.2618E-02
0.1490E-01	0.2315E-01	0.2193E-01	0.2941E-02	0.9025E-06	0.1509E-03	0.4083E-05	0.2237E-01	0.8639E-01	-0.1943E-01
0.4130E-02	0.0000E+00	0.8763E-02	0.1319E-01	0.5011E-08	0.1297E-03	0.3511E-05	0.3204E-01	0.2027E-01	-0.2410E-01
0.1043E-01	0.0000E+00	0.1143E-01	0.8629E-02	0.4790E-07	0.1225E-03	0.3314E-05	0.2863E-01	0.3655E-02	-0.1689E-02
0.2633E-01	0.0000E+00	0.3330E-01	0.3527E-01	0.1586E-04	0.1260E-03	0.3410E-05	0.2105E-01	0.3998E-01	0.3400E-01
0.2109E-01	0.0000E+00	0.3601E-01	0.8902E-01	0.7231E-04	0.1172E-03	0.3172E-05	0.1963E-01	0.1307E+00	-0.3972E-02
0.1346E-01	0.0000E+00	0.1914E-01	0.6012E-01	0.1031E-06	0.1270E-03	0.3435E-05	0.1534E-01	0.8046E-01	-0.2950E-02
0.1537E-01	0.1602E-01	0.1993E-01	0.4566E-01	0.2341E-05	0.1273E-03	0.3444E-05	0.8245E-02	0.9534E-01	0.3530E-02
0.4645E-02	0.2006E-01	0.1294E-01	0.4638E-01	0.6225E-07	0.1319E-03	0.3569E-05	0.0000E+00	0.8966E-01	-0.5508E-02
0.4535E-02	0.2283E-01	0.9928E-02	0.3301E-01	0.7056E-06	0.1341E-03	0.3628E-05	0.0000E+00	0.7429E-01	-0.3861E-02
0.0000E+00	0.4742E-02	0.1129E-02	0.1442E-01	0.1519E-16	0.1199E-03	0.3244E-05	0.0000E+00	0.2735E-01	-0.6940E-02
0.1043E-01	0.6760E-01	0.1531E-01	0.1638E-01	0.3722E-05	0.1354E-03	0.3663E-05	0.0000E+00	0.8821E-01	0.2166E-01
0.1346E-01	0.2071E-01	0.2367E-01	0.5891E-01	0.7697E-06	0.1256E-03	0.3398E-05	0.1267E-01	0.1179E+00	-0.1366E-01
0.7006E-02	0.0000E+00	0.5761E-02	0.2600E-01	0.2015E-06	0.1273E-03	0.3444E-05	0.2963E-01	0.2819E-01	-0.1693E-01
0.1744E-01	0.0000E+00	0.2746E-01	0.4870E-01	0.5275E-04	0.1222E-03	0.3307E-05	0.2984E-01	0.5373E-01	0.1019E-01
0.2157E-01	0.0000E+00	0.2572E-01	0.3774E-01	0.2501E-04	0.1284E-03	0.3474E-05	0.2718E-01	0.4763E-01	0.1037E-01
0.8736E-02	0.0000E+00	0.1497E-01	0.5145E-01	0.1327E-06	0.1272E-03	0.3441E-05	0.2252E-01	0.6384E-01	-0.1108E-01
0.2761E+00	0.4361E+00	0.4193E-00	0.7723E+00	0.4011E-03	0.3658E-02	0.9900E-04	0.3311E+00	0.1596E+01	-0.1908E-01

Note: Unit: m of water per month (over the entire watershed-207 ha)

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Out 2: Evaporation from the Lake,

Out 3: Outflow from the Lake,

Storage: Change in Lake storage

Table 5. Monthly Alkalinity Budget of Lake Panther

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Input 7	Out 2	Reaction	Storage
-0.2081E+04	0.0000E+00	-0.2700E+04	-0.2284E+04	-0.2313E+02	0.5721E+02	0.1305E+01	-0.8640E+03	0.9134E+04	0.2273E+05	0.5699E+04
-0.1277E+04	0.0000E+00	-0.2986E+04	-0.3361E+04	-0.2043E+00	0.5519E+02	0.1319E+01	-0.5468E+03	0.8656E+04	0.1940E+05	0.2626E+04
-0.3291E+03	-0.3336E+01	-0.1201E+04	-0.2227E+04	-0.3845E+02	0.4943E+02	0.1264E+01	-0.6048E+03	0.5084E+04	0.1861E+05	0.9208E+04
-0.2383E+03	-0.1199E+04	-0.8046E+03	-0.1670E+04	-0.9747E+03	0.5044E+02	0.1300E+01	-0.5189E+03	0.1125E+05	0.1527E+05	-0.3618E+03
-0.1040E+03	-0.3788E+03	-0.6543E+03	-0.9919E+03	-0.9846E+03	0.4799E+02	0.1289E+01	-0.6919E+03	0.6444E+04	0.1360E+05	0.4384E+04
-0.3134E+02	-0.2063E+03	-0.6779E+02	-0.6179E+03	-0.1509E+04	0.4178E+02	0.1190E+01	-0.3328E+03	0.5839E+04	0.1698E+05	0.9928E+04
-0.1450E+04	-0.2531E+04	-0.1123E+04	-0.1386E+04	-0.1202E+00	0.4321E+02	0.1239E+01	-0.4799E+03	0.2014E+05	0.1899E+05	-0.9133E+04
-0.6739E+03	-0.8721E+04	-0.1478E+04	-0.1415E+04	-0.3192E+00	0.4166E+02	0.9307E+00	-0.4644E+03	0.4716E+05	0.2330E+05	0.3661E+05
-0.1638E+04	-0.1670E+04	-0.1713E+04	-0.1261E+04	-0.8109E+01	0.3332E+02	0.3579E+00	-0.9486E+03	0.1126E+04	0.2144E+05	0.8040E+04
-0.7739E+03	0.0000E+00	-0.4998E+03	-0.7244E+03	-0.5373E+03	0.3088E+02	0.5919E+00	-0.8748E+03	0.3255E+04	0.2296E+05	0.1686E+05
-0.9922E+03	0.0000E+00	-0.1934E+04	-0.5295E+03	-0.4307E+02	0.2867E+02	0.7136E+00	-0.8147E+03	0.7721E+03	0.2322E+05	0.1819E+05
-0.2216E+04	0.0000E+00	-0.5016E+04	-0.6729E+04	-0.1289E+01	0.2941E+02	0.7890E+00	-0.8872E+03	0.9081E+04	0.2371E+05	-0.1945E+05
-0.9474E+03	0.0000E+00	-0.3019E+04	-0.1122E+05	-0.2366E+01	0.2733E+02	0.6168E+00	-0.8586E+03	0.2551E+05	0.2373E+05	-0.1780E+05
-0.1019E+04	0.0000E+00	-0.2017E+04	-0.6035E+04	-0.5080E+02	0.2961E+02	0.6072E+00	-0.1328E+04	0.1424E+05	0.1996E+05	-0.4648E+04
-0.1068E+04	-0.4324E+03	-0.2803E+04	-0.5354E+05	-0.4282E+01	0.2970E+02	0.5771E+00	-0.1058E+04	0.1416E+05	0.1947E+05	-0.5383E+04
-0.3001E+03	-0.1367E+04	-0.1102E+04	-0.5118E+04	-0.2374E+02	0.3080E+02	0.5268E+00	-0.3292E+03	0.1322E+05	0.1652E+05	-0.4888E+04
-0.1950E+03	-0.1094E+04	-0.5739E+03	-0.2861E+04	-0.3033E+01	0.3132E+02	0.5131E+00	-0.3404E+03	0.1041E+05	0.1505E+05	-0.3929E+03
0.0000E+00	-0.6750E+03	-0.1954E+02	-0.9201E+03	0.0000E+00	0.2803E+02	0.5015E+00	-0.3228E+03	0.4193E+04	0.1822E+05	0.1212E+05
-0.3457E+03	-0.3942E+04	-0.3829E+03	-0.1014E+04	-0.4733E+01	0.3167E+02	0.6332E+00	-0.3069E+03	0.1432E+05	0.1988E+05	-0.4010E+03
-0.1068E+04	-0.2154E+03	-0.1117E+04	-0.2806E+04	-0.5202E+01	0.2940E+02	0.4972E+00	-0.3618E+03	0.1719E+05	0.2410E+05	0.1369E+04
-0.8507E+03	0.0000E+00	-0.1209E+02	-0.4719E+03	-0.2935E+01	0.2982E+02	0.5934E+00	-0.3906E+03	0.4686E+04	0.2392E+05	0.1756E+05
-0.1186E+04	0.0000E+00	-0.2442E+04	-0.2475E+04	-0.3208E+01	0.2864E+02	0.6414E+00	-0.6750E+03	0.1038E+05	0.2296E+05	0.5831E+04
-0.2350E+04	0.0000E+00	-0.4022E+04	-0.4367E+04	-0.2891E+01	0.3009E+02	0.7302E+00	-0.1356E+04	0.9931E+04	0.2379E+05	0.1788E+04
-0.1558E+04	0.0000E+00	-0.2183E+04	-0.7528E+04	-0.1376E+01	0.2980E+02	0.6827E+00	-0.1244E+04	0.1262E+05	0.2448E+05	-0.6250E+03
-0.2269E+05	-0.2245E+05	-0.3987E+05	-0.7340E+05	-0.3384E+02	0.8691E+03	0.1961E+02	-0.1680E+05	0.2889E+06	0.4953E+06	0.3216E+05

Note: Unit: eq per month

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Input 7: Dry deposition to the Lake,

Out 2: Outflow from the Lake,

Reaction: Internal production in the Lake compartment,

Storage: Change in Lake storage

Table 6. Monthly Sulfate Budget of Lake Panther

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Input 7	Out 2	Reaction	Storage
0.3318E+04	0.0000E+00	0.6382E+04	0.6502E+04	0.4207E+02	0.2570E+02	0.8198E+00	0.1604E+04	0.5859E+04	-0.4171E+04	0.7944E+04
0.1121E+04	0.0000E+00	0.4637E+04	0.6248E+04	0.1412E+00	0.2472E+02	0.8913E+00	0.8816E+03	0.5873E+04	-0.1477E+03	0.6890E+04
0.3125E+03	0.3461E+01	0.1972E+04	0.3533E+04	0.2859E-02	0.2207E+02	0.8711E+00	0.7560E+03	0.3507E+04	0.0000E+00	0.3091E+04
0.1713E+03	0.1262E+04	0.1203E+04	0.2402E+04	0.6439E-03	0.2242E+02	0.9287E+00	0.6194E+03	0.8073E+04	0.4027E+04	0.1634E+04
0.9026E+02	0.2667E+03	0.8517E+03	0.1284E+04	0.1064E-02	0.2125E+02	0.9319E+00	0.5134E+03	0.4667E+04	0.5598E+04	0.3958E+04
0.8602E+02	0.1487E+03	0.2068E+03	0.8685E+03	0.5212E-04	0.1839E+02	0.8189E+00	0.3074E+03	0.4049E+04	0.1863E+03	-0.2229E+04
0.1021E+04	0.1945E+04	0.8926E+03	0.1255E+04	0.8825E-01	0.1971E+02	0.8308E+00	0.7888E+03	0.1359E+05	0.0000E+00	-0.7669E+04
0.7878E+03	0.7949E+04	0.1908E+04	0.1777E+04	0.4236E+00	0.1782E+02	0.6694E+00	0.7344E+03	0.3641E+05	-0.4501E+04	-0.2774E+05
0.1701E+04	0.2434E+04	0.3017E+04	0.2756E+04	0.6790E-01	0.1492E+02	0.5191E+00	0.1272E+04	0.1101E+05	-0.4236E+04	-0.4046E+04
0.8764E+03	0.0000E+00	0.1960E+04	0.2552E+04	0.6251E-03	0.1267E+02	0.4581E+00	0.1566E+04	0.2620E+04	-0.4102E+04	0.2445E+03
0.9442E+03	0.0000E+00	0.3711E+04	0.2602E+04	0.3879E-02	0.1198E+02	0.4588E+00	0.1546E+04	0.5030E+03	-0.4358E+04	0.3953E+04
0.2198E+04	0.0000E+00	0.7531E+04	0.1048E+05	0.1265E+01	0.1237E-02	0.5130E+00	0.1406E+04	0.6118E+04	-0.4927E+05	0.1058E+05
0.8181E+03	0.0000E+00	0.4252E+04	0.1603E+05	0.1842E+01	0.1154E+02	0.4845E+00	0.9126E+03	0.1997E+05	-0.4992E+04	-0.2937E+04
0.9862E+03	0.0000E+00	0.3017E+04	0.9351E+04	0.5284E-02	0.1251E+02	0.5253E+00	0.1741E+04	0.1228E+05	-0.1622E+03	0.2578E+04
0.9431E+03	0.3823E+03	0.3552E+04	0.8001E+04	0.4787E-01	0.1255E+02	0.5484E+00	0.1123E+04	0.1361E+05	0.0000E+00	0.4053E+03
0.2901E+03	0.1349E+04	0.1766E+04	0.7612E+04	0.2081E-02	0.1301E+02	0.5886E+00	0.4576E+03	0.1476E+05	0.4091E+03	0.8161E+03
0.2721E+03	0.1743E+04	0.9796E+03	0.4547E+04	0.2677E-01	0.1322E+02	0.6262E+00	0.3571E+03	0.1283E+05	0.5704E+04	0.6829E+03
0.0000E+00	0.5939E+03	0.1043E+03	0.1783E+04	0.0000E+00	0.1182E+02	0.5696E+00	0.2923E+03	0.4803E+04	0.1876E+03	-0.1831E+04
0.2357E+03	0.3533E+04	0.3116E+04	0.1208E+04	0.4720E-01	0.1335E+02	0.6296E+00	0.3962E+03	0.1474E+05	0.0000E+00	-0.9040E+04
0.8868E+03	0.3049E+03	0.1445E+04	0.3191E+04	0.4186E-01	0.1239E+02	0.4949E+00	0.6750E+03	0.1736E+05	-0.4588E+04	-0.1541E+05
0.1979E+04	0.0000E+00	0.9426E+03	0.2060E+04	0.8092E-01	0.1256E+02	0.4610E+00	0.8537E+03	0.3785E+04	-0.4381E+04	-0.2318E+04
0.1085E+04	0.0000E+00	0.5394E+04	0.8530E+04	0.2889E+01	0.1208E+02	0.4584E+00	0.1037E+04	0.7440E+04	-0.4463E+04	0.4158E+04
0.2294E+04	0.0000E+00	0.5856E+04	0.8530E+04	0.2617E+01	0.1273E+02	0.5110E+00	0.1908E+04	0.7079E+04	-0.4870E+04	0.8654E+04
0.1310E+04	0.0000E+00	0.3787E+04	0.1266E+05	0.1522E-01	0.1266E+02	0.5508E+00	0.1920E+04	0.1013E+05	-0.5336E+04	0.4229E+04
0.2354E+05	0.2192E+05	0.6568E+03	0.1258E+06	0.3168E+02	0.3744E+03	0.1516E+02	0.2367E+05	0.2411E+06	-0.3542E+05	-0.1550E+05

Note: Unit: m of water per month (over the entire watershed-207 ha)

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Out 2: Evaporation from the Lake,

Out 3: Outflow from the Lake,

Storage: Change in Lake storage

Table 7. MSE Evaluation for the Calibration Period.

Variable	Units	n	MSE	RMSE
Discharge	m ³ /s	730	0.0012	0.034
Cum. Discharge	m/yr	730	0.003	0.056
Chloride	μeq/L	102	26.3	5.13
Alkalinity	μeq/L	102	6828.0	82.6
Sulfate	μeq/L	102	128	11.3

Table 8. MSE Evaluation for the Verification Period.

Variable	Units	n	MSE	RMSE
Discharge	m ³ /s	365	0.0014	0.038
Cum. Discharge	m/yr	365	0.0026	0.052
Chloride	μeq/L	52	5.85	2.42
Alkalinity	μeq/L	52	4619.2	70.0
Sulfate	μeq/L	52	136.2	11.7

Table 9. Sensitivity Analysis of Hydrological Parameters for Outflow.

PERCENT MSE OF OUTFLOW CHANGE*

Parameter	$\bar{x} + 10\%$	$\bar{x} - 10\%$
BETA	-0.8	-1.7
KAPPA	13.5	11.3
KPAN2	-0.2	0.0
KPAN3	-0.4	0.3
KPAN5	-0.1	0.0
KLAT3	-10.1	-0.4
KLAT4	-10.1	-0.4
KPERC3	-0.3	-7.4
KPERC4	-0.1	-7.5
D1	0.0	0.0
FRAX	0.0	0.0
ALF1	0.0	0.0
ALF2	0.0	0.0

$$* \%MSE \text{ Change} = \left(\frac{MSE_{NEW} - MSE_{opt}}{MSE_{opt}} \right) * 100$$

Table 10. Sensitivity Analysis of Chemical Parameters for Alkalinity

PERCENT MSE OF ALKALINITY CHANGE*

Parameter	$\bar{x} + 10\% \bar{x}$	$\bar{x} - 10\% \bar{x}$
CF	0.4	0.9
RE3	0.2	-0.2
KH4	0.0	0.0
KH5	12.8	-1.6
KH6	0.0	0.0
K04	0.0	12.8
K05	9.0	-4.9
K06	0.0	0.0
KP3	-0.2	0.2
KP4	-0.1	0.1
K	-1.0	1.0
KP6	0.0	0.0

$$* \%MSE \text{ Change} = \left(\frac{MSE_{NEW} - MSE_{opt}}{MSE_{opt}} \right) * 100$$

**LAKE PANTHER
PERIOD : 9/78 - 8/81**

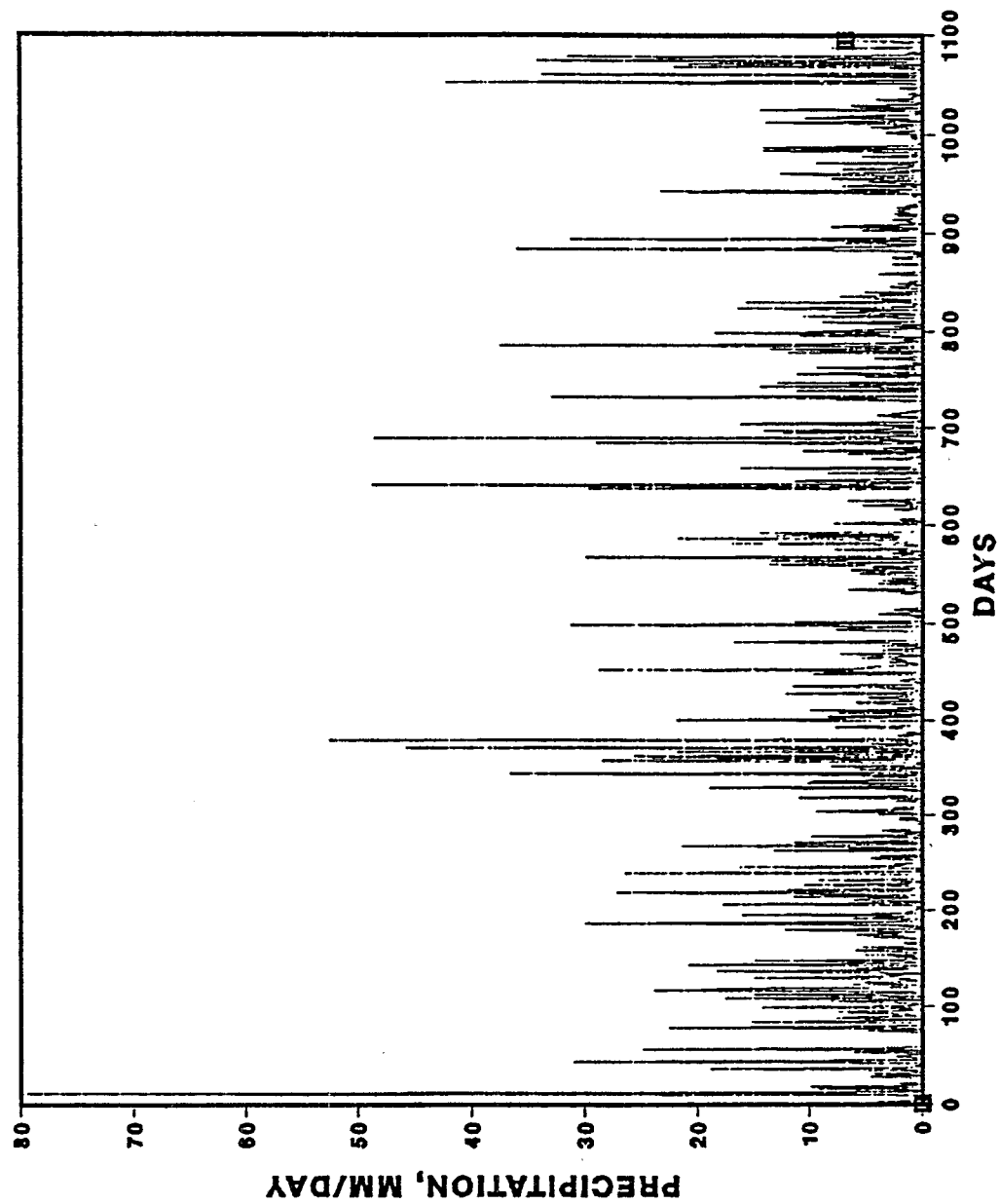


Figure 1. Precipitation data.

**LAKE PANTHER
PERIOD : 9/78 - 8/81**

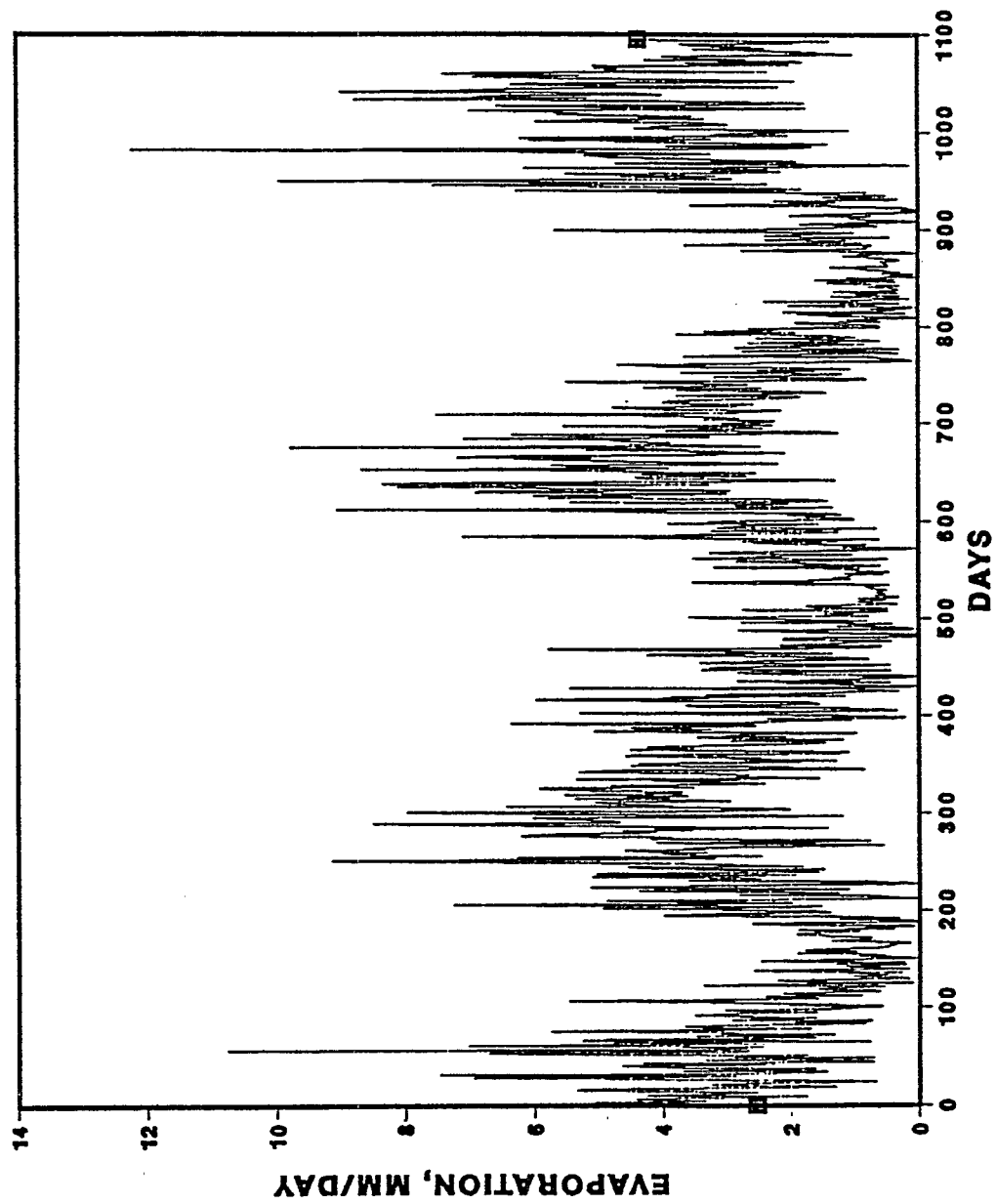


Figure 2. Evaporation data.

**LAKE PANTHER
PERIOD : 9/78 - 8/81**

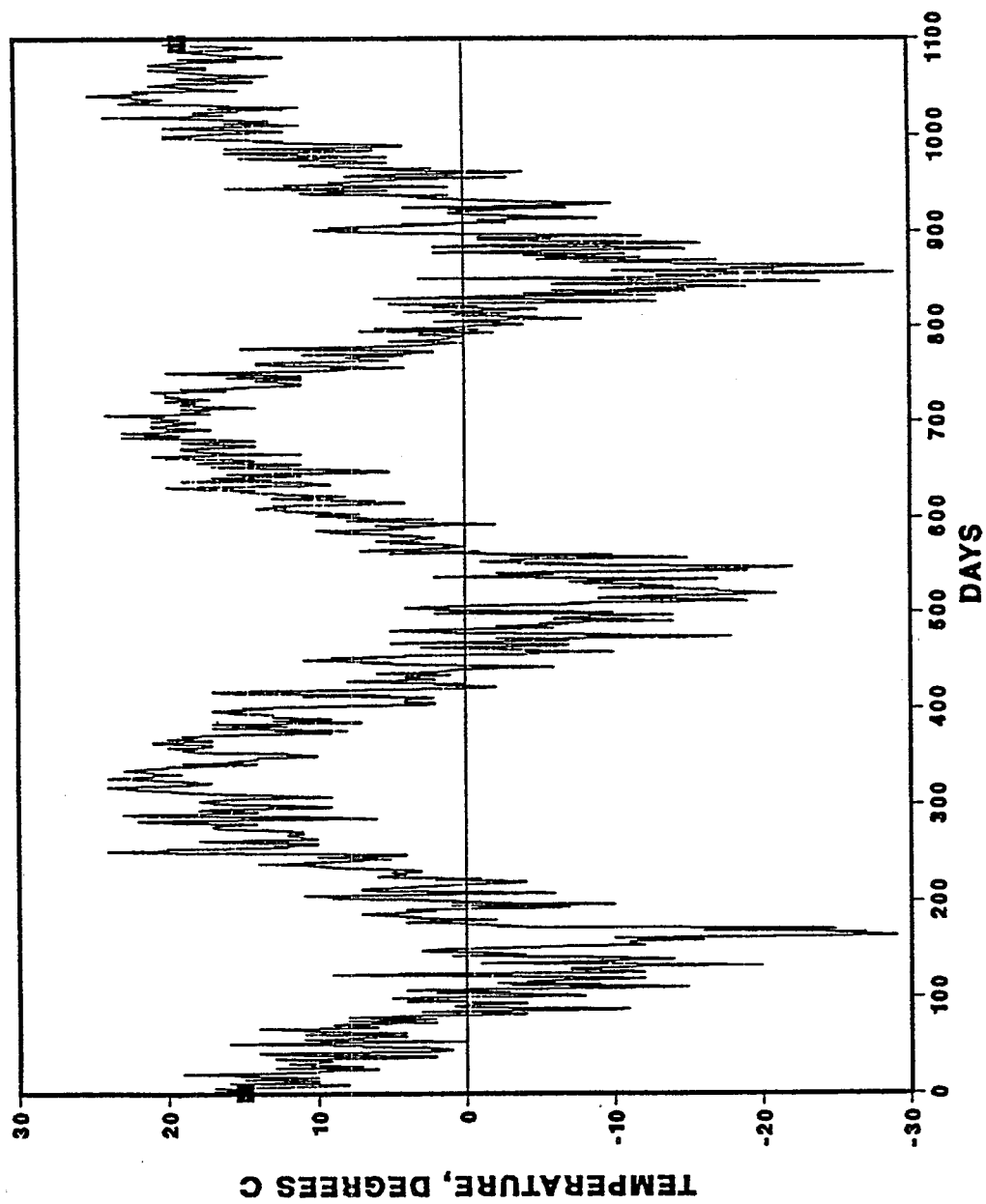


Figure 3. Temperature data.

**LAKE PANTHER
TIME SERIES OF SULFATE DEPOSITION
SIMULATION PERIOD: 9/1/78 - 8/31/81**

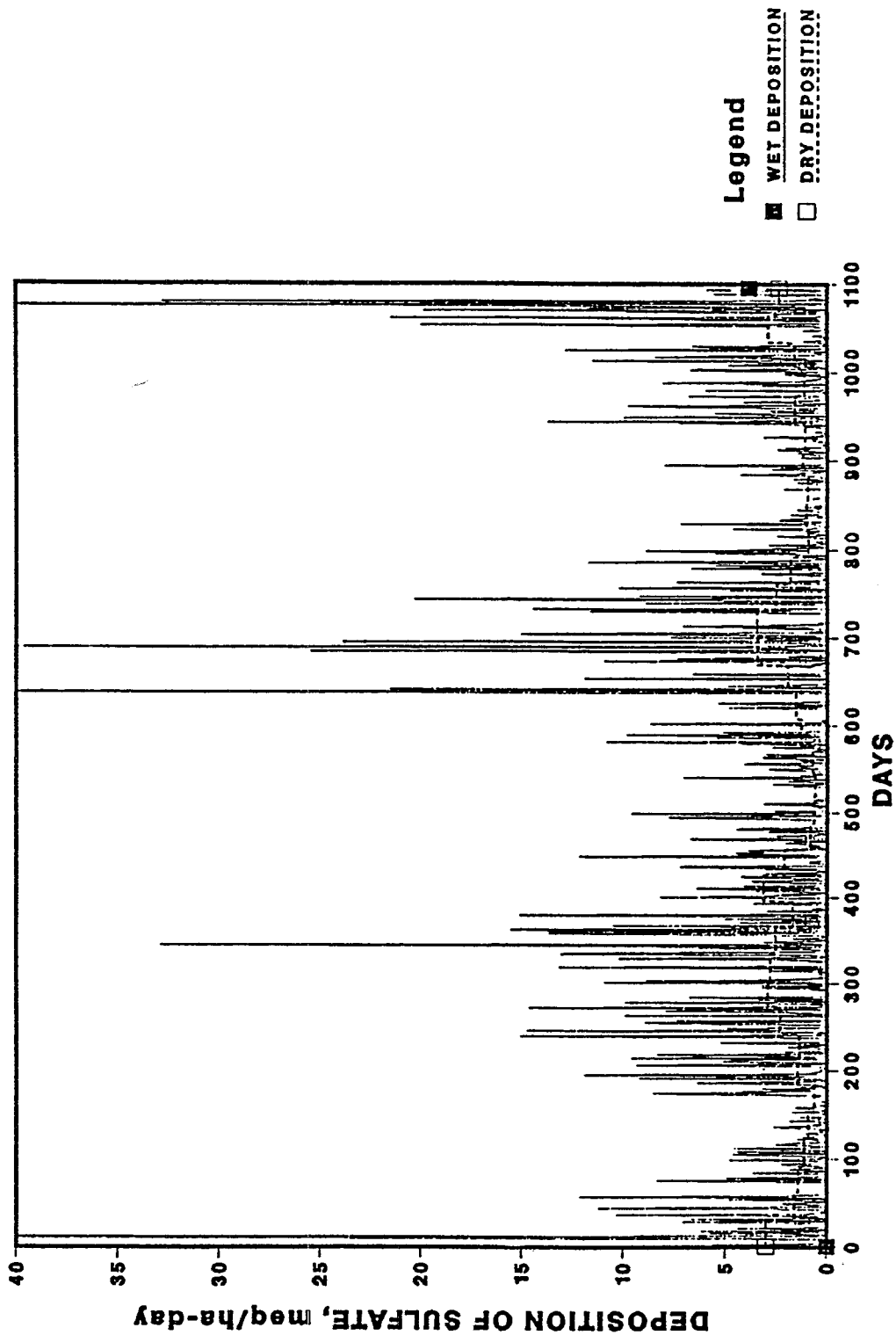


Figure 4. Wet and dry sulfate loading.

**LAKE PANTHER
TIME SERIES OF ACID DEPOSITION
SIMULATION PERIOD: 9/1/78 - 8/31/81**

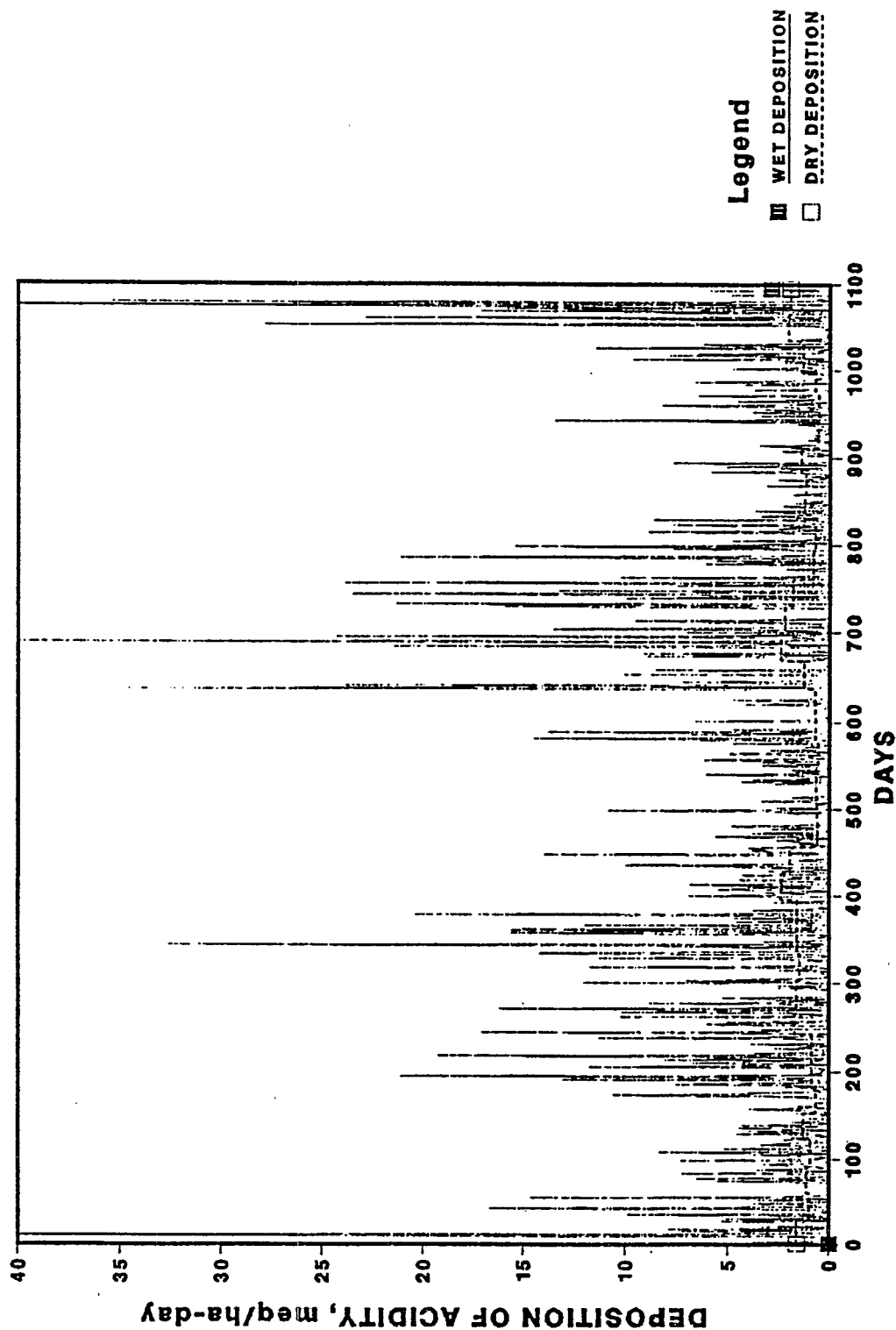


Figure 5. Wet and dry acidity loading.

LAKE PANTHER COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS PERIOD : 9/78 - 8/80

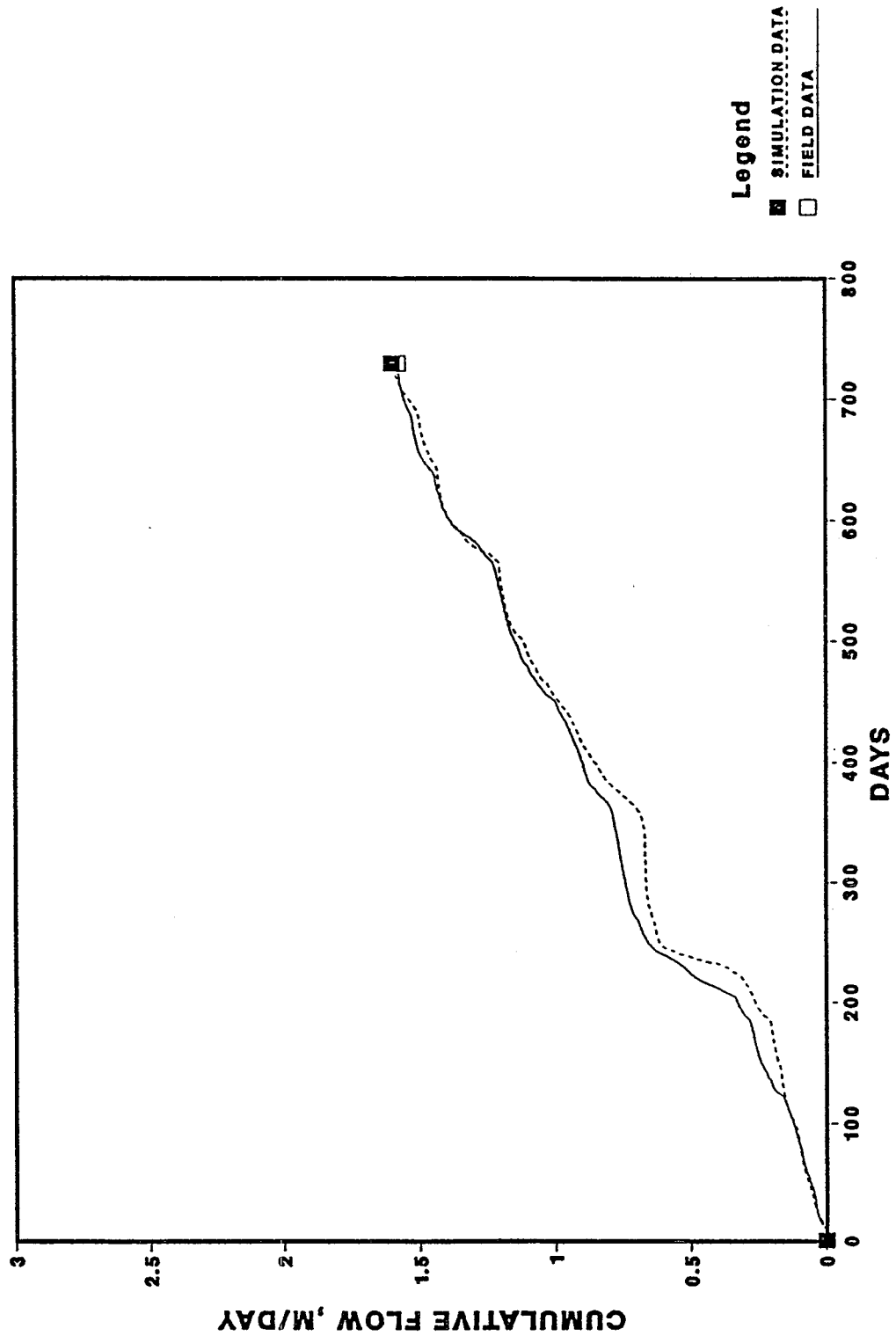


Figure 6. Calibration results of cumulative outflow.

LAKE WOODS **COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS** **PERIOD : 9/78 - 8/80**

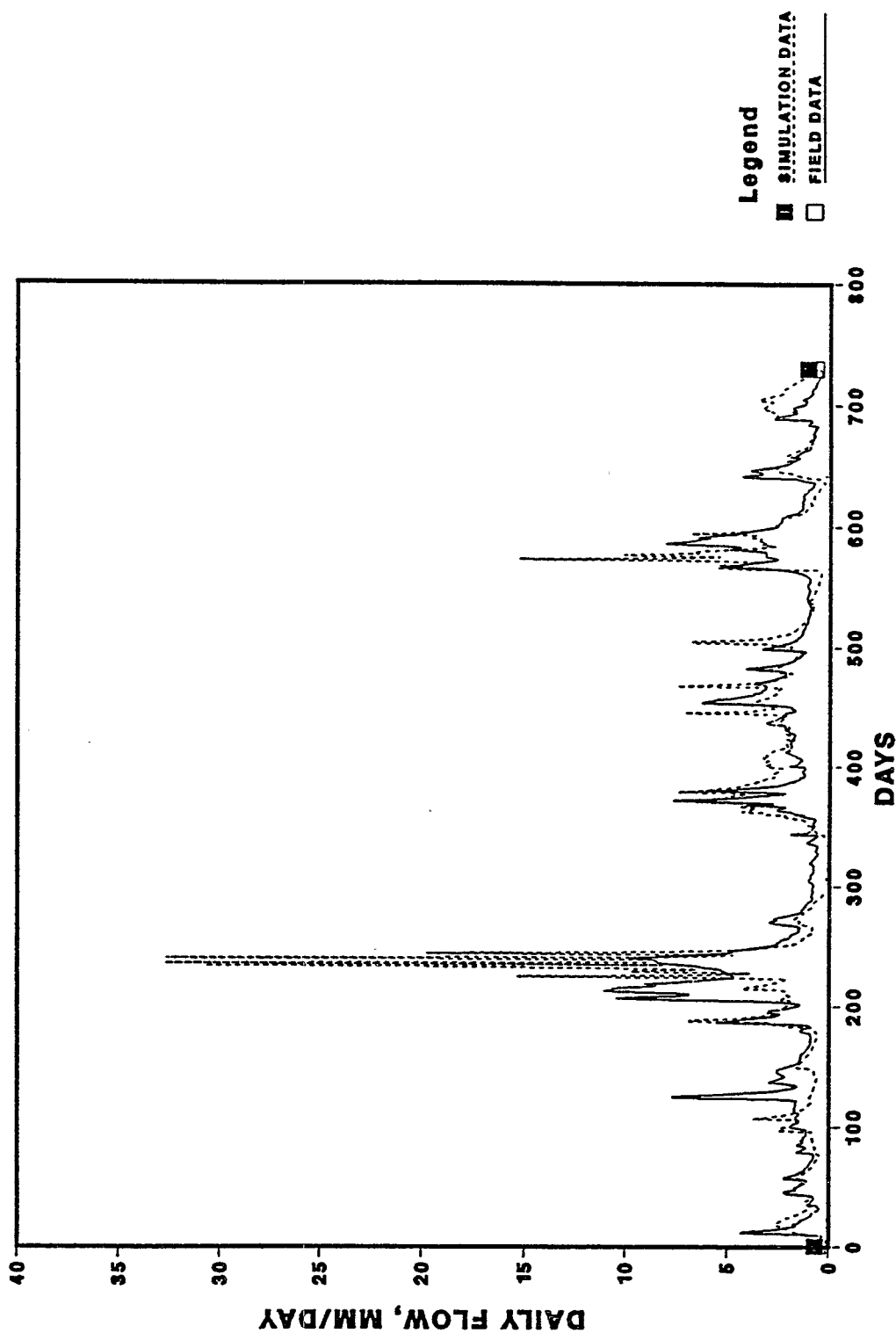


Figure 7. Calibration results of daily outflow.

LAKE WOODS
COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS
PERIOD : 9/78 - 8/80

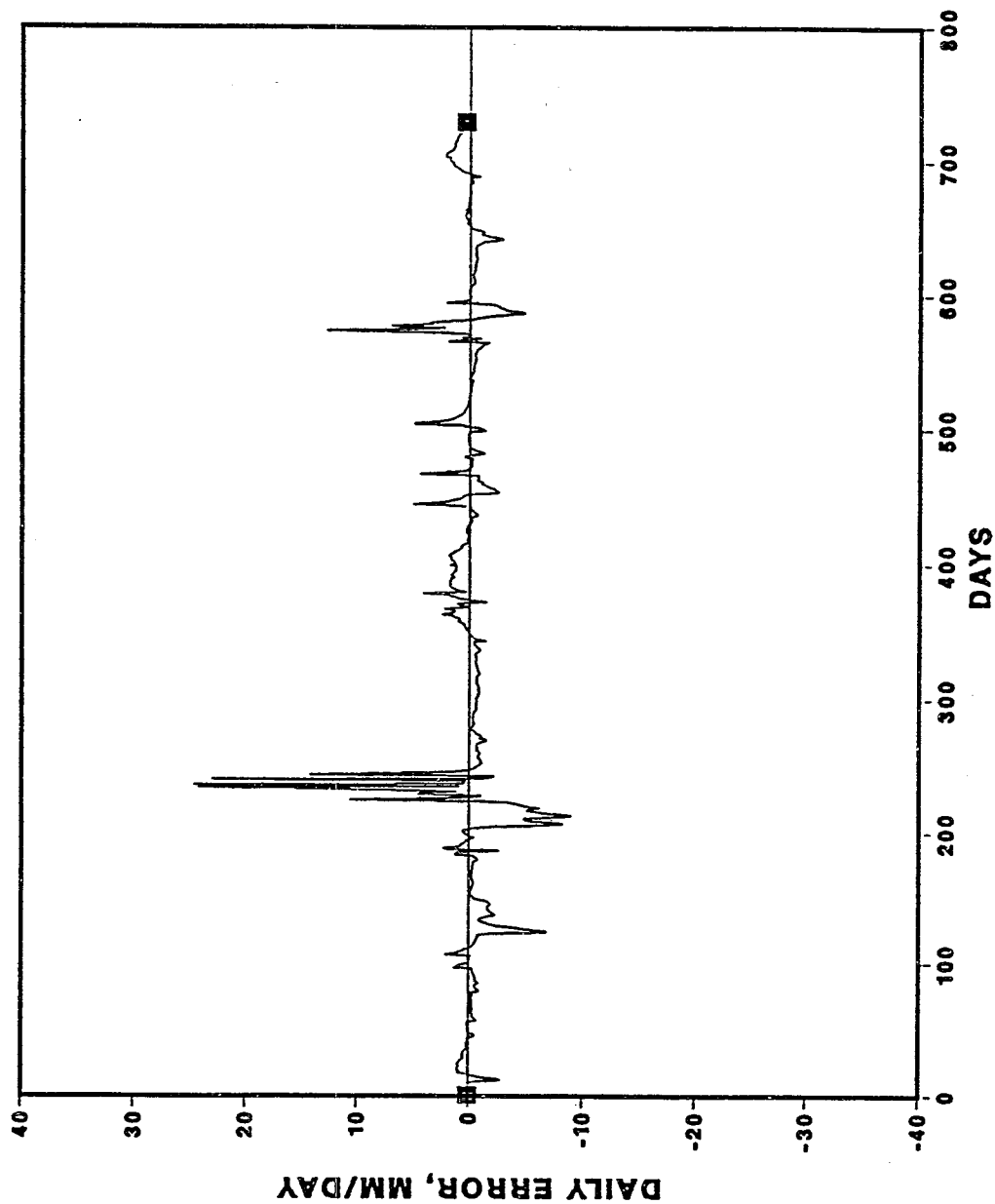


Figure 8. Calibration results of daily outflow error.

**LAKE PANTHER
COMPARISON OF SIMULATION AND FIELD CHLORIDE
CALIBRATION PERIOD: 9/1/78 - 8/31/80**

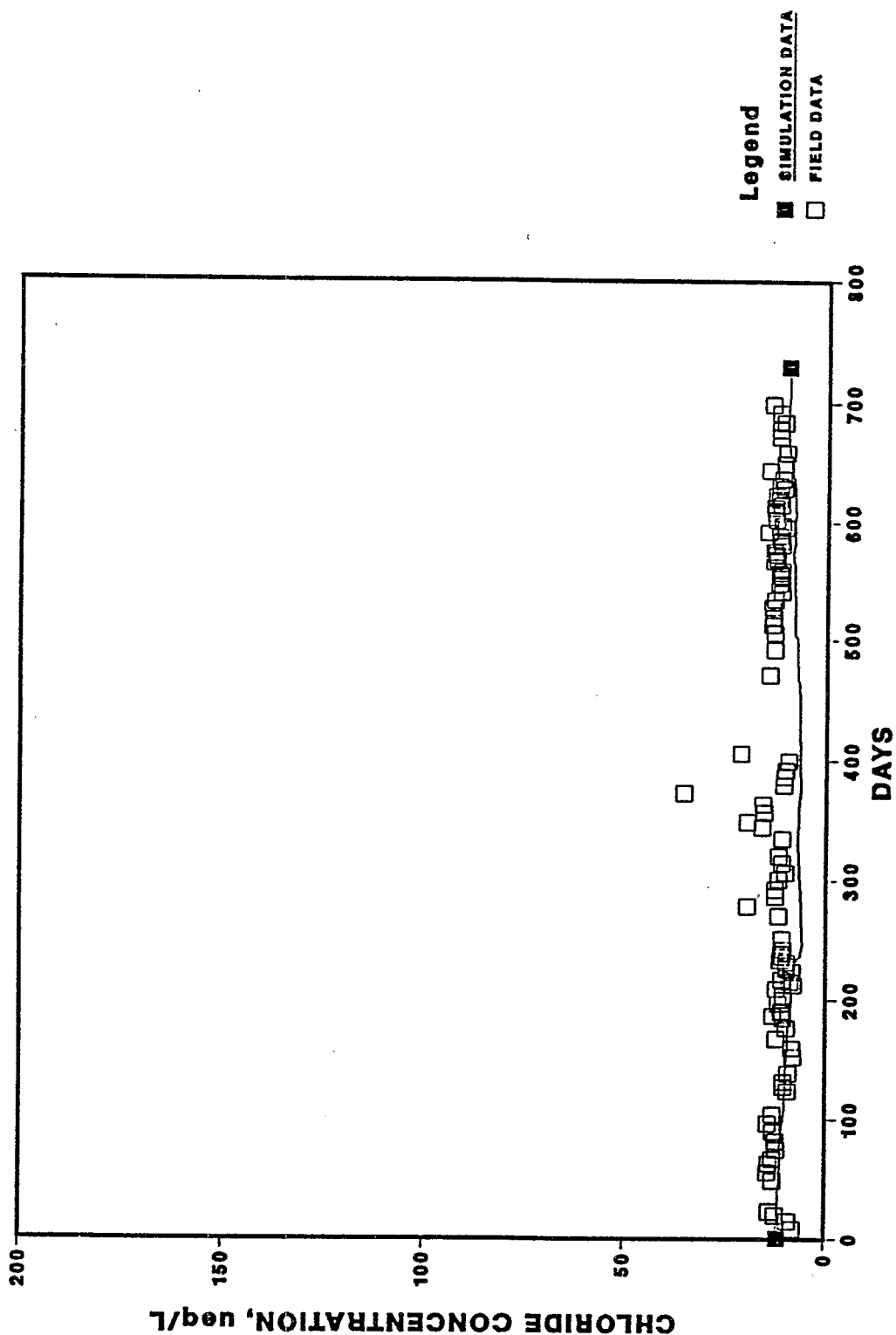


Figure 9. Calibration results of lake chloride.

LAKE PANTHER COMPARISON OF SIMULATION AND FIELD SULFATE CALIBRATION PERIOD: 9/1/78 - 8/31/80

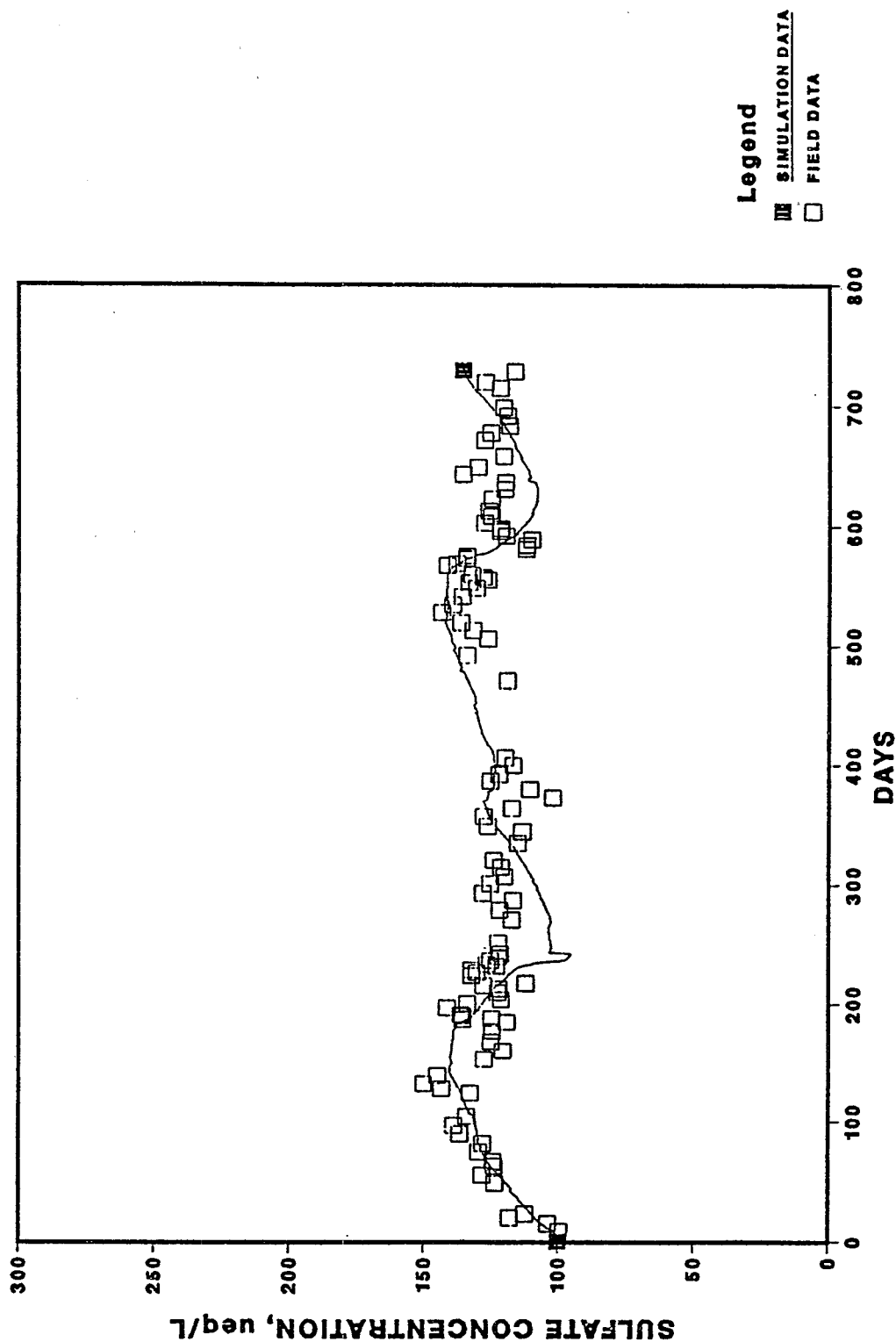


Figure 10. Calibration results of lake sulfate.

LAKE PANTHER COMPARISON OF SIMULATION AND FIELD ALKALINITY CALIBRATION PERIOD: 9/1/78 - 8/31/80

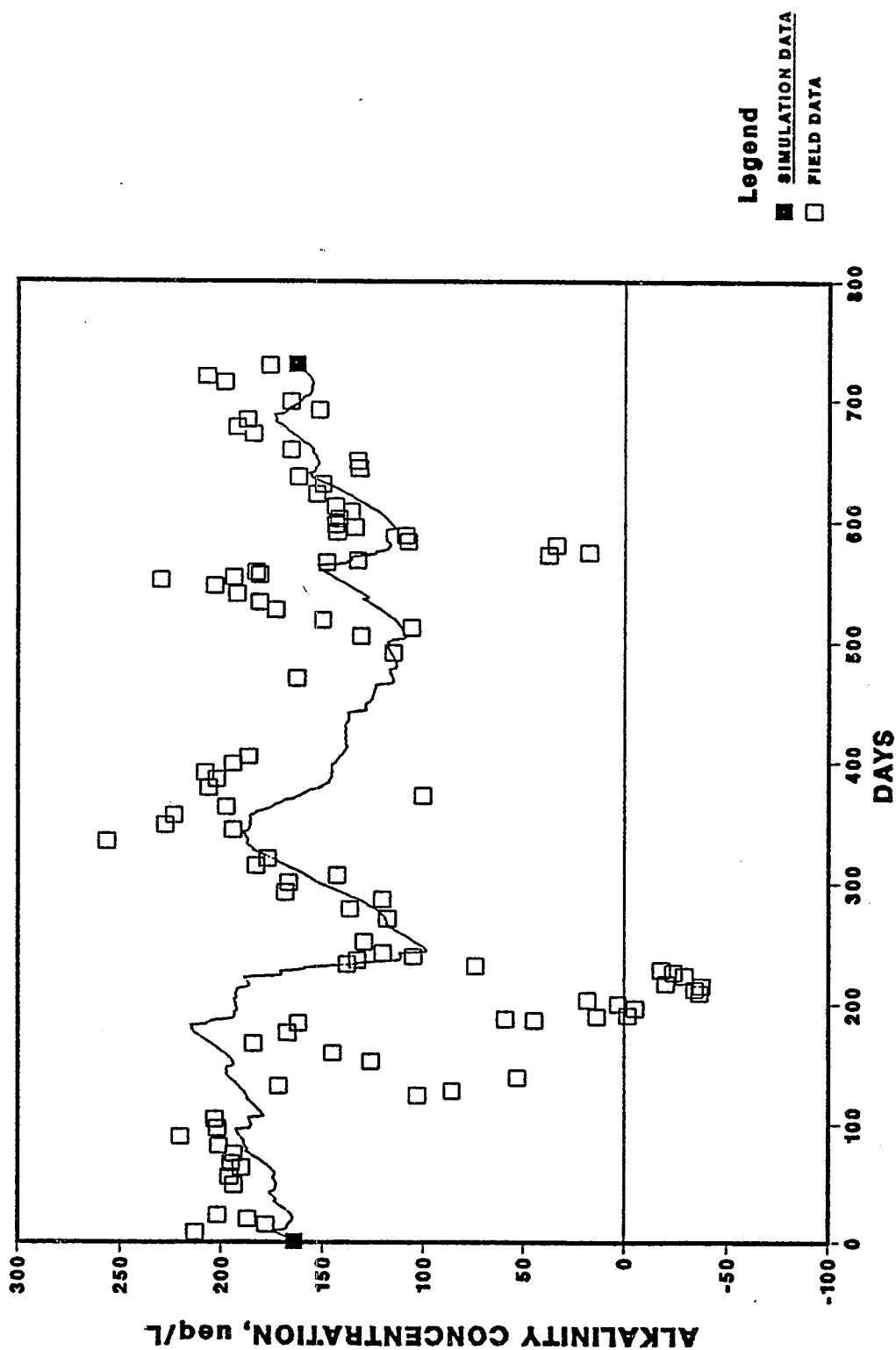


Figure 11. Calibration results of lake alkalinity.

LAKE PANTHER COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS PERIOD : 9/80 - 8/81

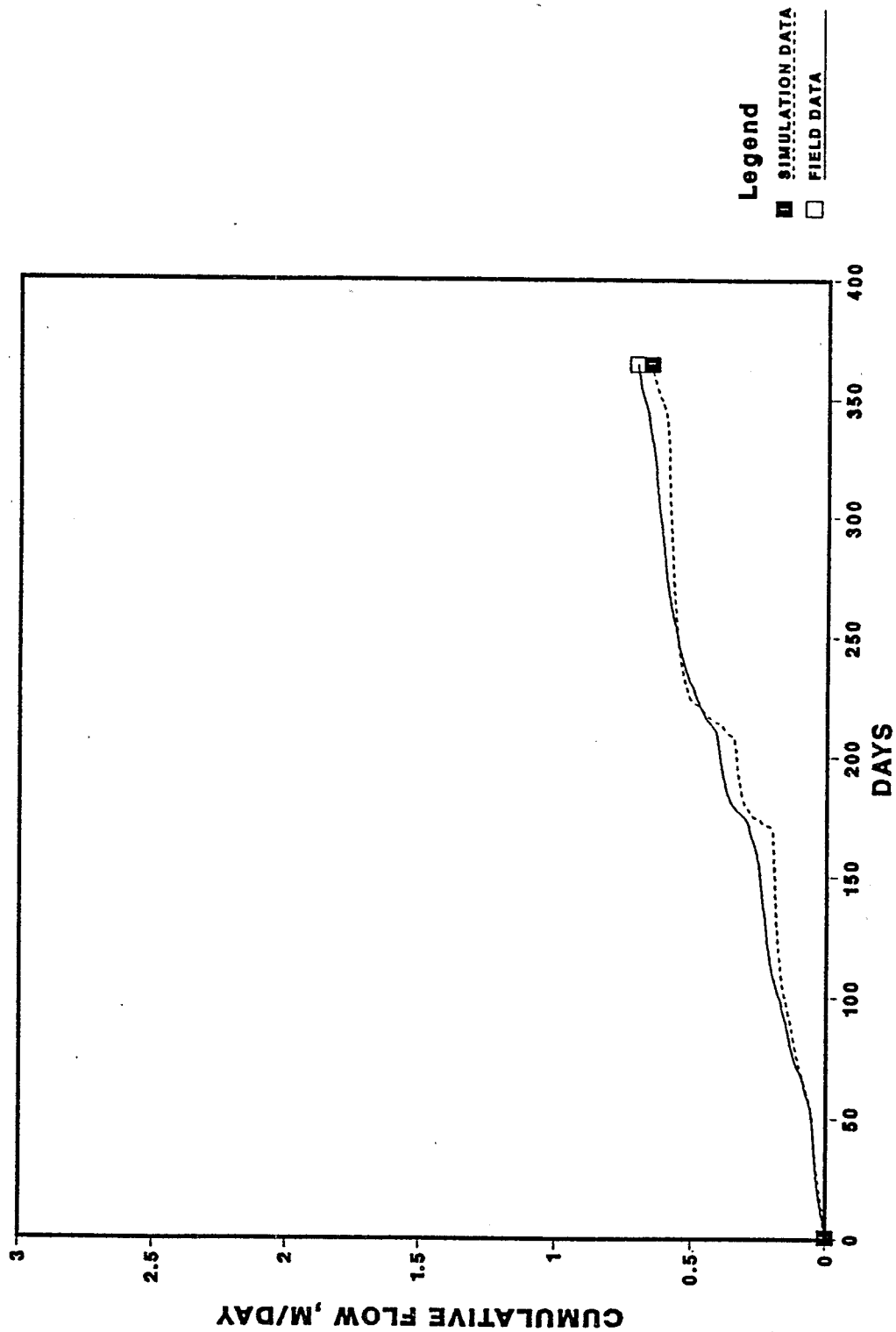


Figure 12. Verification results of cumulative outflow.

LAKE WOODS **COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS** **PERIOD : 9/80 - 8/81**

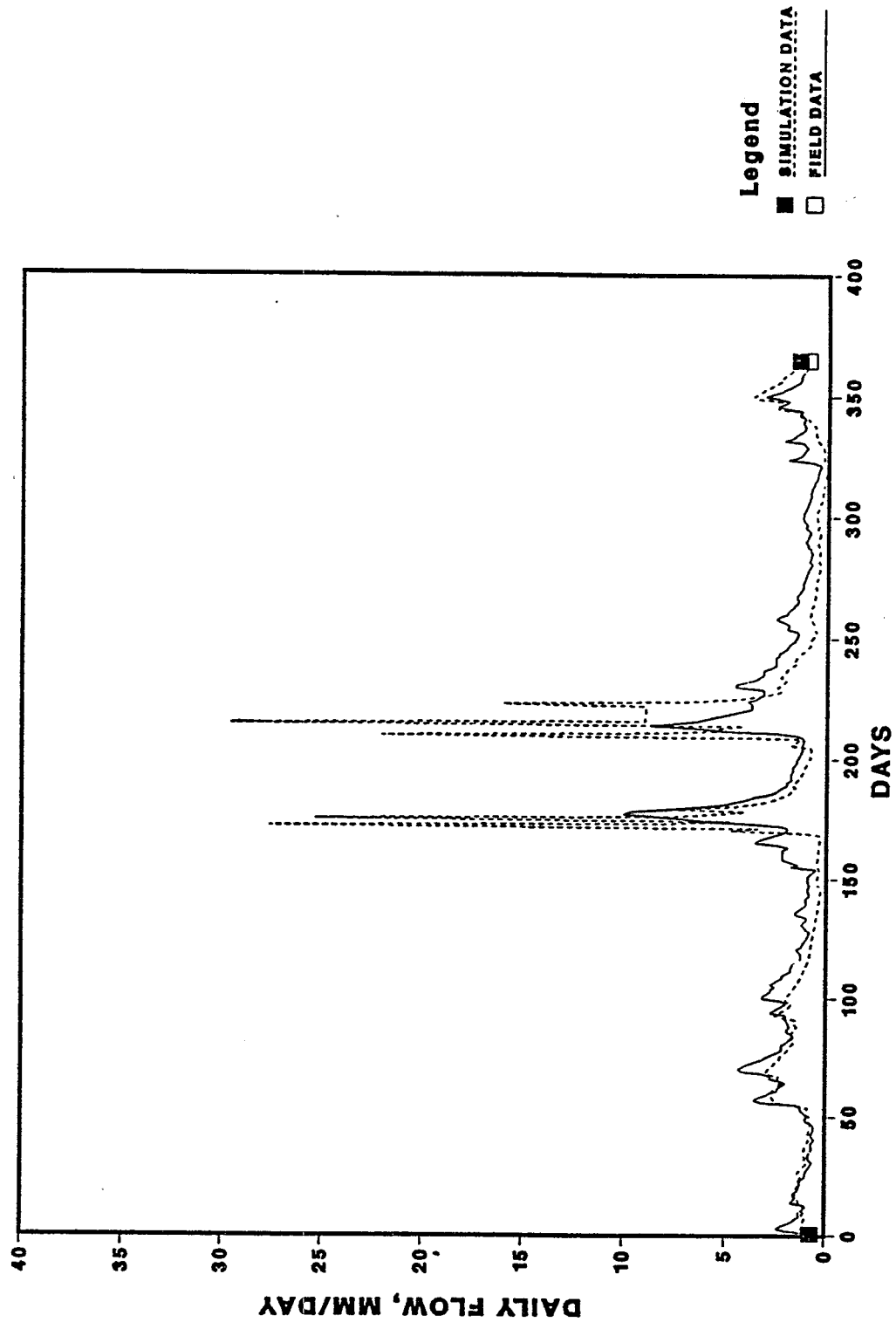


Figure 13. Verification results of daily outflow.

LAKE WOODS
COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS
PERIOD : 9/80 - 8/81

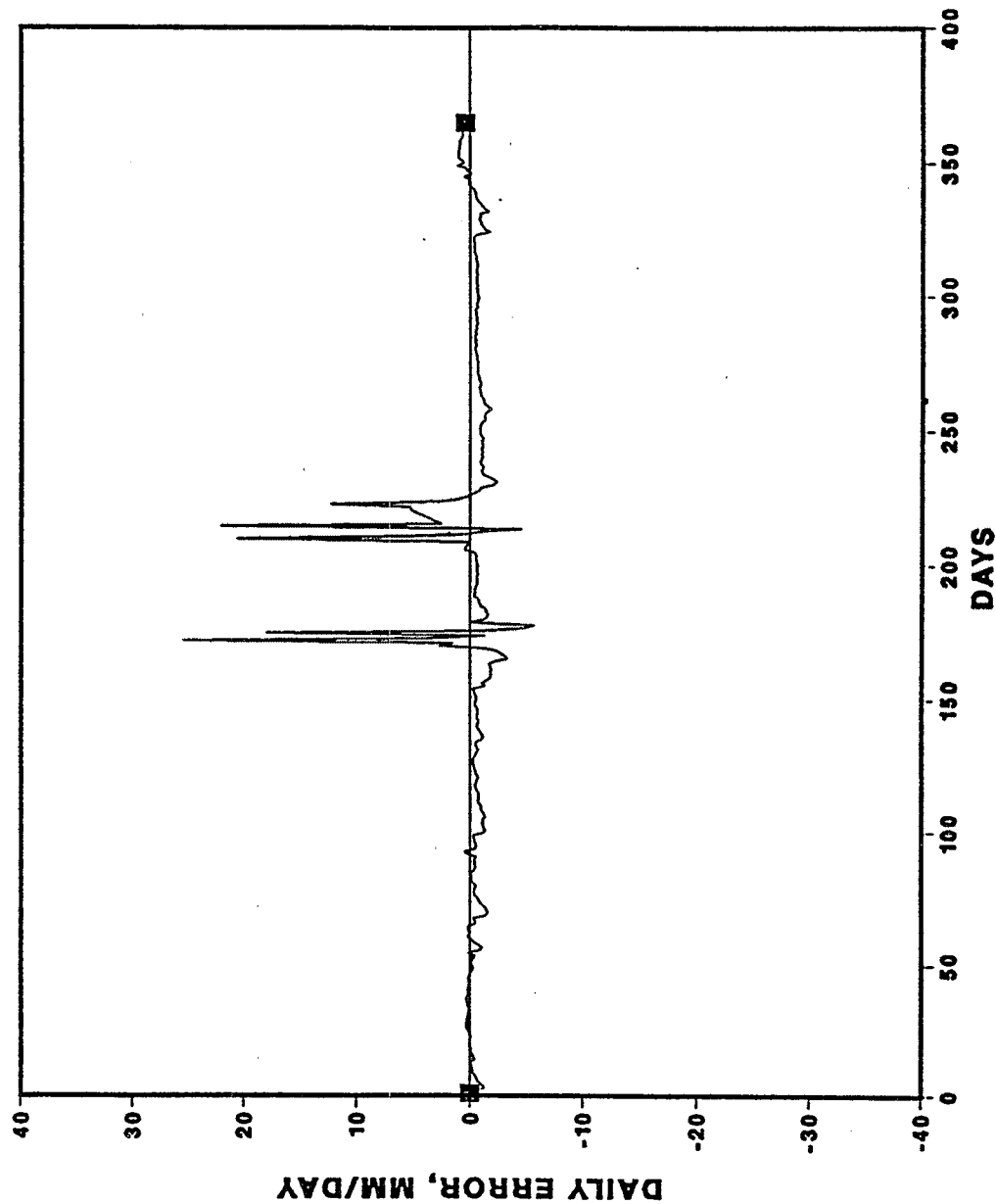


Figure 14. Verification results of daily outflow error.

LAKE PANTHER COMPARISON OF SIMULATION AND FIELD CHLORIDE CALIBRATION PERIOD: 9/1/80 - 8/31/81

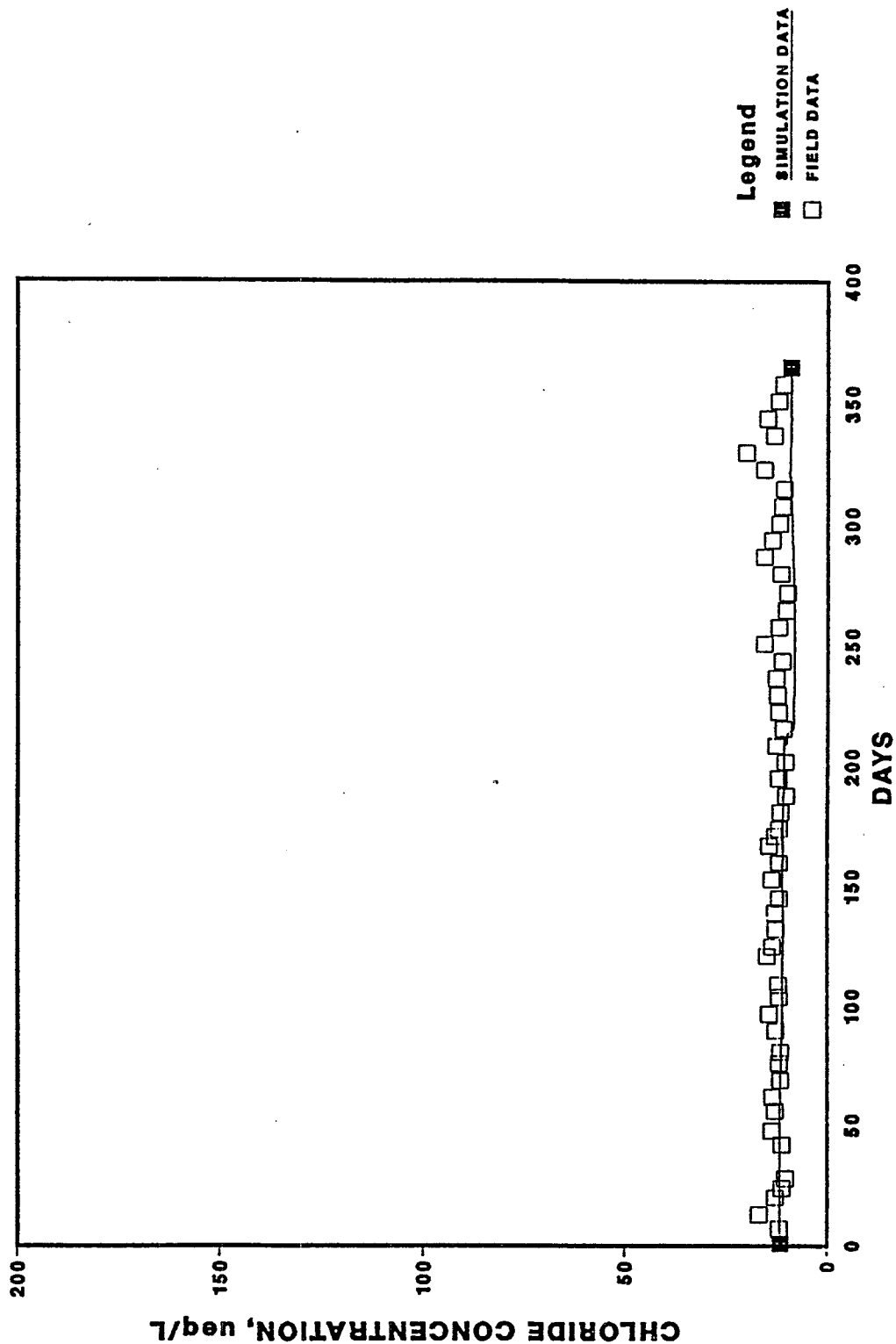


Figure 15. Verification results of lake chloride.

LAKE PANTHER COMPARISON OF SIMULATION AND FIELD SULFATE VERIFICATION PERIOD: 9/1/80 - 8/31/81

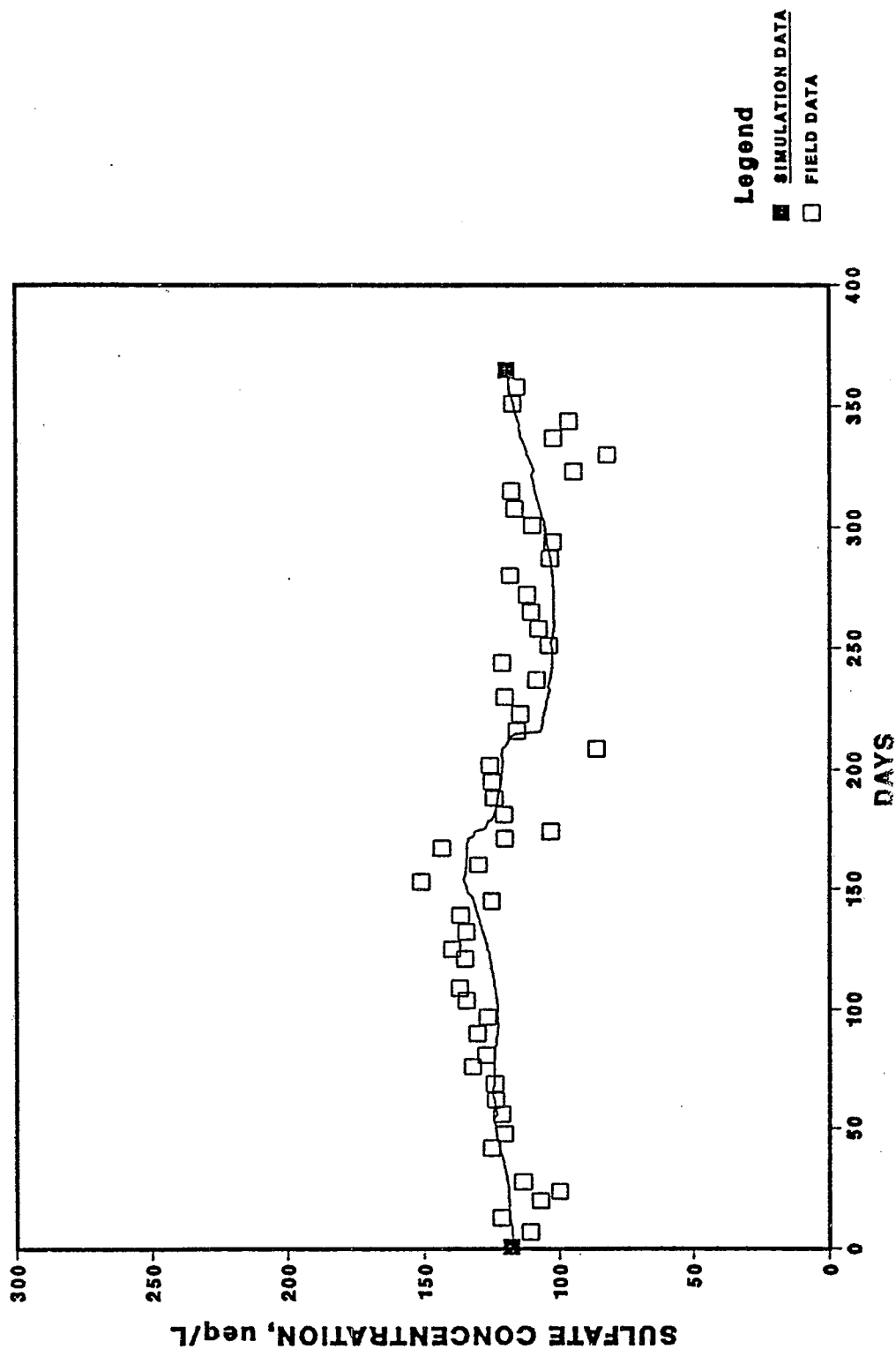


Figure 16. Verification results of lake sulfate.

LAKE PANTHER COMPARISON OF SIMULATION AND FIELD ALKALINITY VERIFICATION PERIOD: 9/1/80 - 8/31/81

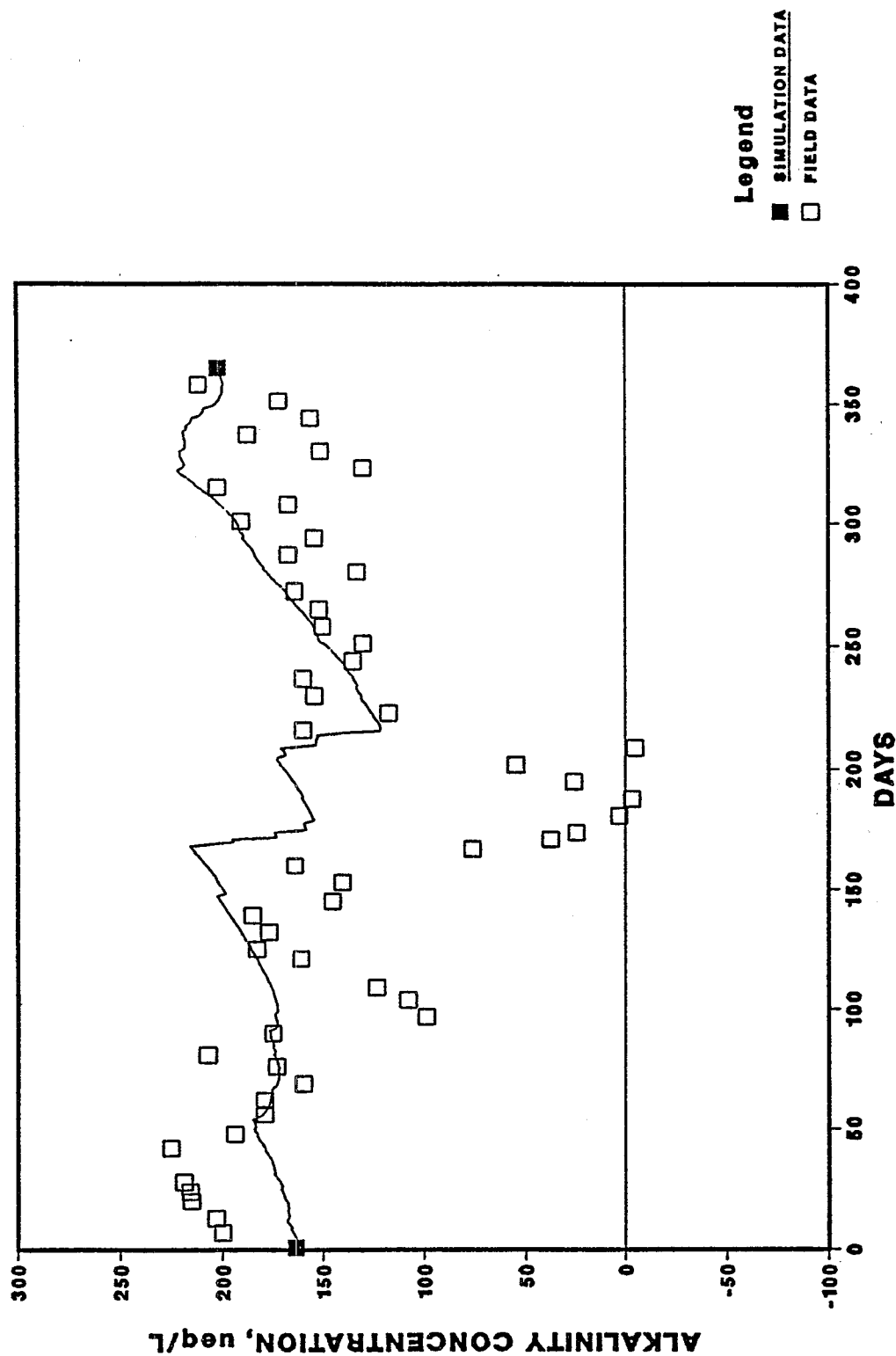


Figure 17. Verification results of lake alkalinity.

LAKE PANTHER, NEW YORK STATE **PROJECTION OF LAKE SULFATE UNDER VARIOUS LOADING SCENARIOS**

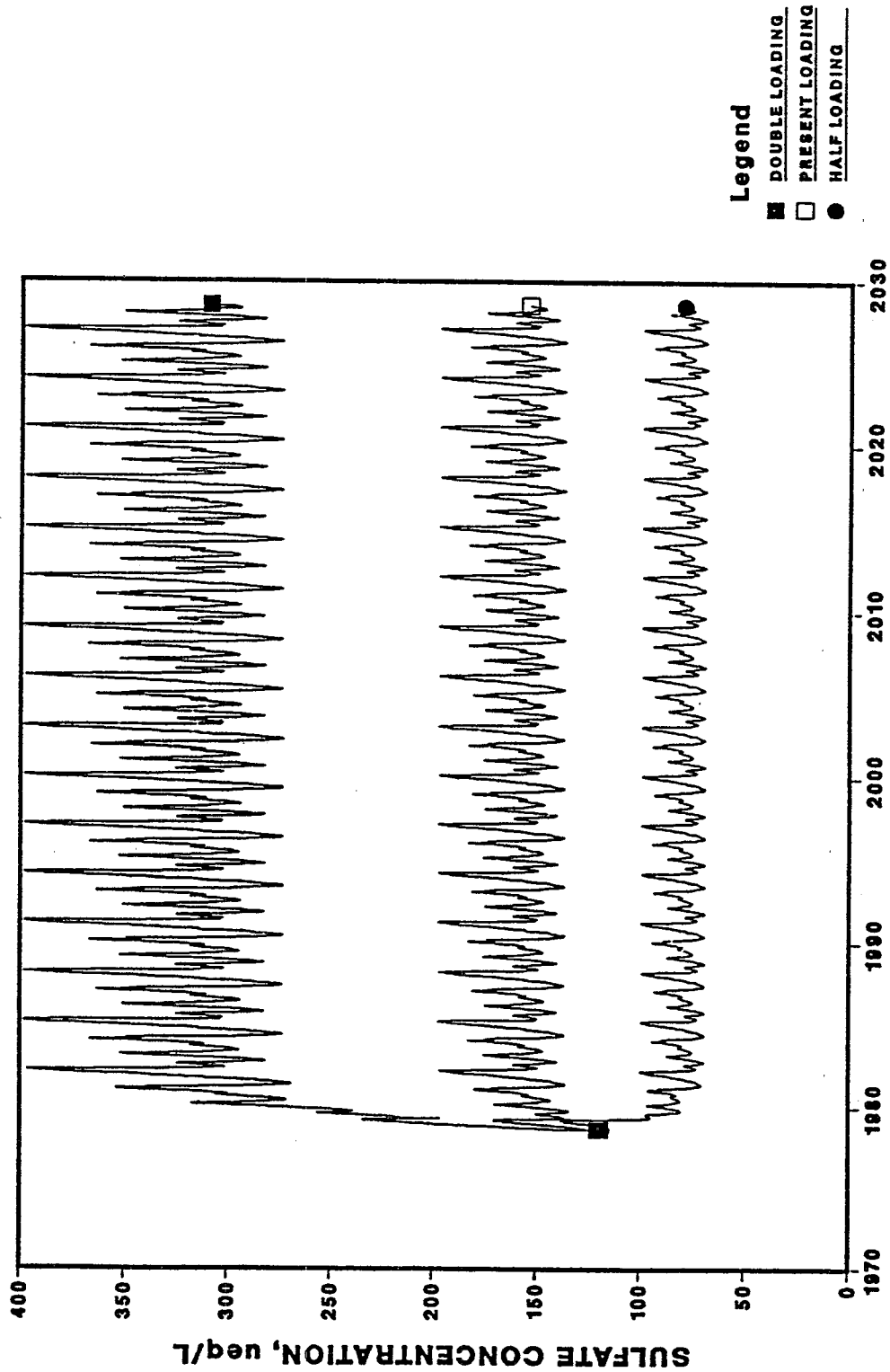


Figure 18. Lake sulfate projection under various loading scenarios.

LAKE PANTHER, NEW YORK STATE PROJECTION OF LAKE ALKALINITY UNDER VARIOUS LOADING SCENARIOS

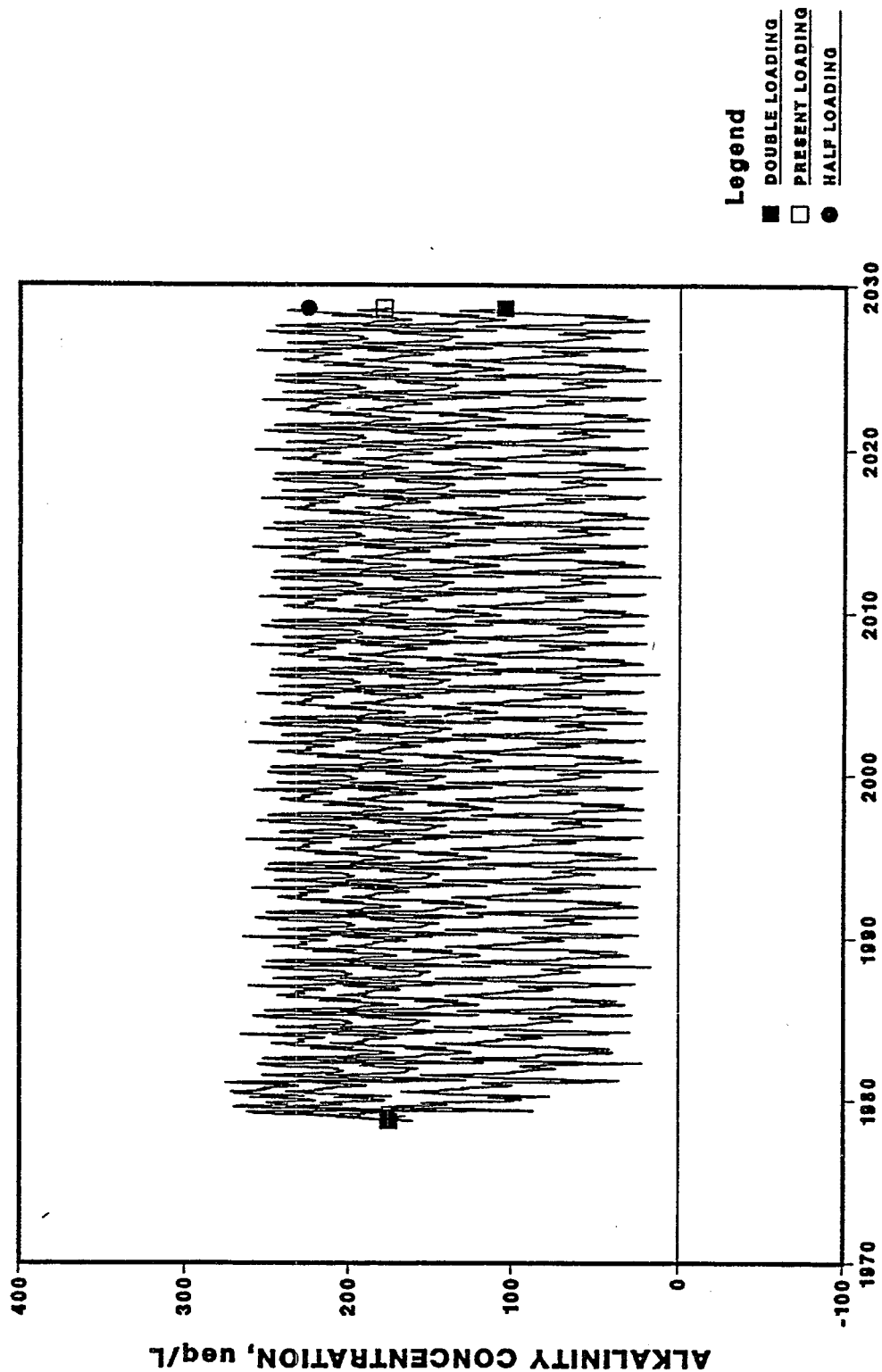


Figure 19. Lake alkalinity projection under various loading scenarios.

LAKE PANTHER CALIBRATION PERIOD: 9/1/78 - 8/31/80

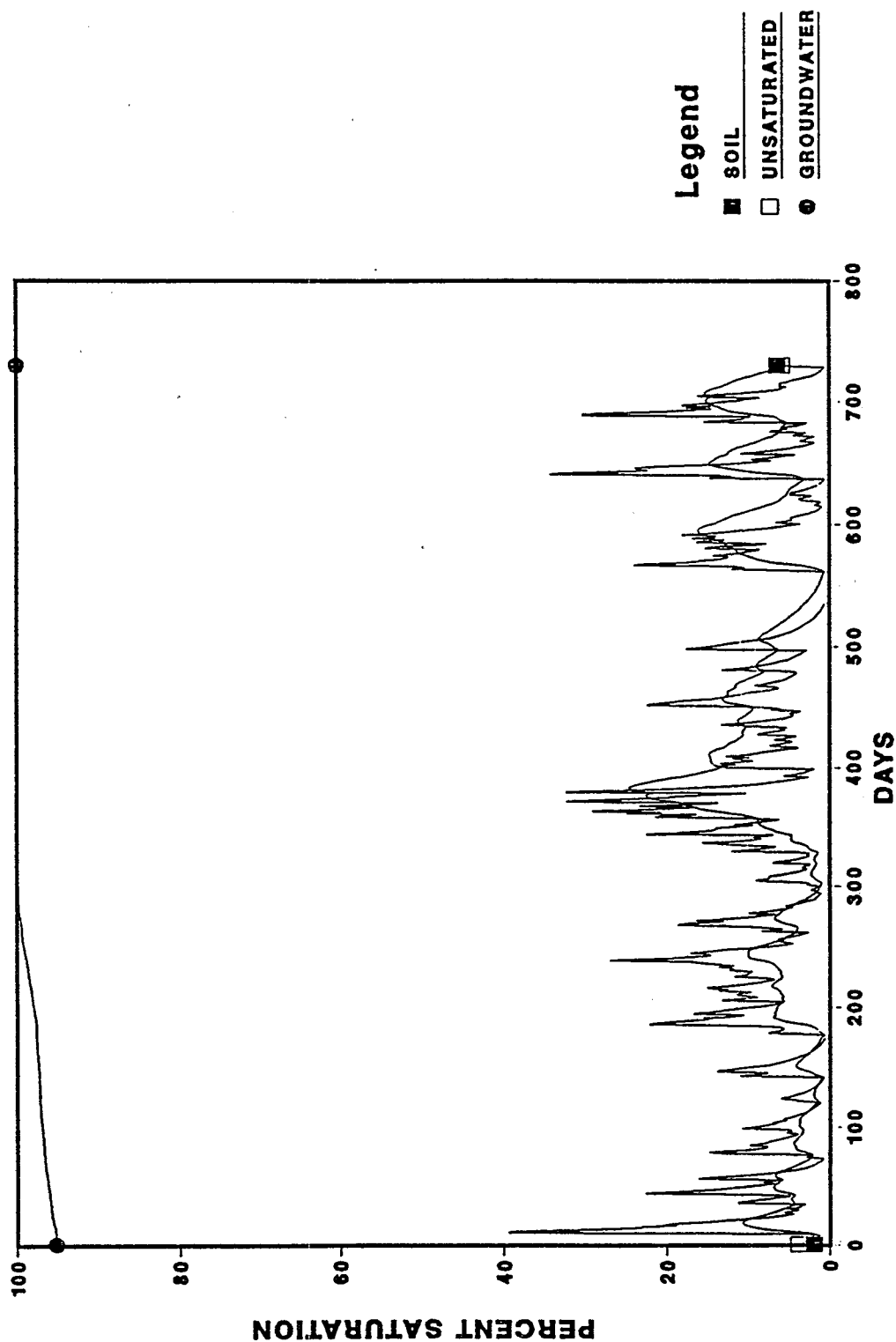
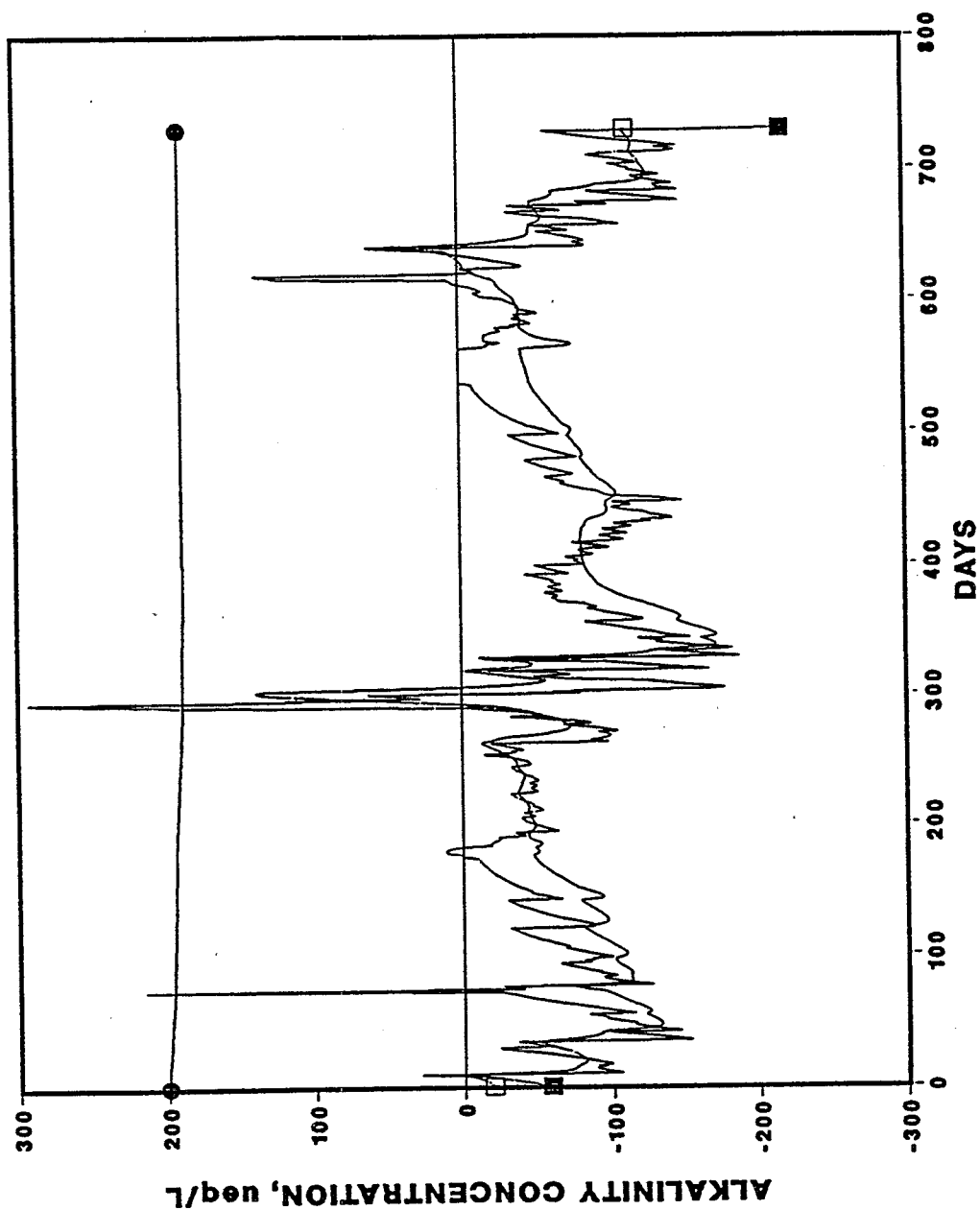


Figure 20. Percent moisture saturation of terrestrial compartment.

LAKE PANTHER CALIBRATION PERIOD: 9/1/78 - 8/31/80



Legend

- SOIL
- UNSATURATED
- GROUNDWATER

Figure 21. Alkalinity concentration of terrestrial compartments.

LAKE PANTHER CALIBRATION PERIOD: 9/1/78 - 8/31/80

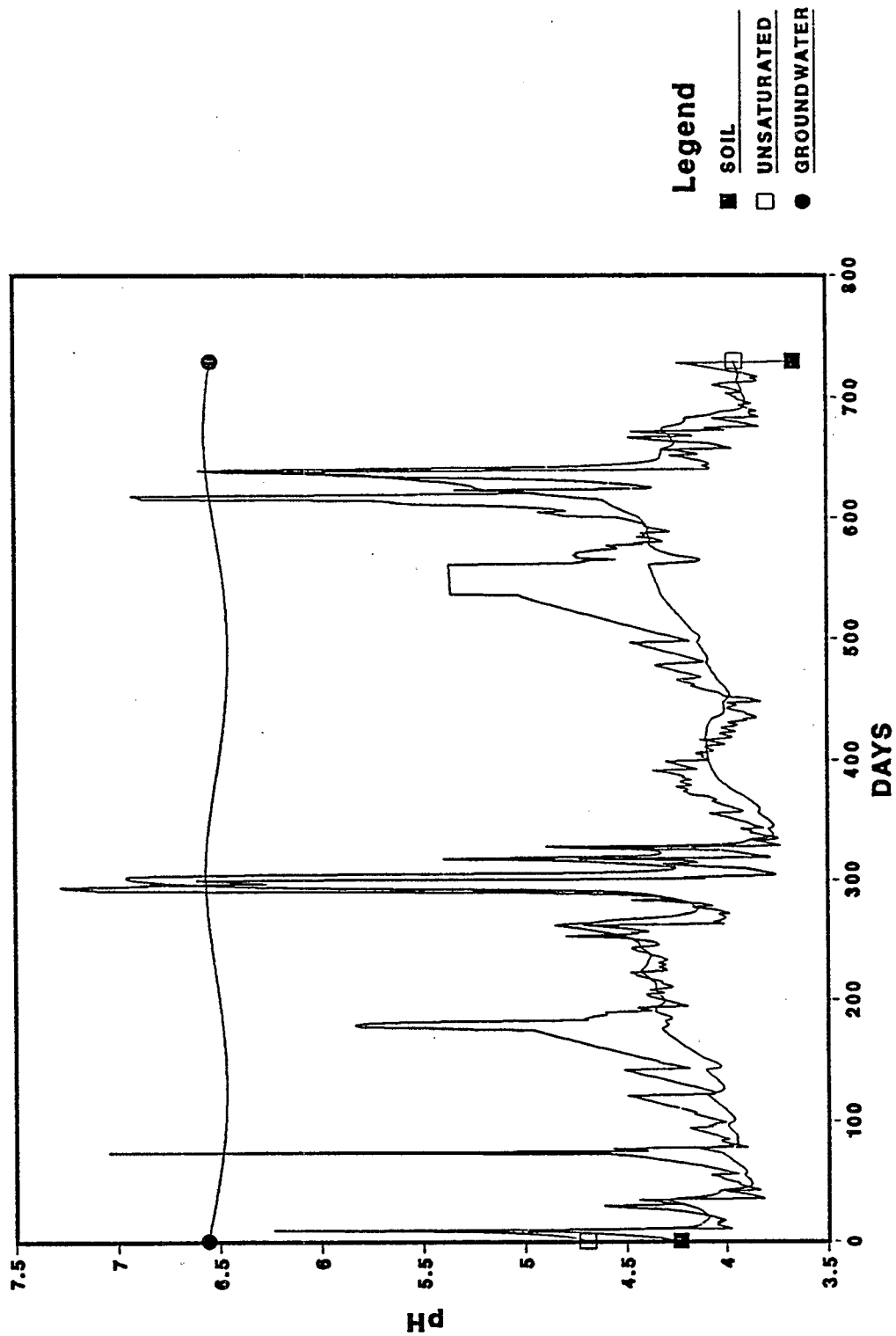


Figure 22. pH of terrestrial compartments.

LAKE PANTHER CALIBRATION PERIOD: 9/1/78 - 8/31/80

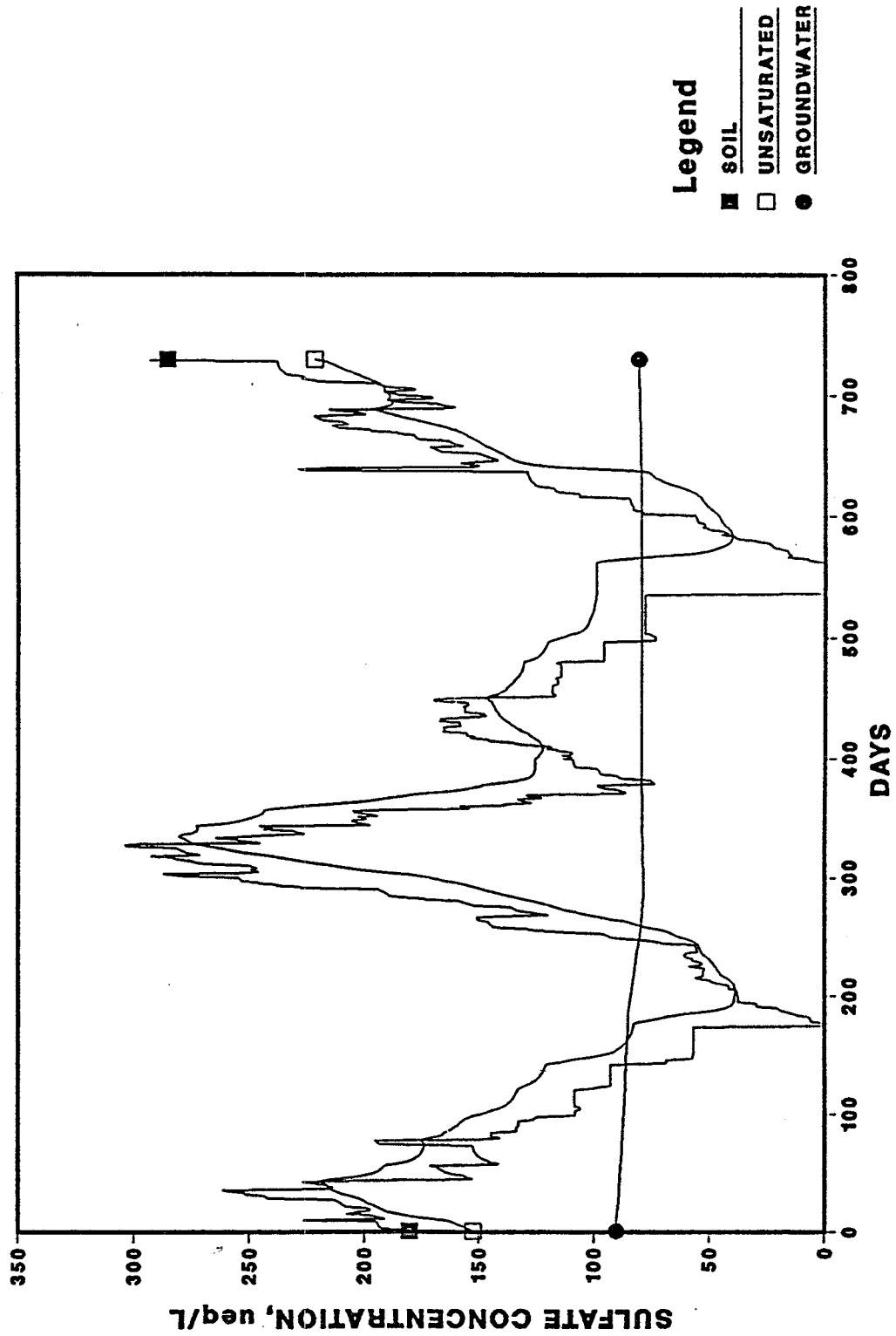


Figure 23. Sulfate concentration of terrestrial compartment.

Technical Report No. CEE-ARRG-86.05

Modeling Short and Long Term Impacts
of Acid Precipitation Using the Enhanced Trickle-Down Model
Clear Pond Case Study

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MODELING SHORT AND LONG TERM IMPACTS OF ACID PRECIPITATION USING THE ENHANCED TRICKLE-DOWN MODEL: CLEAR POND CASE STUDY

INTRODUCTION

The Enhanced Trickle-Down (ETD) model (Nikolaidis et al. 1986a) was used to calibrate a two year record of Clear Pond watershed. Clear Pond is 5.21 km² forested watershed located in the Adirondack Park region of New York State. The pond is considered neutral with a mean ANC of 100±19 µeg/L. It receives on the average of 1 m of annual precipitation. The vegetation of the watershed is dominated by Northern white Cedar, Paper and Yellow Birch, Red Spruce, Sugar maple, Beech, and Balsam Fir. The watershed is underlain by metanorthosite and anorthositic gneiss bedrock. The depth to bedrock is 6.3 m. The predominant soil series is Becket fine sandy loam. Clear Pond is located about 60 miles northeast of Lake Woods and Panther.

MODEL CALIBRATION

PROCEDURE

The calibration of ETD for Lake Panther was obtained by decoupling the hydrologic, sulfate and alkalinity submodels, similar to the calibration of Lake Panther (Nikolaidis et al. 1986b). Keeping the same guideline for establishing the optimum value of discharge, by trial and error the lateral and vertical percolation flow parameters were adjusted. These adjustments helped in capturing the seasonal variability as well as the peaks and valleys of the daily discharge. In order to obtain closure of the cumulative flow during the calibration period, the evaporation and snowmelt parameters were adjusted as well. Continuous refinements of the hydrologic parameters were applied until agreement between the simulation and field data was achieved. Trial and error adjustments to sulfate and alkalinity parameters were made starting with the initial values of Lake Panther in a similar manner.

INPUT DATA

The time series data of surface precipitation, evaporation and temperature for the calibration and verification periods are presented in Figures 1, 2 and 3. Precipitation and temperature data were collected as part of the RILWAS project. Evaporation measurements were obtained by using van Bavel's combination method (Nikolaidis 1986c).

Figures 4 and 5 present the wet and dry daily sulfate and acidity loading time series. An analysis of wet and dry deposition is presented in Table 1. Approximately 29.5% of the total acidity is dry deposition and 40% of the total sulfate loading is dry sulfate. The total acidity loading is 849 eg/ha/yr and the total sulfate loading is 790.2 eg/ha/yr.

RESULTS

Table 2 presents a partial list of the hydrologic and chemical watershed descriptors that were input to the model. The optimum values of the calibrated parameters are presented in Table 3. Comparison between lake discharge and field data are presented in figures 6, 7 and 8. Figure 6 contains the cumulative discharge of simulation and field data only for the 443 days of measured discharge. The missing data days were eliminated from the simulation results in order to construct this plot. Figure 8 shows the daily error between simulation and field data.

Figures 9 through 11 present the chloride, sulfate and alkalinity simulations and field data comparison. In order to obtain these simulations the sulfate loading was increased 1.5 times, and the alkalinity and chloride loading was increased 1.3 times the loading of the field data presented in Table 1 and Figures 4 and 5. The rationale of increasing the measured loading of Clear Pond is partially presented in Figure 12. Figure 12 presents a simulation of sulfate under actual measured data. In this simulation, there is a definite trend of sulfate decline in the lake. When a calibration of the terrestrial

compartments was attempted, it was found that the sorption partitioning coefficients had to be at least 2 orders of magnitude less than the optimum coefficients of Woods and Panther lakes and still there was a definite trend of decline. This prompted the fact that a definite increase in loading is necessary.

Table 4 contains a complete hydrologic budget for Lake Panther. Direct precipitation accounts for 11.2% of the total inflow to the lake. The majority of the water is coming through the unsaturated zone (36.0%). Finally, 26.1% is due to snowmelt and 26.7% is from the soil compartment.

An alkalinity budget for Lake Panther is presented in Table 5. The majority of the acidity input to the lake is coming through soil and unsaturated zone, with 41.6 and 22.6%, respectively. Wet deposition contributes 13.8% and dry 7.8% of the total acidity input.

A sulfate budget is shown in Table 6. The majority of sulfate input to the lake is coming through the soil and unsaturated zone with 40 and 46.6%, respectively. Wet and dry deposition contribute 5% each. The net sulfate reduction in the lake sediments is 13.6% of the total sulfate deposition.

Table 7 presents the MSE evaluation for the calibration period for discharge, chloride, alkalinity and sulfate.

REFERENCES

Nikolaidis, N. P., Rajaram, H., Schnoor, J. L. and Georgakakos, K. P. (1986a) Enhanced Trickle-Down model description. Civil and Environmental Engineering, University of Iowa, Technical Report No. CEE-ARRG-86.01.

Nikolaidis, N. P., Georgakakos, K. P., and Schnoor, J. L. (1986b) . Modeling Short and long term impacts of acid precipitation using the Enhanced Trickle- Down model: Lake Panther case study. Civil and Environmental Engineering, University of Iowa, Technical Report No. CEE-ARRG-86.04.

Nikolaidis, N. P. (1986c). Estimation of daily potential evaporation. Civil and Environmental Engineering, University of Iowa, Technical Report No. CEE- ARRG-86.02.

Table 1. Clear Pond analysis of wet and dry deposition.

Period	ACIDITY (eg/ha-yr)		SULFATE (eg/ha-yr)	
	Wet	Dry	Wet	Dry
8/82-7/83	507.0	259.8	447.2	320.3
7/83-8/84	<u>690.0</u>	<u>241.3</u>	<u>503.4</u>	<u>309.5</u>
Average	598.5	250.5	475.3	314.9

Total average Acidity = 849 eg/ha-yr
 Dry deposition = 29.5% of total deposition

Total average Sulfate = 790.2 eg/ha-yr
 Dry deposition = 40.0% of total deposition

Sulfate Loading (Average)

Wet = 22.82 kg/ha-yr
 Dry = 15.12 kg/ha-yr
 Total = 37.94 kg/ha-yr

On the average, 19.4 metric tons of sulfate are deposited on Clear Pond watershed (or 6.5 metric tons of sulfur).

Table 2. List of watershed descriptors used for model calibration.

GENERAL WATERSHED CHARACTERISTICS:

AQUATIC AREA =	0.7300E+06 SQUARE METERS
TERRESTRIAL AREA =	0.4480E+07 SQUARE METERS
CHARACTERISTIC DISTANCE =	0.1100E+4 METERS
DEPTH TO BEDROCK =	6.3000 METERS
PARTIAL PRESSURE OF ATM CO2 =	0.0003 ATMOSPHERES
SURFACE WATER PCO2 IS 1.50 TIMES SATURATED PCO2	

SOIL COMPARTMENT CHARACTERISTICS:

POROSITY =	0.2700
DEPTH OF SOIL LAYER =	0.5500 METERS
SUM OF BASES =	33.8000 EQUIVALENTS/KILOGRAM
SOIL DENSITY =	1140.0000 KILOGRAMS/CU. METER

UNSATURATED ZONE COMPARTMENT CHARACTERISTICS:

POROSITY =	0.2000
TRANSPORTATION COEFFICIENT =	0.0010 INCHES/DAY
BARE=GROUND FROST COEFFICIENT =	0.1000
REDUCTION IN FROST COEFFICIENT =	0.0800
DAILY THAW RATE =	0.1200 DEGREES C
INITIAL FROST INDEX =	0.0000 DEGREES C
LIMITING FROST INDEX =	-3.0000 DEGREES C
THAW COEFFICIENT =	0.2000
BULK DENSITY =	1590.0000 KILOGRAMS/CU. METER

SURFACE WATER BODIES CHARACTERISTICS:

STREAM BED ELEVATION AT OUTFLOW =	18.0000 METERS
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GROUNDWATER COMPARTMENT CHARACTERISTICS:

POROSITY =	0.2000
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Table 3. List of optimum values of the calibrated parameters.

a) Hydrologic Parameters

-Snow:

BETA = 0.8095
KAPPA = 1.1423
KPAN2 = 0.1766

-Evaporation

KPAN3 = 1.3171
KPAN5 = 1.0381

-Lateral and Vertical Flows:

KLAT3 = 54.781
KLAT4 = 55.791
KPERC3 = 2.3117E-2

-Groundwater

D1 = 0.6963
FRAX = 0.6804
ALF1 = 6.2375E-4
ALF2 = 3.4045E-2

b) Alkalinity Parameters

RE3 = 5.5E-7 m³/eq/day
KH4 = 9.0E-2 meq/m²/day
KH5 = 3.1E-1 meq/m²/day
KH6 = 2.0E-3 meq/m²/day
K04 = 4.1E-2 meq/m²/day
K05 = 7.0E-2 meq/m²/day
K06 = 0.1E-3 meq/m²/day

c) Sulfate Parameters

CF = 2.0247
KP3 = 5.0E-4 eg/kg/eq/m³
KP4 = 4.0E-4 eg/kg/eq/m³
K = 1.033E-3 1/day
KP6 = 9.0E-6 eg/kg/eq/m³

Table 4. Monthly Hydrologic Budget of Clear Pond

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Out 2	Out 3	Storage
0.4498E-02	0.0000E+00	0.2888E-02	0.7018E-02	0.5571E-06	0.2562E-05	0.1076E-06	0.2415E-02	0.1898E-02	0.1009E-01
0.1165E-01	0.0000E+00	0.2471E-01	0.3402E-01	0.7742E-05	0.1613E-04	0.6773E-06	0.1773E-01	0.4773E-01	0.4946E-02
0.6907E-02	0.0000E+00	0.1435E-01	0.2056E-01	0.6829E-06	0.1558E-04	0.6544E-06	0.1350E-01	0.3049E-01	-0.2163E-02
0.6969E-02	0.0000E+00	0.1862E-01	0.2330E-01	0.5056E-05	0.1613E-04	0.6775E-06	0.1091E-01	0.3907E-01	-0.1061E-02
0.9561E-02	0.2994E-02	0.2080E-01	0.2812E-01	0.1002E-01	0.1563E-04	0.6564E-06	0.8889E-02	0.4717E-01	0.5439E-02
0.1340E-02	0.1964E-01	0.6252E-02	0.1924E-01	0.7200E-09	0.1614E-04	0.6778E-06	0.2447E-02	0.4010E-01	0.3943E-02
0.1118E-02	0.5243E-03	0.5291E-02	0.1105E-01	0.2575E-08	0.1613E-04	0.6775E-06	0.0000E+00	0.3169E-01	-0.1369E-01
0.2753E-02	0.1627E-01	0.7341E-02	0.1059E-01	0.2105E-06	0.1456E-04	0.6113E-06	0.0000E+00	0.2591E-01	0.1166E-01
0.3589E-02	0.5693E-01	0.1293E-01	0.1601E-01	0.1401E-06	0.1633E-04	0.6358E-06	0.1785E-02	0.7432E-01	-0.6627E-02
0.1478E-01	0.7734E-02	0.2238E-01	0.8023E-01	0.8846E-06	0.1566E-04	0.6578E-06	0.5147E-02	0.4923E-01	0.1093E-01
0.1608E-01	0.8108E-01	0.4094E-01	0.4694E-01	0.1098E-03	0.1637E-04	0.6873E-06	0.1073E-01	0.1749E-00	-0.4386E-03
0.5668E-02	0.0000E+00	0.2244E-01	0.3900E-01	0.8764E-05	0.1564E-04	0.6567E-06	0.1943E-01	0.6174E-01	-0.1404E-01
0.1231E-01	0.0000E+00	0.1214E-01	0.1161E-01	0.8570E-04	0.1601E-04	0.6726E-06	0.2355E-01	0.1402E-01	-0.1484E-02
0.8179E-01	0.0000E-00	0.3300E-01	0.2932E-01	0.1439E-03	0.1617E-04	0.6791E-06	0.1584E-01	0.5408E-01	0.4336E-02
0.8075E-02	0.0000E+00	0.1626E-01	0.2013E-01	0.2863E-04	0.1558E-04	0.6545E-06	0.1530E-01	0.3063E-01	-0.1431E-02
0.1128E-01	0.0000E+00	0.2586E-01	0.3086E-01	0.1494E-04	0.1616E-04	0.6788E-06	0.1122E-01	0.5479E-01	0.2019E-02
0.1694E-01	0.1407E-01	0.3489E-01	0.3903E-01	0.2036E-03	0.1571E-04	0.6600E-06	0.3398E-02	0.9142E-01	0.1033E-01
0.1102E-01	0.2930E-03	0.3164E-01	0.5474E-01	0.1548E-02	0.1623E-04	0.6819E-06	0.0000E+00	0.1038E-02	-0.4506E-02
0.0000E+00	0.4040E-03	0.1248E-01	0.3477E-01	0.0000E+00	0.1615E-04	0.6783E-06	0.0000E+00	0.5450E-01	-0.6834E-02
0.5555E-02	0.4208E-01	0.1422E-01	0.1941E-01	0.1737E-05	0.1467E-04	0.6160E-06	0.0000E+00	0.7148E-01	0.9794E-02
0.7496E-03	0.1321E-01	0.9240E-02	0.2152E-01	0.2254E-08	0.1620E-04	0.6802E-06	0.0000E+00	0.5499E-01	-0.1026E-01
0.1481E-01	0.2189E+00	0.3538E-01	0.2873E-01	0.1782E-03	0.1604E-04	0.6736E-06	0.0000E+00	0.2169E+00	0.8117E-01
0.1772E-01	0.0000E+00	0.4114E-01	0.5654E-01	0.1643E-03	0.1637E-04	0.6877E-06	0.1524E-01	0.1886E+00	-0.6324E-01
0.8021E-02	0.0000E+00	0.1334E-01	0.3261E-01	0.1190E-04	0.1281E-04	0.5255E-06	0.1740E-01	0.3438E-01	-0.6782E-02
0.2042E+00	0.4742E+00	0.4850E+00	0.6554E+00	0.2612E-02	0.3647E-03	0.1332E-04	0.1949E+00	0.1610E-01	-0.1709E-01

Note: Unit: m of water per month (over the entire watershed-207 ha)

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Out 2: Evaporation from the Lake,

Out 3: Outflow from the Lake,

Storage: Change in Lake storage

Table 5. Monthly Alkalinity Budget of Clear Pond

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Input 7	Out 2	Reaction	Storage
0.1659E+04	0.0000E+00	-0.1115E+04	-0.2944E+03	-0.2055E+00	0.2001E+01	0.5286E-01	-0.6114E+03	0.9331E+03	0.1379E+05	0.9180E+04
0.4470E+04	0.0000E+00	-0.5450E+04	-0.5705E+03	-0.3222E+01	0.1261E+02	0.3439E+00	-0.3791E+04	0.2425E+05	0.8554E+05	0.4816E+05
0.1970E+04	0.0000E+00	-0.3453E+04	-0.4795E+04	-0.1043E+00	0.1221E+02	0.3646E+00	-0.3857E+04	0.1693E+05	0.8082E+05	0.5942E+05
0.2842E+04	0.0000E+00	-0.7320E+04	-0.1052E+04	-0.1899E+01	0.1266E+02	0.4061E+00	-0.1446E+04	0.2341E+05	0.7607E+05	0.4212E+05
0.4216E+04	0.0000E+00	-0.1177E+05	-0.3657E+04	-0.3131E+03	0.1228E+02	0.3976E+00	-0.6285E+03	0.2855E+05	0.4515E+05	-0.3673E+04
0.6446E+03	-0.4149E+04	-0.2150E+04	-0.4416E+03	-0.1426E+03	0.1269E+02	0.4095E+00	-0.8894E+03	0.2408E+05	0.4200E+05	0.9657E+04
0.2019E+03	-0.2134E+03	-0.2203E+04	-0.7022E+03	-0.4651E-03	0.1270E+02	0.4075E+00	-0.7558E+03	0.1899E+05	0.4198E+05	0.1893E+05
0.3953E+03	-0.5312E+04	-0.3502E+04	-0.1435E+04	-0.2818E-01	0.1147E+02	0.3784E+00	-0.5233E+03	0.1596E+05	0.4403E+05	0.1691E+05
0.8144E+03	-0.6308E+04	-0.5845E-04	-0.2859E-04	-0.3551E-01	0.1283E+02	0.4074E-00	-0.6110E+03	0.5592E+05	0.8074E+05	0.8202E+04
0.3506E+04	-0.1160E+04	-0.1035E-05	-0.4130E+04	-0.2512E+02	0.1237E+02	0.4026E+00	-0.1084E+04	0.3013E+05	0.7523E+05	0.2485E+05
0.4703E+04	-0.5108E-04	-0.1376E+05	-0.1003E+05	-0.2606E+02	0.1293E+02	0.3708E+00	-0.1496E-04	0.9408E+05	0.3274E+05	-0.4646E+05
0.2274E+04	0.0000E+00	-0.3601E+04	-0.2628E+04	-0.3461E+01	0.1236E+02	0.3507E+00	-0.1507E+04	0.3267E-05	0.7876E+05	0.3619E+05
0.5041E+04	0.0000E+00	-0.8582E+03	-0.6501E+04	-0.4989E+02	0.1270E+02	0.4020E+00	-0.2028E+04	0.8316E+04	0.7872E+05	0.6894E+05
0.6674E+04	0.0000E+00	-0.1772E+05	-0.3707E+04	-0.7372E+02	0.1287E+02	0.4181E+00	-0.4010E+04	0.3326E-05	0.7936E+05	0.1393E+05
0.2680E+04	0.0000E+00	-0.8666E+04	-0.3283E+03	-0.5176E+01	0.1242E+02	0.4215E+00	-0.2284E+04	0.1972E-05	0.7632E+05	0.4330E+05
0.1961E+04	0.0000E+00	-0.1181E+05	-0.2612E+04	-0.2961E+01	0.1289E+02	0.4496E+00	-0.9369E+03	0.3628E+05	0.7301E+05	0.1942E+05
0.2818E+04	-0.1364E+04	-0.2050E+05	-0.8757E+04	-0.3495E+02	0.1255E+02	0.4239E+00	-0.6745E+03	0.5791E+05	0.4373E+05	-0.4832E+05
0.1654E+04	-0.9256E+02	-0.1229E+05	-0.1766E+05	-0.1640E+03	0.1297E+02	0.3869E+00	-0.9052E+03	0.5895E+05	0.4489E+05	-0.4682E+05
0.0000E+00	-0.1045E+03	-0.1462E+04	-0.5712E+04	0.0000E+00	0.1292E+02	0.3709E+00	-0.1021E+04	0.2977E+05	0.4604E+05	0.7987E+04
-0.1971E+04	-0.1356E+05	-0.6098E+04	-0.3749E+04	-0.3938E+00	0.1175E+02	0.3362E+00	-0.6970E+03	0.3790E+05	0.4815E+05	-0.1582E+05
-0.2700E+03	-0.3447E+04	-0.2849E+04	-0.6469E+04	-0.6978E-03	0.1298E+02	0.3587E+00	-0.4232E+03	0.2890E+05	0.8349E+05	0.4114E+05
-0.3331E+04	-0.2088E+05	-0.1451E+05	-0.1215E+05	-0.2847E+02	0.1286E+02	0.3347E+00	-0.1172E+04	0.1005E+06	0.8032E+05	-0.7222E+05
-0.4048E+04	0.0000E+00	-0.8198E+04	-0.1817E+05	-0.3142E+02	0.1313E+02	0.2688E+00	-0.4435E+03	0.6571E+05	0.8984E+05	-0.6756E+04
-0.1341E+04	0.0000E+00	-0.3520E+04	-0.5411E+04	-0.1605E+01	0.1003E+02	0.2167E+00	-0.1218E+04	0.2064E+05	0.6701E+05	0.3489E+05
-0.5933E+05	-0.6290E+05	-0.1780E+06	-0.9735E-05	-0.4659E+03	0.2892E+03	0.8690E+01	-0.3301E+05	0.8637E-06	0.1538E+07	0.2632E+06

Note: Unit: eq per month

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Input 7: Dry deposition to the Lake,

Out 2: Outflow from the Lake,

Reaction: Internal production in the Lake compartment,

Storage: Change in Lake storage

Table 6. Monthly Sulfate Budget of Clear Pond

Input 1	Input 2	Input 3	Input 4	Input 5	Input 6	Out 1	Input 7	Out 2	Reaction	Storage
0.1787E+04	0.0000E+00	0.1838E+04	0.4024E+04	0.2213E+00	0.1281E+01	0.6995E+01	0.6683E+03	0.1234E+04	-0.3464E+04	0.3621E+04
0.5523E+04	0.0000E+00	0.1803E+05	0.1967E+05	0.3997E+01	0.8098E+01	0.4389E+00	0.4144E+04	0.3093E+05	-0.2159E+05	-0.5133E+04
0.1895E+04	0.0000E+00	0.1246E+05	0.1208E+05	0.1132E+00	0.7858E+01	0.4237E+00	0.4240E+04	0.1974E+05	-0.1978E+05	-0.8845E+04
0.2285E+04	0.0000E+00	0.1668E+05	0.1392E+05	0.1473E+01	0.8158E+01	0.4359E+00	0.1620E+04	0.2514E+05	-0.1325E+05	-0.3872E+04
0.2466E+04	0.0000E+00	0.1819E+05	0.1704E+05	0.1493E+01	0.7911E+01	0.4319E+00	0.7687E+03	0.3104E+05	0.1680E+05	0.2423E+05
0.3951E+03	0.3376E-04	0.5413E+04	0.1175E+05	0.9044E-04	0.8169E+01	0.4640E+00	0.8441E+03	0.2747E+05	0.2283E+05	0.1714E+05
0.1347E+03	0.1927E-03	0.4474E+04	0.6789E+04	0.3103E-03	0.8165E+01	0.4768E+00	0.7717E+03	0.2223E-05	0.2288E+05	0.1300E+05
0.2639E+03	0.4642E+04	0.6262E+04	0.6505E+04	0.1831E-01	0.7367E+01	0.4400E+00	0.5498E+03	0.1859E+05	0.1297E+05	0.1260E-05
0.6084E+03	0.6330E+04	0.9819E+04	0.9878E+04	0.1861E-01	0.8266E+01	0.4777E+00	0.7875E+03	0.6591E+05	-0.1794E-03	-0.5643E+04
0.2753E+04	0.1162E+04	0.1544E+05	0.1257E+05	0.2490E+02	0.7934E+01	0.4441E+00	0.1288E+04	0.3314E+05	-0.1716E+05	-0.1706E+03
0.4217E+04	0.6222E-04	0.2636E+05	0.2928E+05	0.2307E+02	0.8316E+01	0.4357E+00	0.2075E+04	0.1111E+06	-0.2083E-05	-0.6371E+05
0.2693E+04	0.0000E-00	0.1540E+05	0.2453E+05	0.3884E+01	0.7987E+01	0.4085E+00	0.2656E+04	0.3839E+05	-0.1960E+05	-0.1271E+05
0.4454E+04	0.0000E+00	0.9892E+04	0.7380E+04	0.3868E+02	0.8231E+01	0.4197E+00	0.3408E+04	0.8793E+04	-0.2063E+04	-0.4246E+04
0.4159E+04	0.0000E+00	0.2924E+05	0.1908E+05	0.4616E+02	0.8363E+01	0.4273E+00	0.5076E+04	0.3403E+05	-0.2099E+05	0.2593E+04
0.2014E+04	0.0000E-00	0.1379E+03	0.1332E+05	0.3640E+01	0.8099E+01	0.4141E+00	0.2906E+04	0.1938E+05	-0.1933E+05	-0.4460E+04
0.2543E+04	0.0000E-00	0.2431E+05	0.2081E+05	0.4075E+01	0.8425E+01	0.4301E+00	0.1113E+04	0.3471E+05	-0.1308E+05	0.1196E+04
0.1048E+04	0.4118E+03	0.2738E+05	0.2665E+05	0.8989E+01	0.8201E+01	0.4244E+00	0.6592E+03	0.5877E+05	0.1652E+05	0.1392E+05
0.1039E+04	0.6481E+02	0.1953E+05	0.3740E+05	0.1033E+03	0.8475E+01	0.4436E+00	0.5476E+03	0.6746E+05	0.2195E+05	0.1319E+05
0.0000E+00	0.5155E+02	0.7358E+04	0.2367E+05	0.0000E+00	0.8431E+01	0.4539E+00	0.6363E+03	0.3640E+05	0.2187E+05	0.1722E+05
0.1249E+04	0.8031E+04	0.8099E+04	0.1318E+05	0.2211E+00	0.7657E+01	0.4199E+00	0.6091E+03	0.4859E+05	0.1242E+05	-0.4995E+04
0.2011E+03	0.2309E+04	0.5136E+04	0.1457E+05	0.5332E-03	0.8456E+01	0.4514E+00	0.4322E+03	0.3651E+05	-0.1700E+05	-0.3085E+05
0.2463E+04	0.1618E+05	0.1717E+05	0.1934E+05	0.3256E+02	0.8378E+01	0.4175E+00	0.1180E+04	0.1298E+06	-0.1608E+05	-0.8947E+05
0.4053E+04	0.0000E+00	0.1946E+05	0.3755E+05	0.2782E+02	0.8581E+01	0.3666E+00	0.1928E+04	0.8993E+05	-0.1756E+05	-0.4445E+05
0.1537E+04	0.0000E+00	0.1004E+05	0.2157E+05	0.1414E+01	0.6587E+01	0.2801E+00	0.1763E+04	0.2684E+05	-0.1340E+05	-0.5310E+04
-0.2322E+06	0.4980E+05	0.4897E-03	0.3442E+06	0.4225E+06	0.3260E+03	0.1874E+03	0.9896E+01	0.4069E+05	0.1016E+07	-0.2358E+06

Note: Unit: m of water per month (over the entire watershed-207 ha)

Input 1: Atmospheric compartment to Lake,

Input 2: Snow compartment to Lake,

Input 3: Soil compartment to Lake,

Input 4: Unsaturated zone compartment to Lake,

Input 5: Overland flow to Lake,

Input 6: Groundwater compartment to Lake

Out 1: Lake compartment to Groundwater,

Out 2: Evaporation from the Lake,

Out 3: Outflow from the Lake,

Storage: Change in Lake storage

Table 7. MSE Evaluation for the Calibration Period.

Variable	Units	n	MSE	RMSE
Discharge	m ³ /s	443	0.026	0.16
Chloride	μeq/L	24	5.61	2.37
Alkalinity	μeq/L	24	8294.0	18.6
Sulfate	μeq/L	24	79.7	8.9

CLEAR POND
PERIOD : 7/82 - 7/84

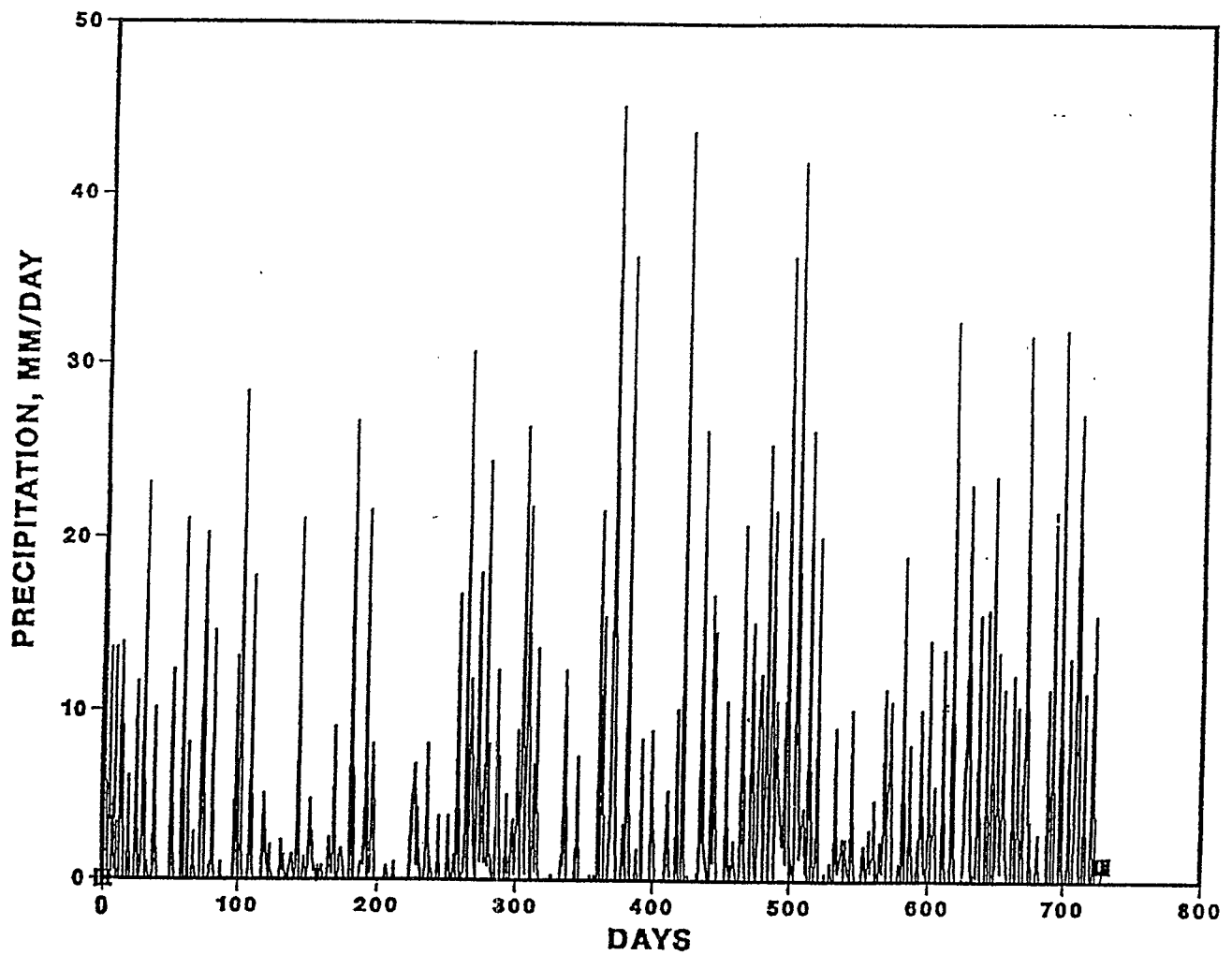


Figure 1. Precipitation data.

**CLEAR POND
PERIOD : 7/82 - 7/84**

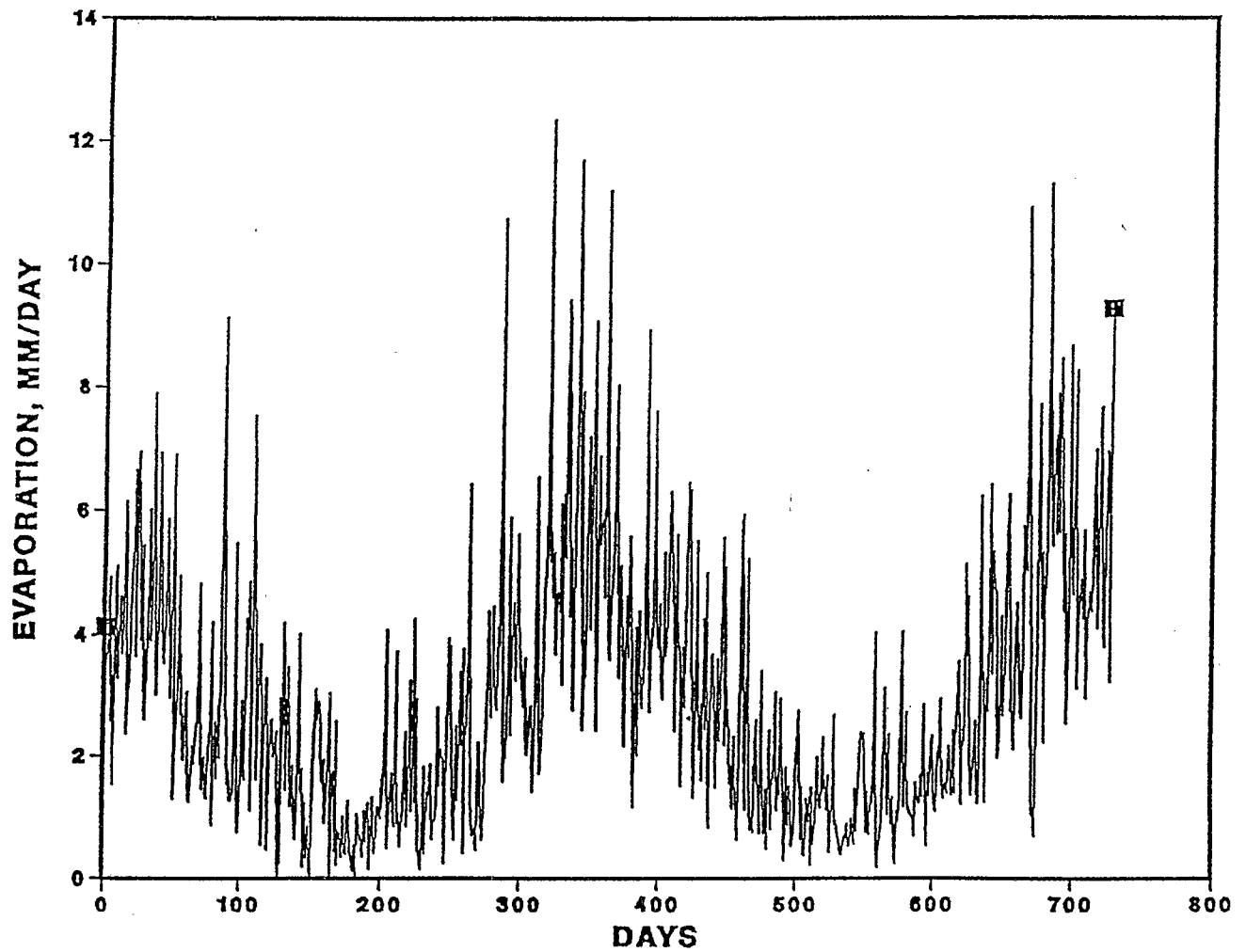
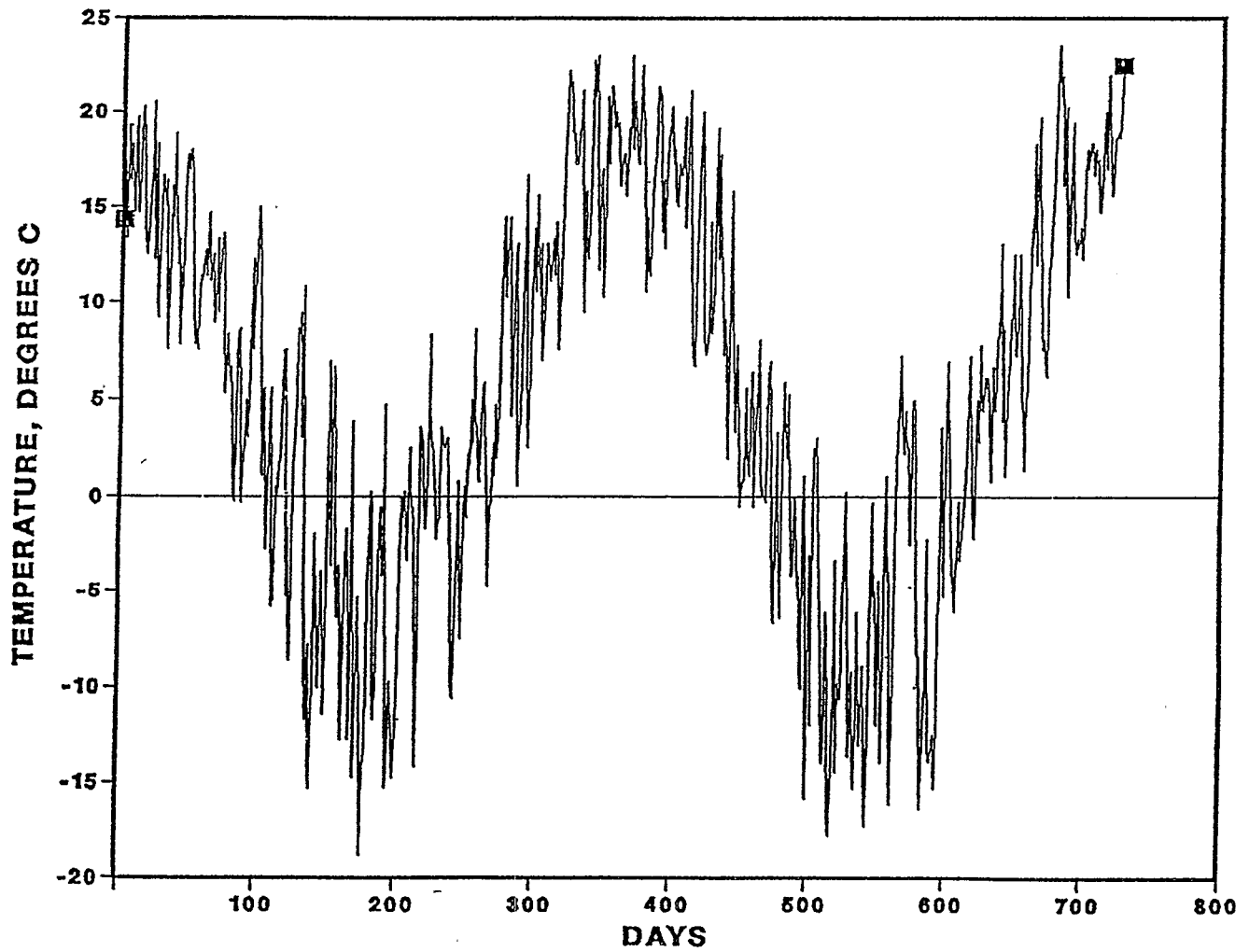


Figure 2. Evaporation data.

**CLEAR POND
PERIOD : 7/82 - 7/84**



3. Temperature data.

**CLEAR POND
TIME SERIES OF SULFATE DEPOSITION
SIMULATION PERIOD: 7/27/82 - 7/24/84**

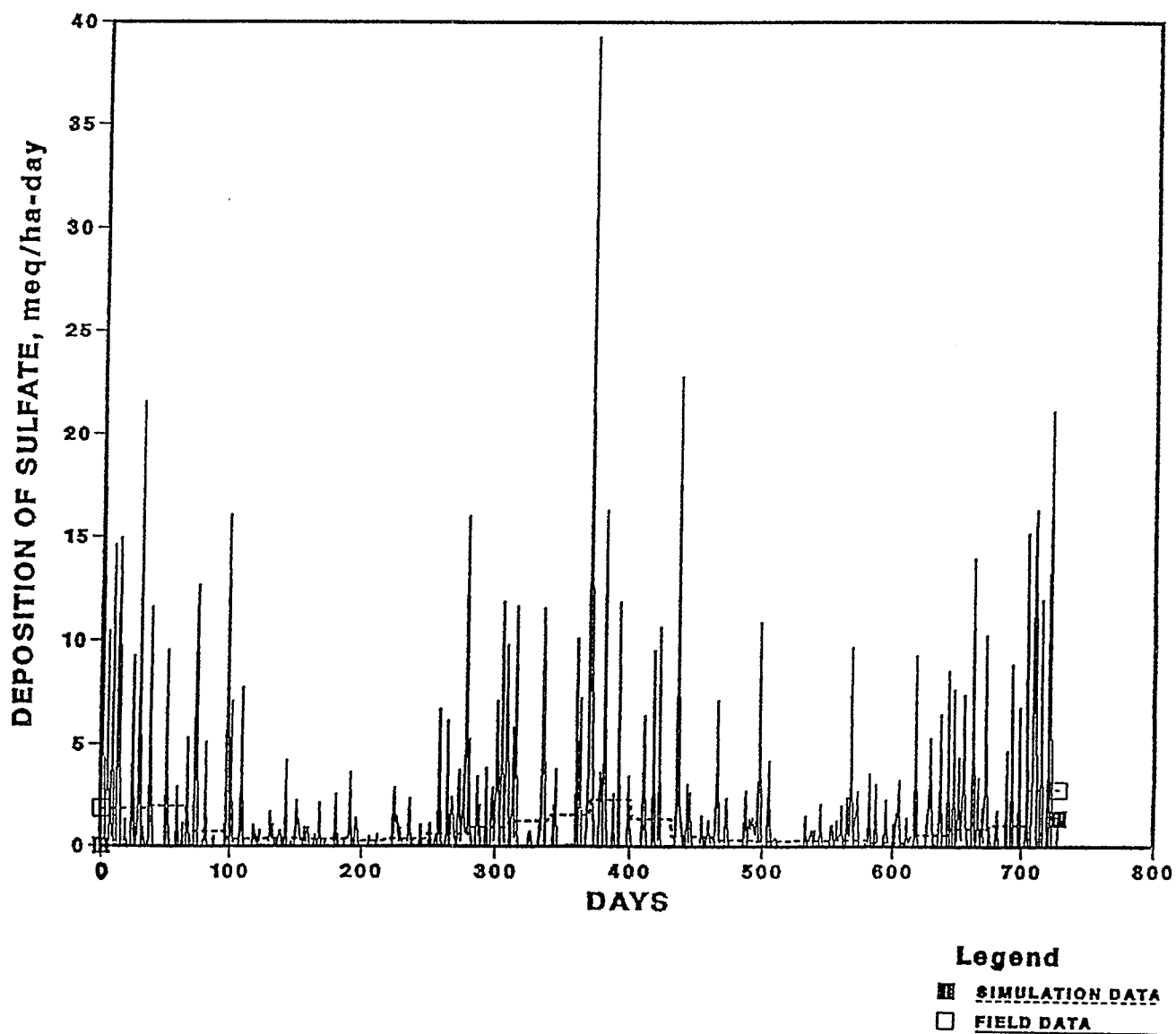


Figure 4. Wet and dry sulfate loading.

**CLEAR POND
TIME SERIES OF ACID DEPOSITION
SIMULATION PERIOD: 7/27/82 - 7/24/84**

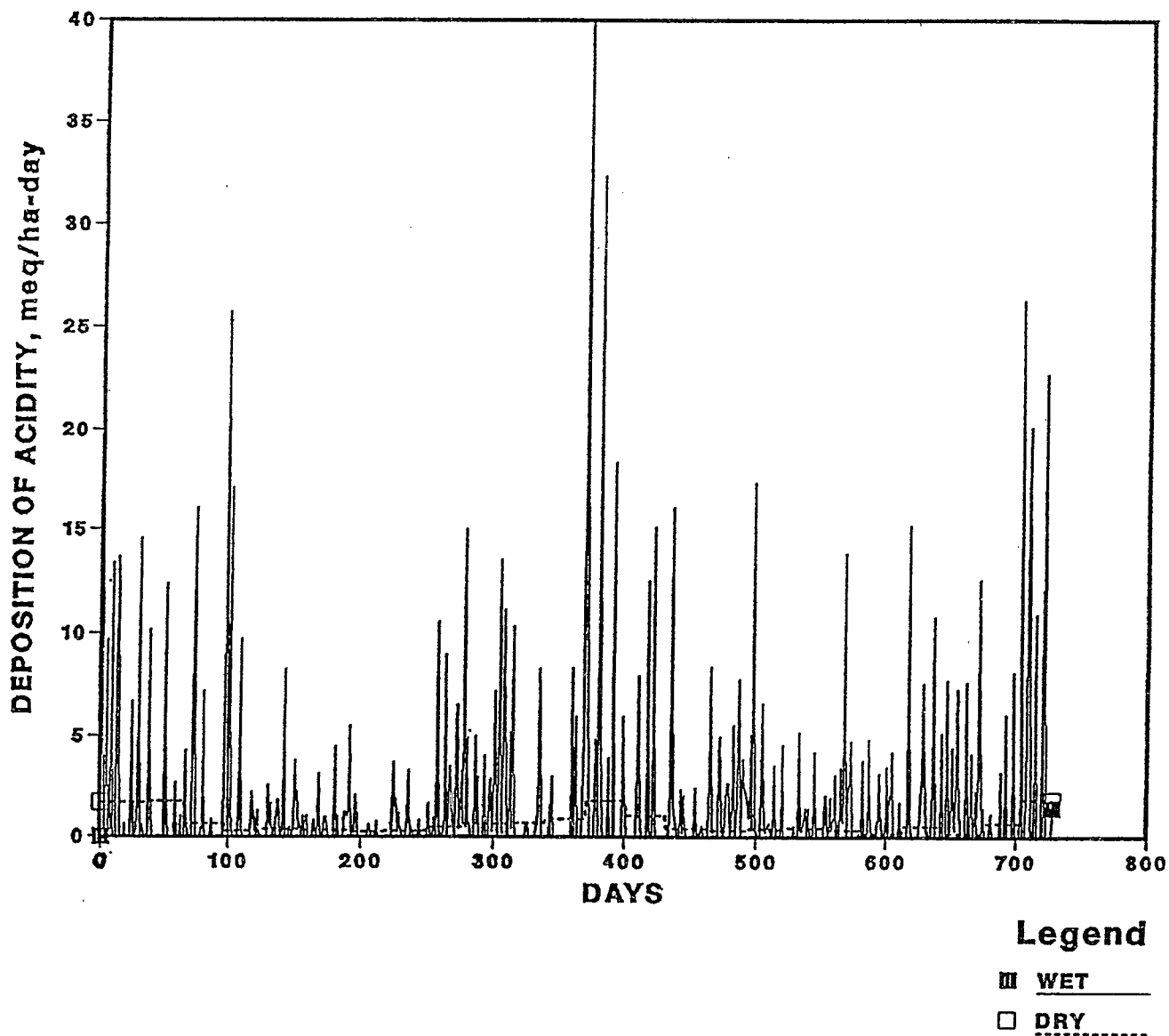


Figure 5. Wet and dry acidity loading.

**CLEAR POND
COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS
CALIBRATION PERIOD : 7/27/82 - 7/24/84**

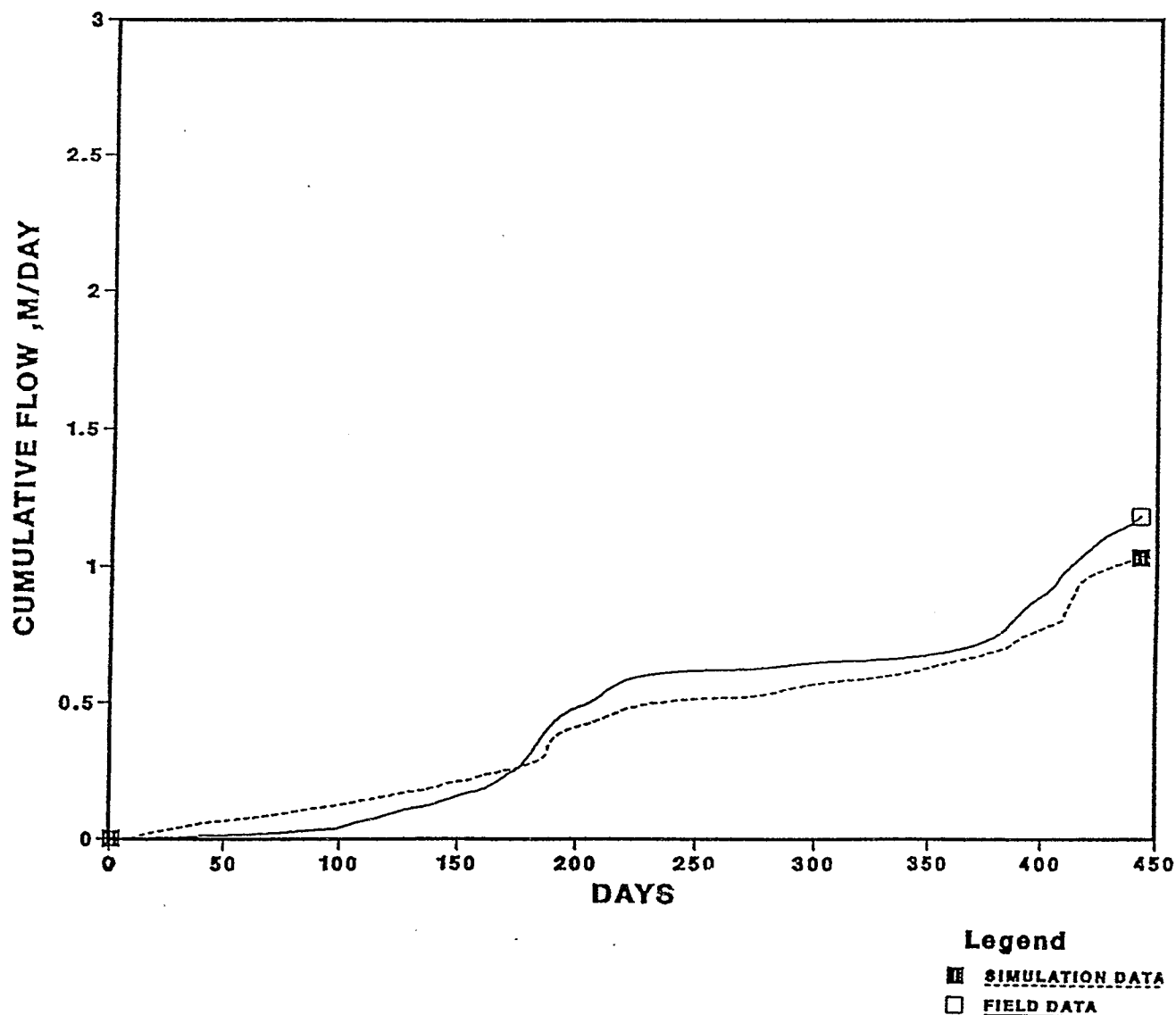


Figure 6. Calibration results of cumulative outflow.

**CLEAR POND
COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS
CALIBRATION PERIOD : 7/27/82 - 7/24/84**

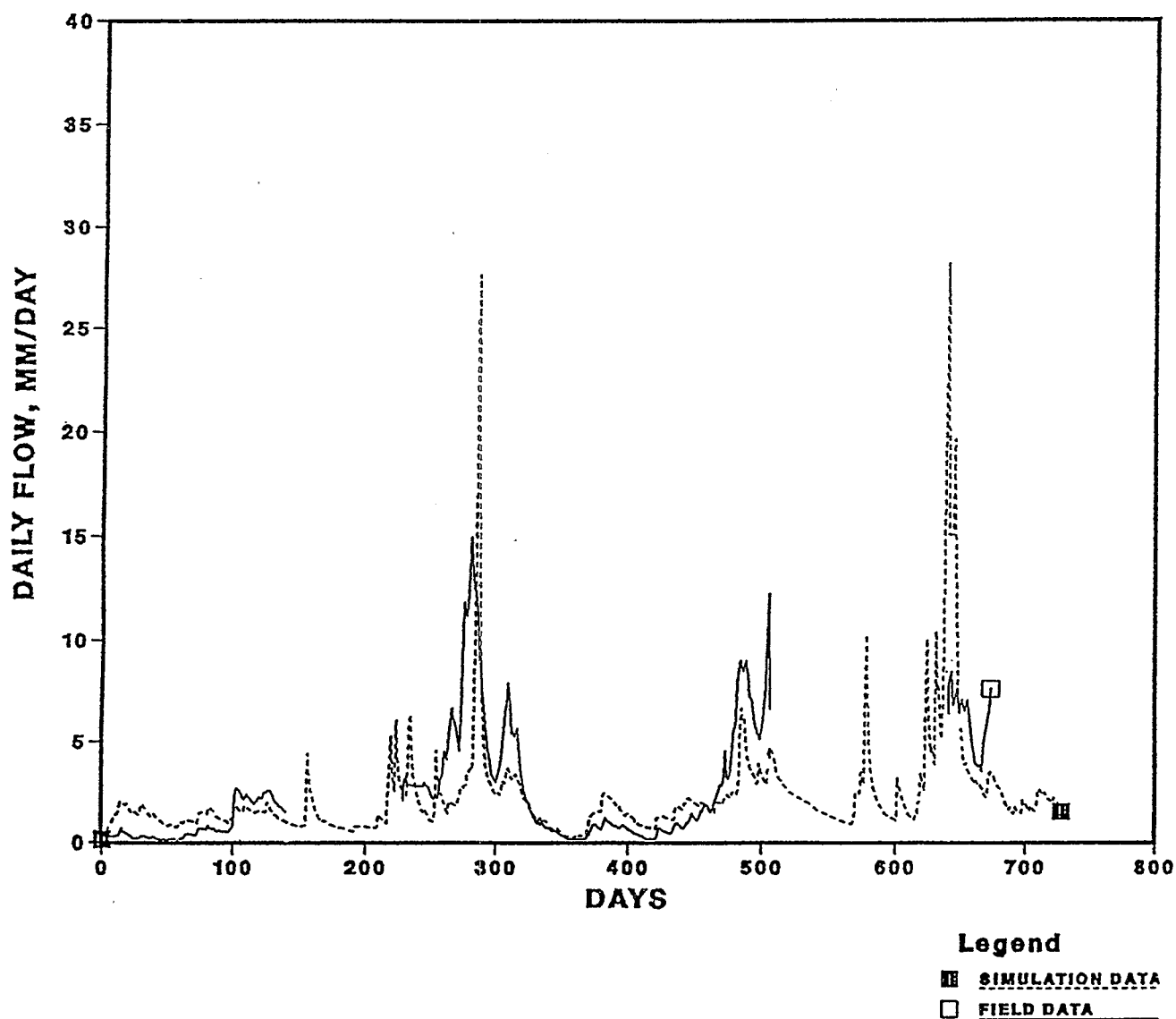


Figure 7. Calibration results of daily outflow.

**CLEAR POND
COMPARISON OF SIMULATED VERSUS FIELD OUTFLOWS
CALIBRATION PERIOD : 7/27/82 - 7/24/84**

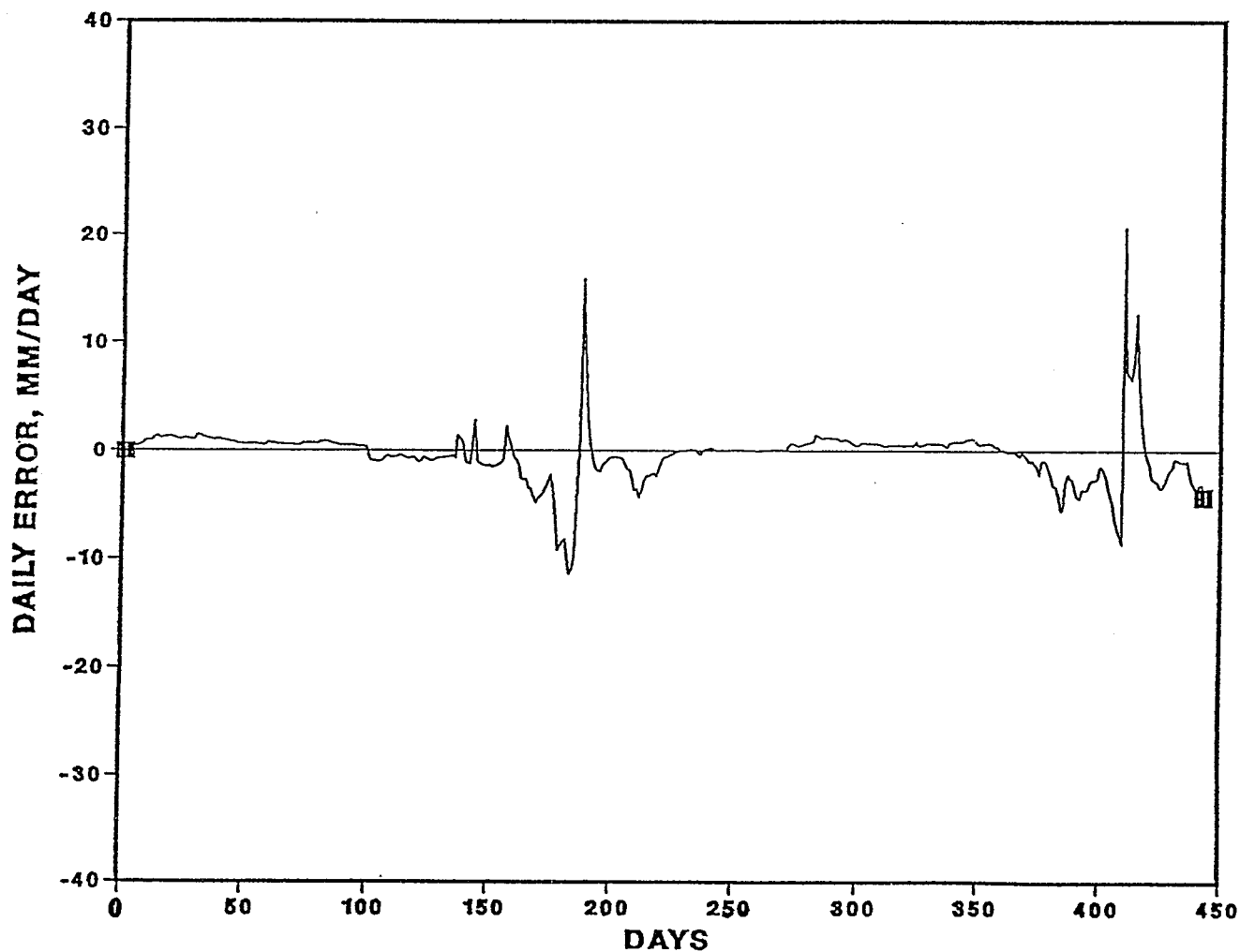


Figure 8. Calibration results of daily outflow error.

**CLEAR POND
COMPARISON OF SIMULATION AND FIELD CHLORIDE
CALIBRATION PERIOD: 7/27/82 - 7/24/84**

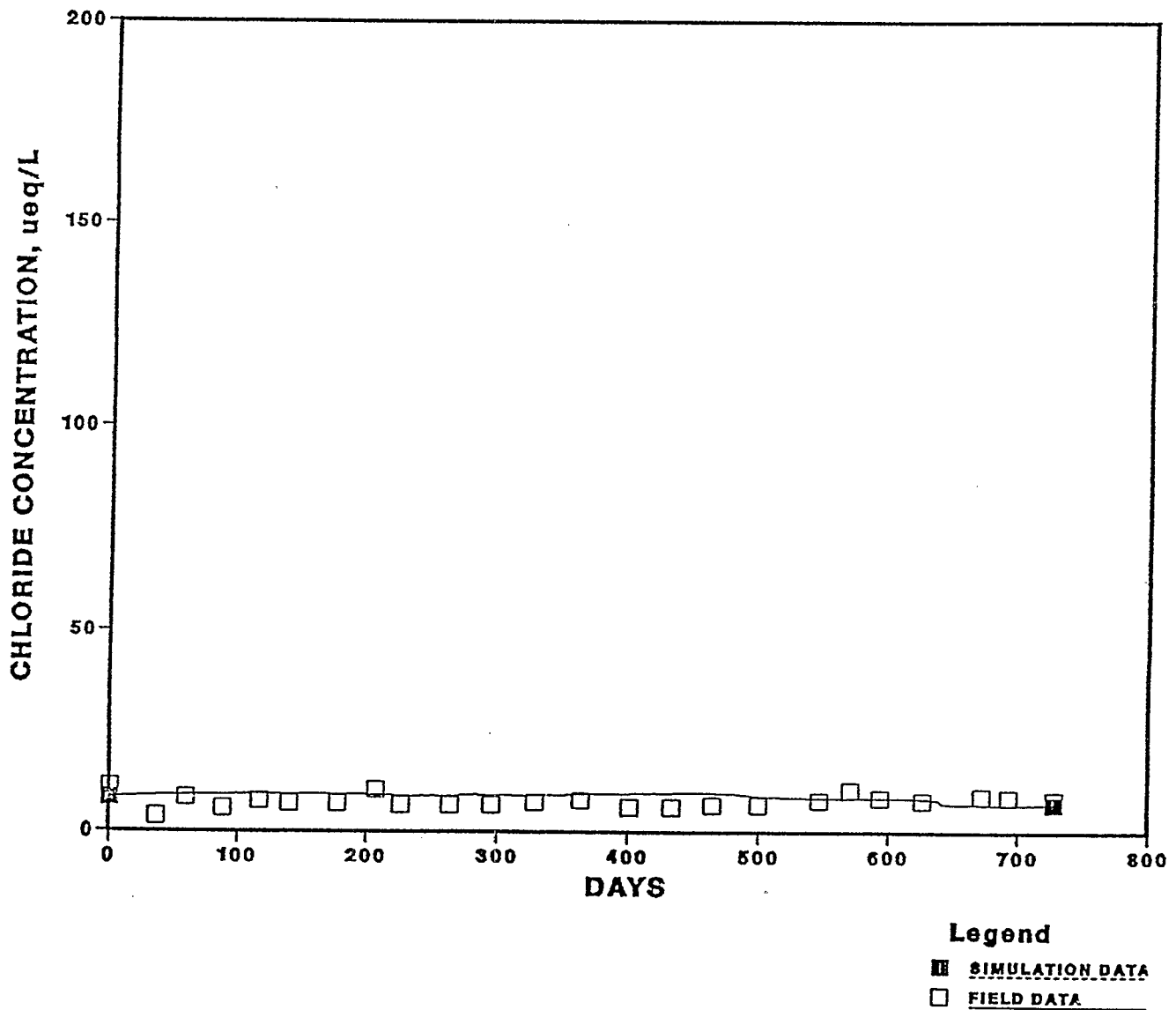


Figure 9. Calibration results of lake chloride

**CLEAR POND
COMPARISON OF SIMULATION AND FIELD SULFATE
CALIBRATION PERIOD: 7/27/82 -7/24/84**

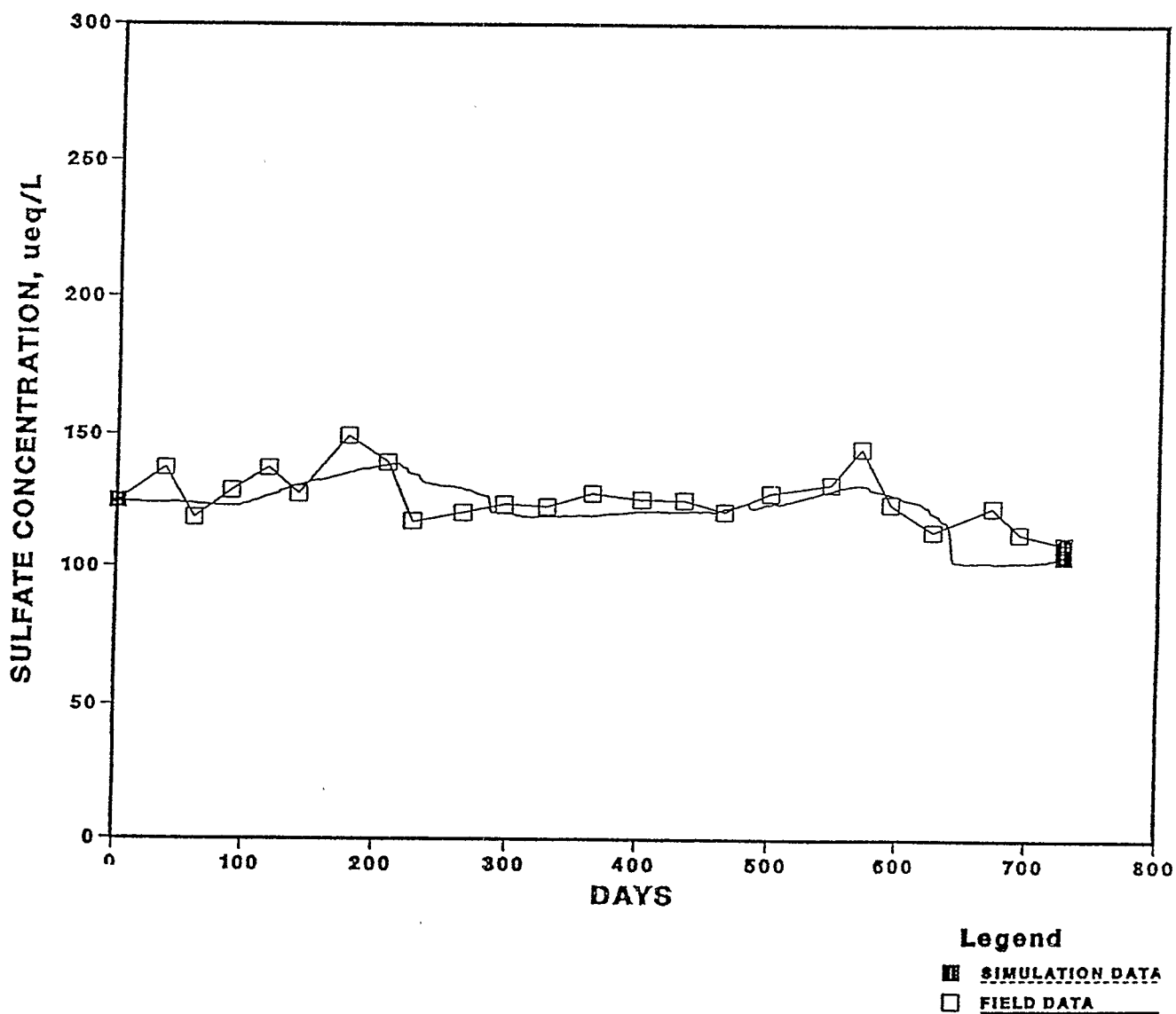


Figure 10. Calibration results of lake sulfate.

**CLEAR POND
COMPARISON OF SIMULATION AND FIELD ALKALINITY
CALIBRATION PERIOD: 7/27/82 - 7/24/84**

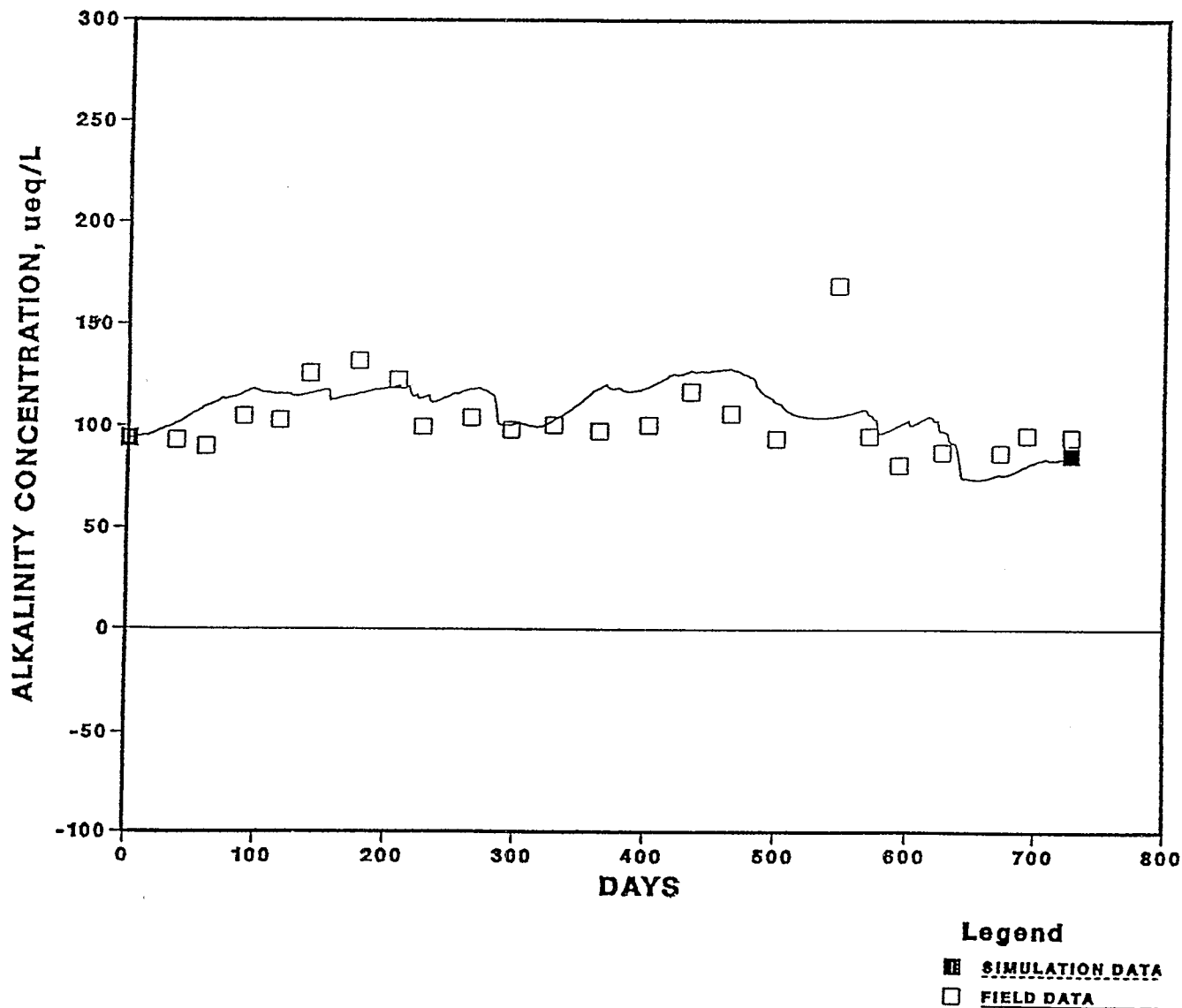


Figure 11. Calibration results of lake alkalinity.

**CLEAR POND
COMPARISON OF SIMULATION AND FIELD SULFATE
CALIBRATION PERIOD: 7/27/82 -7/24/84**

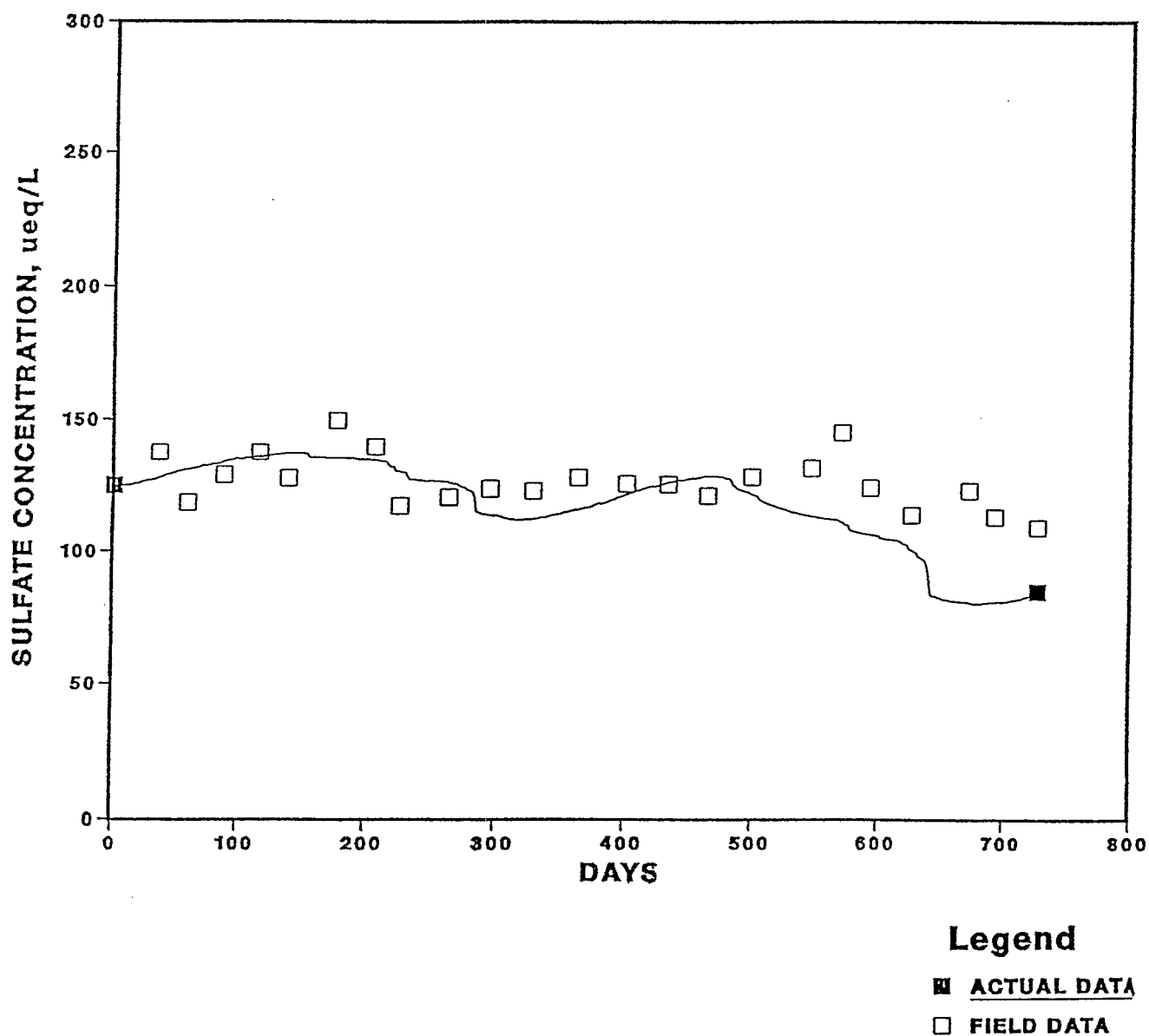


Figure 12. Sulfate simulation without loading increase.

APPENDIX A.1-2

INTEGRATED LAKE-WATERSHED ACIDIFICATION (ILWAS)

Direct/Delayed Response Project

ILWAS MODEL CALIBRATION AND SENSITIVITY ANALYSIS
FOR WOODS LAKE, PANTHER LAKE AND CLEAR POND

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INTRODUCTION

The ultimate goal of the Direct/Delayed Response Project is to provide Congress with a scientifically-based estimate of the degree to which surface waters in the northeast and southeast regions (as defined by U.S. EPA) will be affected by acidic deposition over the next fifty years. This estimate will be based, in part, on the results obtained from dynamic computer simulation models. The models will be applied to several lake and stream watershed systems in both regions. Classification rules will then be developed based on the model simulations and used to predict surface water behavior for the entire regions. Clearly, the application of these models to many watersheds dictates that the data record for calibration will, in most cases, be very short. Therefore, before the models can be applied regionally, their ability to simulate the behavior of single lakes or streams having relatively long data records must be demonstrated. In addition, the sensitivity of the models to various model parameters must also be demonstrated.

The ability of the Integrated Lake-Watershed Acidification Study (ILWAS) model to simulate northeast lakes with relatively long data records has been demonstrated with the calibration of Woods Lake, Panther Lake, and Clear Pond. These calibrations were performed using data generated as a part of the field components of ILWAS and RILWAS (the regionalization of the ILWAS project). The results of the calibrations will be presented below as will a short description of the ILWAS model, a discussion of the physical and chemical characteristics of the three watersheds, and the results of the model sensitivity analyses.

ILWAS MODEL OVERVIEW

ILWAS Model Description

The ILWAS model conceptualization, development, application, and theory have been described elsewhere (Chen, Gherini, and Goldstein, 1979; Goldstein, Gherini, and Chen, 1984; Gherini, Mok, Hudson, Davis, Chen, and Goldstein, 1985; Davis, Whipple, Gherini, Chen, Goldstein, Chan, and Munson, 1986). What follows below is a brief summary of the model.

The ILWAS model was developed to simulate the chemical response of surface waters in forested ecosystems to changes in deposition acidity. To do this the model simulates the major physical and biogeochemical processes occurring in the tributary watersheds as well as in the surface waters. This is achieved in the model by routing incident precipitation through the forest canopy, soil strata, streams and lakes (See Figure 1). Concurrently the model simulates the major processes which add acid or base to the throughflowing water.

The ILWAS project demonstrated that for drainage basin systems, surface water quality is largely determined by where precipitation flows en route to becoming surface water (Goldstein, Gherini, and Chen, 1984; Peters, 1985; Schofield, 1985). To calculate the distribution of water between flow paths the ILWAS model uses various forms of the continuity equation, Darcy's law for flow in unsaturated and saturated permeable media, and Manning's equation, Muskingum routing, and stage-flow relationships for surface waters. Snow and ice formation and melting are simulated by the model using multiple-term heat budgets.

In simulating the acid-base chemistry of the water, the ILWAS model calculates the concentrations of 16 chemical constituents (See Table 1) in throughfall, surface runoff, soil solution, and in surface waters. This is achieved using mass-balance techniques and both kinetic and equilibrium formulations to represent the major processes which add acid or base to the water (Table 2). Concentrations of chemical species which are not readily mass balanced are computed from the concentrations of other constituents. For example, the model calculates H^+ -ion concentration from alkalinity, total inorganic carbon, total monomeric aluminum, and total organic acid analogue.

The model is applied by dividing a lake or stream-watershed system into catchments, each of which

discharge water directly to either a stream or lake. Each catchment is divided vertically into compartments with homogeneous characteristics: forest canopy, vegetation, and separate soil layers. Streams are divided into longitudinal segments and lakes are divided vertically into well-mixed layers.

Input to the model includes time invariant parameters which characterize each compartment (e.g., for a soil layer -- bulk density, organic and mineral composition, cation exchange capacity, etc.) and the initial solution and solid phase concentrations (initial conditions). Time variant model input consists of meteorological data (e.g., daily air temperature and precipitation amounts) and chemical data (monthly dry deposition and precipitation solute concentrations). As output the model calculates the aqueous concentrations of the base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+), strong acid anions (SO_4^{2-} , NO_3^- , Cl^-), alkalinity, silicic acid, organic acid analogue, total monomeric aluminum (Al_T), organically complexed monomeric aluminum, and pH - in throughfall and in soil and surface waters.

BASIN CHARACTERISTICS

Woods Lake, Panther Lake and Clear Pond are all located in the Adirondack Park region of New York State (Figure 2). Woods and Panther Lakes are both in the west central region of the Adirondack Park and are located less than 20 miles from each other. Clear Pond is located near the eastern boundary of the park and is slightly farther north than Woods Lake.

All three sites are forested watersheds with largely deciduous cover. The basins range from 1.2 to 5.7 km_2 in surface area and lie at approximately the same elevation. Clear Pond has 3 to 4 times the relief of the other basins and also has a wider variety of till depths with thin till (less than 1 m) near the top of the watershed and thick till (as deep as 55 m) near the lake (average depth = 6.5 m). Panther Lake soils are more uniformly deep (average depth = 24.5 m) while Woods Lake soils are thin (average depth = 2.3 m). The physical characteristics of all three basins are summarized in Table 3.

Although Woods and Panther Lakes each receive about the same amount of precipitation of nearly identical quality, the alkalinities (ANC) of the lake outlet waters are significantly different. The alkalinity at Woods Lake is about -10 $\mu\text{eq/L}$ while at Panther Lake the average alkalinity is nearly 150 $\mu\text{eq/L}$. Clear Pond receives less total precipitation than Woods and Panther and the acidity of the precipitation is slightly lower as well. The lake outlet alkalinity at Clear Pond averages 100 $\mu\text{eq/L}$. The chemical characteristics of both the wet and dry deposition at all three lakes is summarized in Table 4.

CALIBRATION

Application of the ILWAS model begins with calibration. Basin data are used to quantitatively characterize the system to be simulated. Initial conditions (e.g., lake stage, soil and surface water quality) are established as a simulation starting point. The model is then run using actual meteorological and air quality data as input. The model output, the quantity and quality of water at various points in the system, is made to coincide with observed values by adjustment of calibration parameters (e.g., evapotranspiration coefficients). The simulated results are typically compared to the observed data using graphical procedures. Simultaneous calibration against observed data for several points within a watershed is recommended if data are available. For example, throughfall quantity, snowpack depth, and flows at various points in any streams, should be calibrated together with lake discharge. Since the ILWAS model simulates many processes, calibration of these processes must follow a logical order to proceed with minimal effort. The general rules for calibration are: 1) calibrate the system's hydrologic behavior before calibrating the chemical behavior; 2) calibrate in the same order as water flows through the basin; and 3) calibrate on an annual basis first, then seasonally, and finally calibrate to the instantaneous (daily) behavior.

Hydrologic Calibration

The first step in the hydrologic calibration is the adjustment of the evapotranspiration parameters so

that the predicted cumulative lake outflow matches the observed data. Observed lake outflow is checked against the observed rainfall to ensure that all major storm events cause either increases in lake outflow or at least retard recessions. The seasonal patterns in the predicted cumulative outflow are controlled by the length of the snow cover period and by seasonal variations in evapotranspiration. The snow formation temperature and the snowmelt rate coefficients, along with the sublimation rate, are adjusted to match observed snowpack depth and lake outflow during the snowmelt period. A seasonal calibration parameter is used to adjust the variation in potential evapotranspiration. Canopy interception storage, monthly leaf area indices, and root distribution determine the allocation of evapotranspiration to the different compartments of the system. Depending on the depth of the water table, the distribution of potential evapotranspiration will influence the actual amount of water lost (i.e., a large distribution factor for the upper soil layer together with a deep water table will give a low total evapotranspiration rate despite a high potential).

The peak flow and recession curve characteristics are influenced by the snowpack, soil field capacity, soil-specific yield, and soil hydraulic conductivity. The fine adjustment of the instantaneous lake discharge rate can be performed in conjunction with the chemical calibration. However, the ratio of base flow to the sum of shallow and surface flow should be reasonably estimated using flow separation techniques before proceeding with chemical calibration.

Chemical Calibration

Lake chemical characteristics are primarily determined by the initial lake-water quality, in-lake processes, soil solution quality and the routing of water through the different soil layers. The concentrations of several soil solution constituents is fairly constant with time because of equilibration of the aqueous phase with the solid phase by cation exchange and anion adsorption reactions. Hence, a reasonable calibration of lake outflow chemistry can be obtained by establishing the initial solute concentrations in the soil and lake waters, the soil cation exchange selectivity coefficients and anion adsorption coefficients, and the in-lake rate process coefficients. The initial solute levels in the soil solution must be such that a volumetric flow-weighted average of the soil solution concentrations, plus direct precipitation onto the lake surface, will give the average lake concentrations for species which do not undergo reaction in the lake (e.g., Cl^-). The volumetric flows used in the above averaging are the soil layer lateral flows obtained from the hydrologic calibration. The cation exchange selectivity coefficients and anion adsorption coefficients are adjusted so that the initial soil solution concentrations are at equilibrium with the adsorbed concentrations. The soil nitrification rates, lake nitrification rates, and monthly algal production rates are adjusted to calibrate the ammonium and nitrate concentrations in the lake outflow.

Observed lysimeter and ground water chemical data can be used to check the hydrologic calibration. The concentrations of solutes which do not equilibrate with the solid phase may drift quickly away from their initial levels if the rate processes in the soil are not calibrated properly. The aluminum dissolution rate is adjusted to maintain a fairly constant level of aluminum in the applicable soil layers from year to year (aluminum concentration may fluctuate seasonally with the nitrate cycle). The nitrification rate is adjusted to prevent buildup of nitrate in deep soil layers. The observed silicic acid concentrations are used in setting the mineral weathering rates.

If observed data are available, the throughfall chemistry can be calibrated by adjusting the gas and particulate deposition velocities, canopy nitrification rates, and foliar exudation rates. This also provides a means of quantifying total atmospheric deposition (wet and dry). The snowpack ion levels are calibrated by adjusting a solute leaching coefficient.

The dynamic behavior of the lake outflow water quality is influenced by the lake thermal profile, the fraction of solute retained in the lake ice, and the fraction of flow that comes in as surface runoff or ground water seepage.

The calibrated and observed cumulative lake outflow, instantaneous lake outflow, pH, and concentrations of ANC, NH_4 , Al_T , Ca, Mg, K, Na, SO_4 , NO_3 , Cl, and Silicic Acid are shown in Figures 3 through 16 for Panther Lake, Figures 17 through 29 for Woods Lake and Figures 30 through 42 for Clear Pond. The figures indicate good agreement between simulated and observed dynamic concentrations. The calculated mean square errors between the simulated and observed concentrations are presented in Tables 5, 6, and 7.

Discussion of Results

The results indicate that the primary reason for the difference in the acidity of Woods and Panther lake waters is the depth of till in the watersheds. Panther basin has thick till and thus a larger reservoir of exchangeable bases and weatherable minerals to neutralize acid deposition. Sensitivity analysis indicates that if the depth of till at Panther Lake were reduced, it too would be more acidic (see next section). For both Woods and Panther Lakes, the majority of the base supplied to throughflowing waters comes from cation exchange (70%).

The simulation of Clear Pond led to some interesting comparisons of sources of alkalinity. For example, although the average till thickness at Clear Pond is only 6.5 m, the thick till in the immediate vicinity of the lake provides significant buffering capacity. Another factor in the alkalinity supply at Clear Pond is the presence of anorthosite minerals. These are similar to the minerals at Woods and Panther but have a higher ratio of calcium to sodium. The calcic minerals at Clear Pond weather faster than the sodic minerals at Woods and Panther and thus provide a much larger fraction of the base supply. Mineral weathering contributes is over 50 percent of the base supply at Clear compared to less than 30 percent at Woods and Panther.

Table 1. Solution-Phase Chemical Constituents.

	Cations	Anions	Neutral Species	Analytical Totals	Gases (Input Only)
Solutes tracked by mass balance	Ca _T	SO _{4T}	H ₄ SiO ₄	Alk(ANC)	(SO _x)
	Mg _T	NO _{3T}	CO ₂ (aq)	Org Acid Lig 1 (triprotic, R1)	(NO _x)
	K _T	Cl _T	AlF ₃	Org Acid Lig 2 (monoprotic, R2)	
	Na _T	PO _{4T}	AlR1	Al _T	
	NH _{4T}	F ⁻	Al(R2) ₃	C _T (TIC) F _T	
Solutes which can be calculated from those above	H ⁺	Al(OH) ₄	Al(OH) ₃		
	Al ³⁺	HCO ₃	H ₃ R1		
	Al(OH) ²⁺	CO ₃	HR2		
	Al(OH) ₂	R1 ³⁻			
	AlF ²⁺	HR1 ²⁻			
	Al ₂	H ₂ R1 ⁻			
	Al(SO ₄) ⁺	R2 ⁻			
	AlR2 ²⁺	AlF ₄			
	Al(R2) ₂	AlF ₅			
		AlF ₆			
		Al(SO ₄) ₂			

Note: Subscripted "T" indicates total analytical solution phase concentration.

Table 2. Chemical and Physical Processes Simulated by the ILWAS model.

Canopy Processes

Dry Deposition
Foliar Exudation
Nitrification
Solution Phase Equilibration
Washoff

Snowpack Processes

Accumulation
Sublimation
Leaching
Nitrification

Soil Processes

Heat Transfer
Biomass Loop
 Litter Accumulation
 Litter Decay
 Organic Acid Decay
 Nitrification
 Nutrient Uptake
 Root Respiration
Abiotic Processes
 Mineral Weathering
 Competitive Cation Exchange (Al, Ca, Mg, K, Na, NH_4^+ , H)
 Anion Adsorption (SO_4 , PO_4 , organic acid ligand)
 CO_2 Exchange
 $\text{Al}(\text{OH})_3$ (am) Dissolution-Precipitation
 Solid-Liquid-Gas Phase Equilibration

Surface Water Processes

Gas Transfer
Mixing (Advection & Dispersion)
Heat Exchange
Ice Formation & Melting
Algal Nutrient Uptake
Nitrification
Reductive Loss of Strong Acid Anions
Solution Phase Equilibration

Table 3. Characteristics of Panther, Woods, and Clear Lakes.

	Panther	Woods	Clear
Basin area (km ²)	1.2	2.1	5.7
Lake surface elevation ^a (m)	557	606	580
Relief _b (m)	170	122	518
Forest cover (%)	98	95	95
Coniferous (%)	3	5	0
Deciduous (%)	95	90	95
Mean till depth (m)	24.5	2.3	6.5
Lake			
Area (km ²)	0.18	0.26	0.74
Mean depth (m)	3.5	4.0	6.0
Maximum depth (m)	7	12	24.4
Lake Outlet			
Alkalinity (μeq/L)	-35 to 240	-60 to 30	80 - 170
pH	4.5-7.2	4.4-5.9	6.1-7.4

^a Relative to mean sea level.

^b Difference between highest and lowest elevation in the watershed.

Table 4a. Mean annual wet deposition loading (equivalents/hectare-year).

Constituent	Clear ^a	Panther ^b	Woods ^b
Sulfate	470	670	560
Nitrate	250	370	320
Chloride	46	52	44
Ammonium	130	200	180
Calcium	65	150	110
Magnesium	23	40	36
Sodium	38	49	44
Potassium	14	22	17

Table 4b. Mean annual dry deposition loading (equivalents/hectare-year).

Constituent	Clear ^a	Panther ^b	Woods ^b
Sulfate	83	120	100
Nitrate	39	67	50
Chloride	15	15	15
Ammonium	37	36	29
Calcium	37	89	62
Magnesium	11	18	16
Sodium	14	17	17
Potassium	12	12	12

^a Sampling period was for a two year period from August 1982 through July 1984.

^b Sampling period was from March 1978 through December 1981.

Table 5. Panther Lake Outlet.

Parameter	Number of Data Points, n	Mean Square Error (MSE)*	Standard Estimate of Error (SEE)**
Discharge	547	0.0002 (m ³ /s) ²	0.013 m ³ /sec
Cl	250	20.7 (μeq/l) ²	4.6 μeq/l
NO ₃	247	279	16.8
SO ₄	250	312	17.7
Ca	250	1350	36.9
Mg	250	76.7	8.8
Na	250	66.3	8.2
K	250	4.0	2.0
NH ₄	222	8.3	2.9
pH	159	.28 (S.U.) ²	.53 S.U.
Alk	205	2220 (μeq/l) ²	47.3 μeq/l
Al _T	65	10.5 (μmol/l) ²	3.3 (μmol/l)

$$* \text{MSE} = \Sigma(X_{\text{OBS}} - X_{\text{SIM}})^2 / n$$

$$** \text{SEE} = (\Sigma(X_{\text{OBS}} - X_{\text{SIM}})^2 / (n-2))^{0.5}$$

Table 6. Woods Lake Outlet.

Parameter	Number of Data Points, n	Mean Square Error (MSE)*	Standard Estimate of Error (SEE)**
Discharge	1095	0.0065 (m ³ /s) ²	0.013 m ³ /sec
Cl	263	11.1 (μeq/l) ²	3.3 μeq/l
NO ₃	261	129	11.4
SO ₄	263	301	17.4
Ca	263	277	16.7
Mg	263	44.7	6.7
Na	262	42.0	6.5
K	262	10.5	3.3
NH ₄	263	16.8	4.1
pH	187	0.10 (S.U.) ²	0.32 S.U.
Alk	205	983 (μeq/l) ²	31.5 μeq/l
Al _T	136	12.3 (μmol/l) ²	3.5 (μmol/l)

$$* \text{ MSE} = \Sigma(X_{\text{OBS}} - X_{\text{SIM}})^2 / n$$

$$** \text{ SEE} = (\Sigma(X_{\text{OBS}} - X_{\text{SIM}})^2 / (n-2))^{0.5}$$

Table 7. Clear Pond Outlet.

Parameter	Number of Data Points, n	Mean Square Error (MSE)*	Standard Estimate of Error (SEE)**
Discharge	102	0.0011 (m ³ /s) ²	0.034 m ³ /sec
Cl	23	2.1 (μeq/l) ²	1.5 μeq/l
NO ₃	23	43.3	6.9
SO ₄	23	114.0	11.2
Ca	23	558.0	24.7
Mg	23	25.4	5.3
Na	23	39.9	6.6
K	23	1.0	1.1
NH ₄	11	4.5	2.3
pH	23	0.05 (S.U.) ²	0.24 S.U.
Alk	23	320 (μeq/l) ²	18.7 μeq/l
Al _T	21	1.1 (μmol/l) ²	1.1 (μmol/l)

$$* \text{ MSE} = \Sigma(X_{\text{OBS}} - X_{\text{SIM}})^2/n$$

$$** \text{ SEE} = (\Sigma(X_{\text{OBS}} - X_{\text{SIM}})^2/(n-2))^{0.5}$$

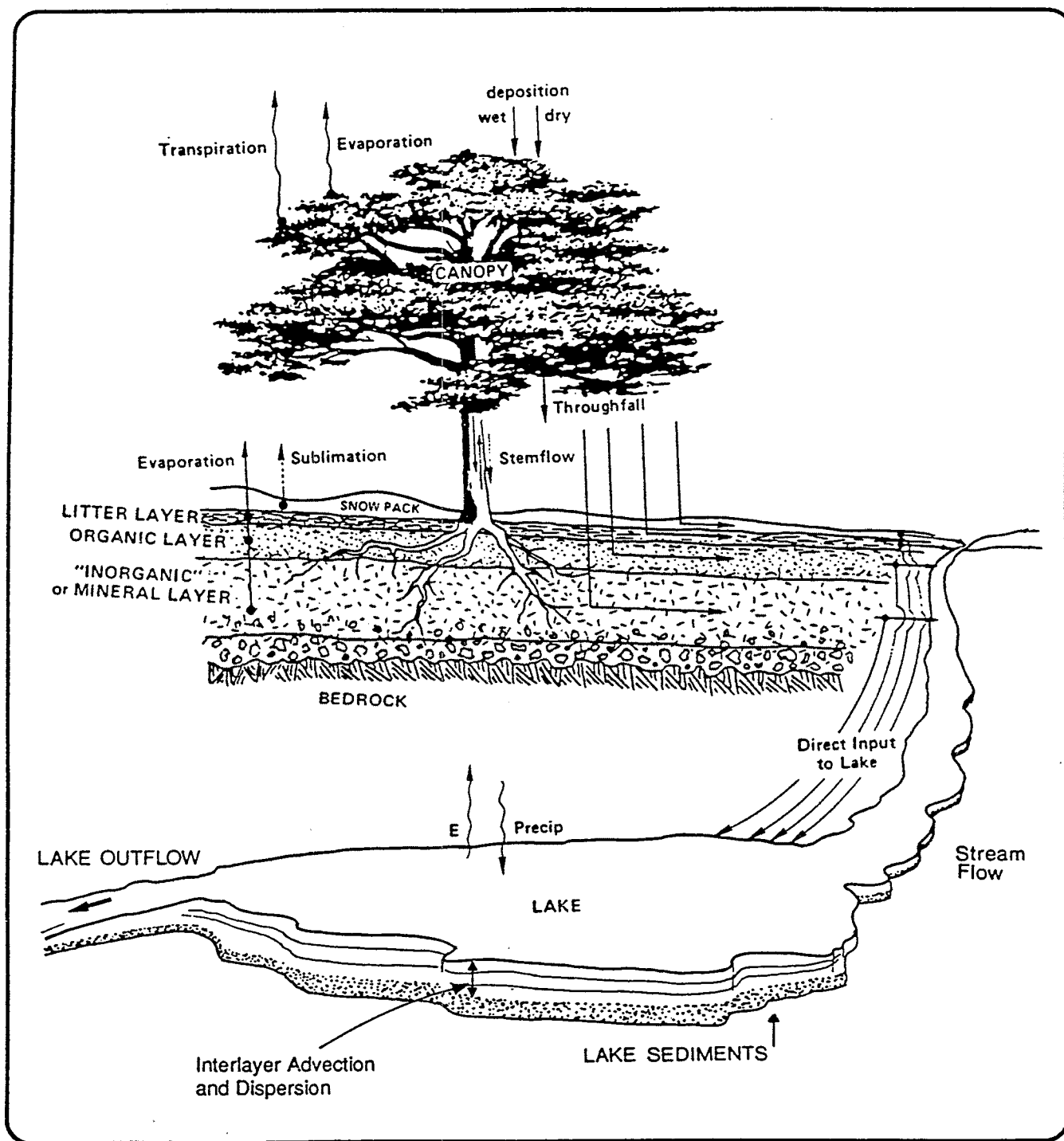


Figure 1. Lake-watershed system showing hydrologic setting.

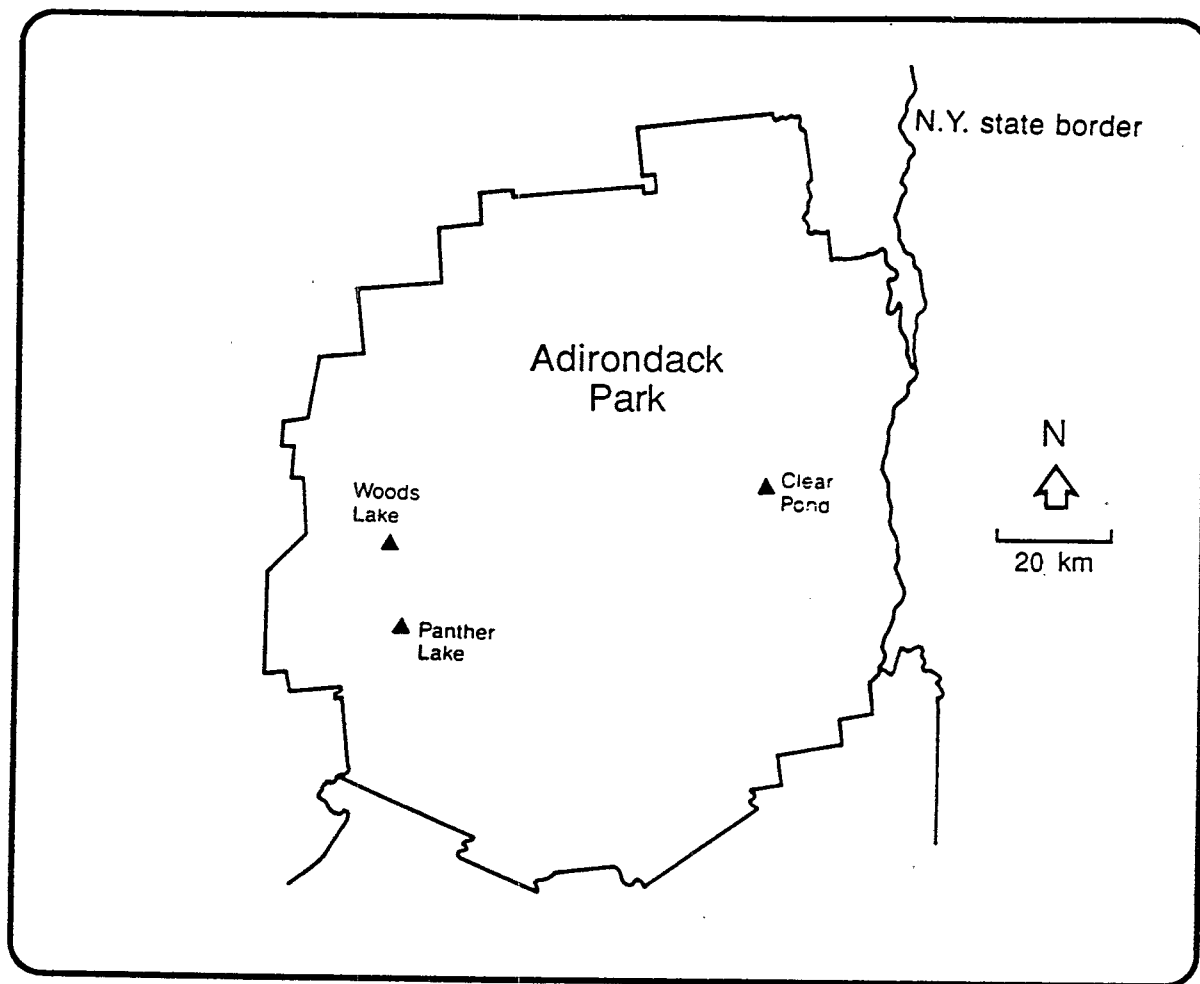


Figure 2. The DDRP Intensively Studied Lakes in the Adirondack Park of New York.

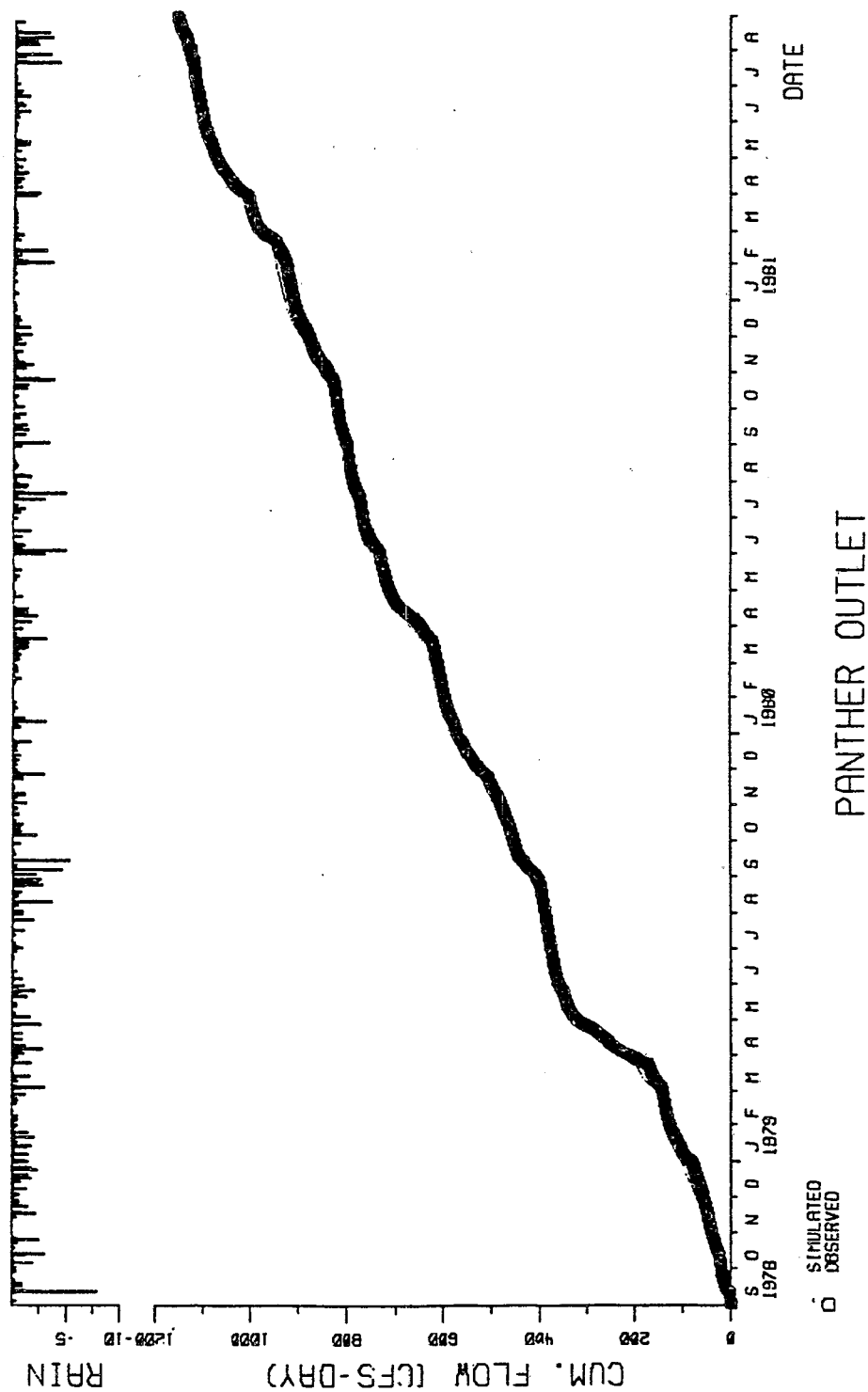


Figure 4. Simulated and observed instantaneous outflow for Panther Lake.

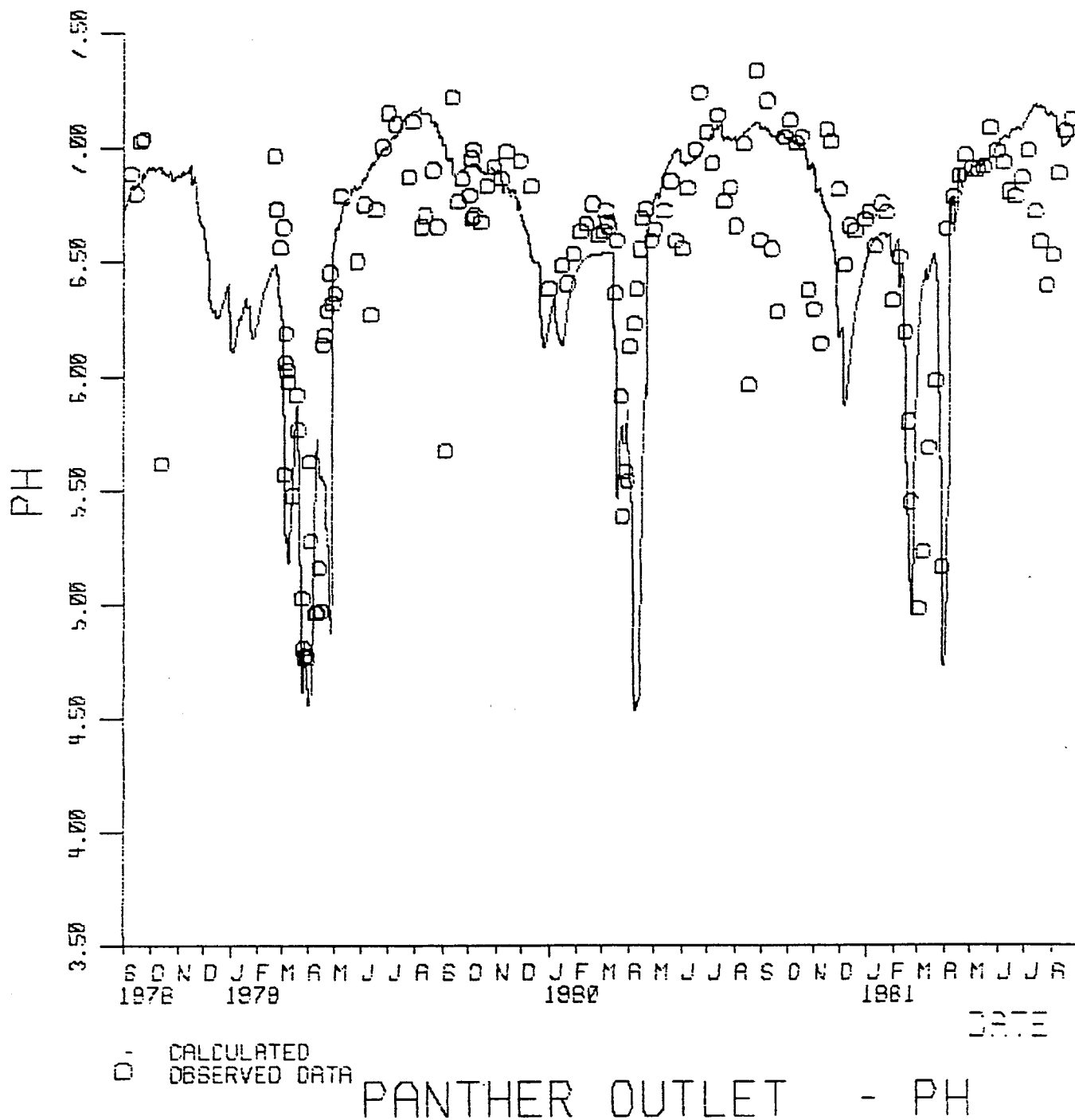


Figure 5. Simulated and observed pH for Panther Lake.

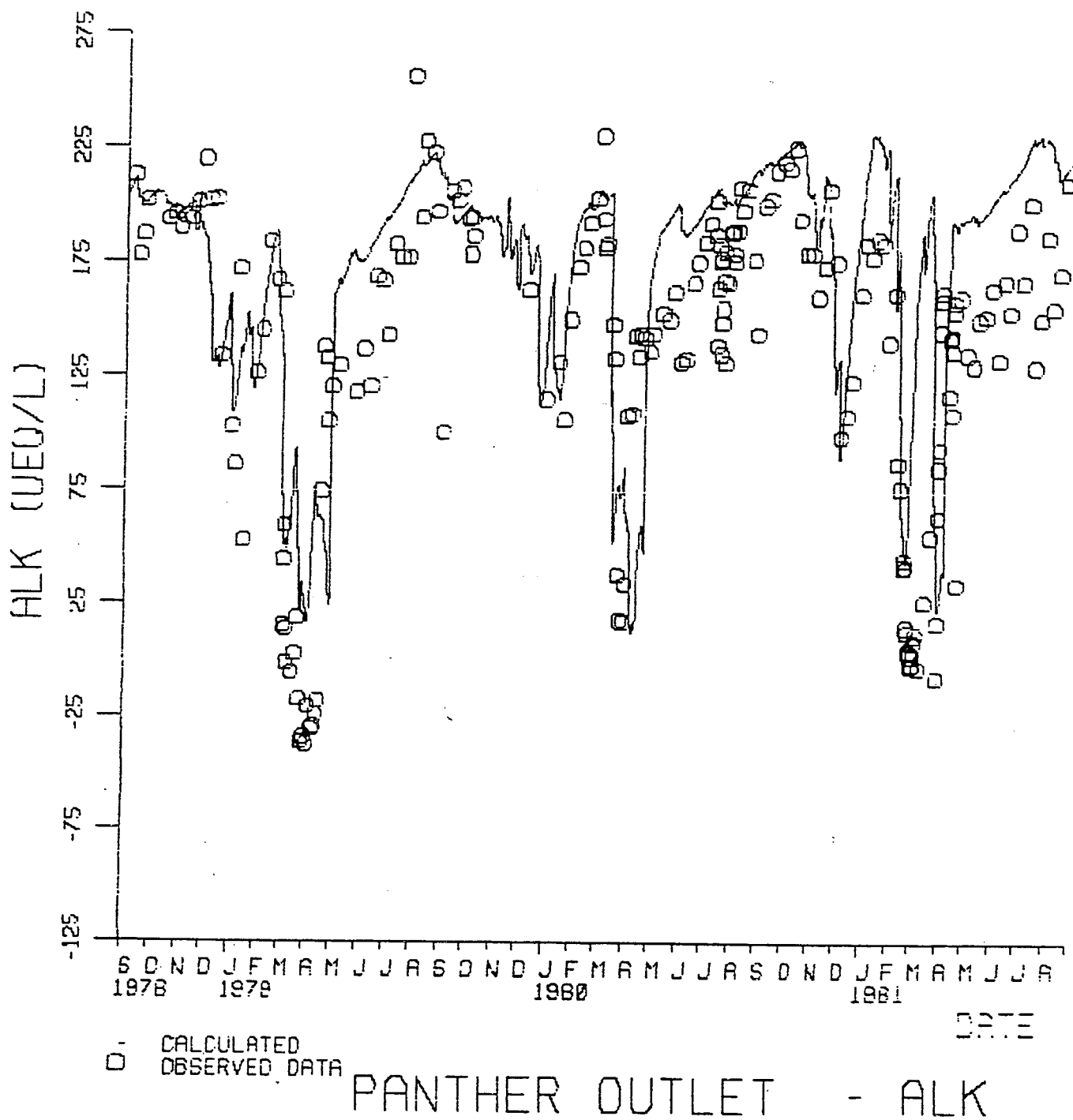


Figure 6. Simulated and observed alkalinity for Panther Lake.

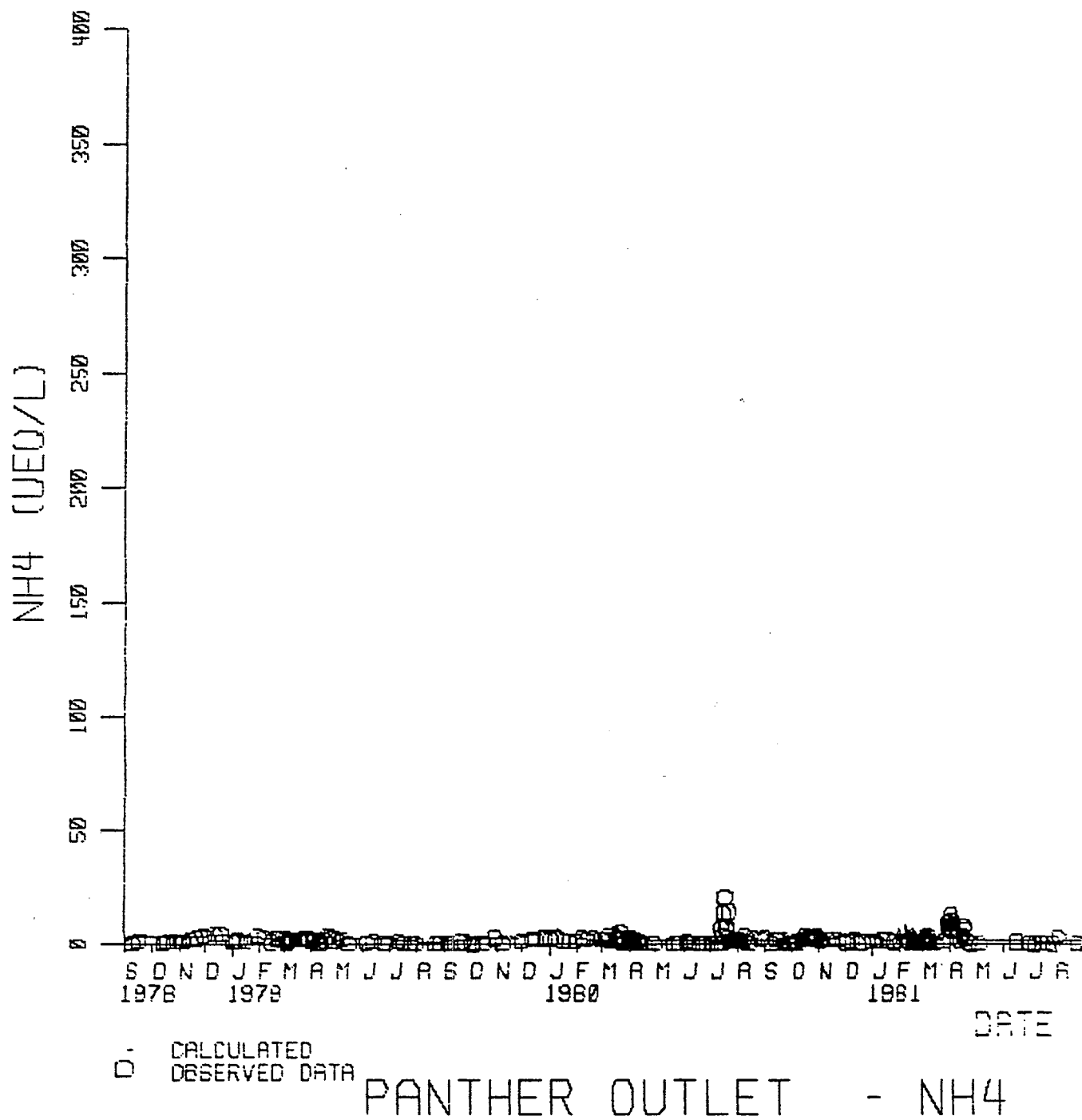


Figure 7. Simulated and observed ammonium concentration for Panther Lake.

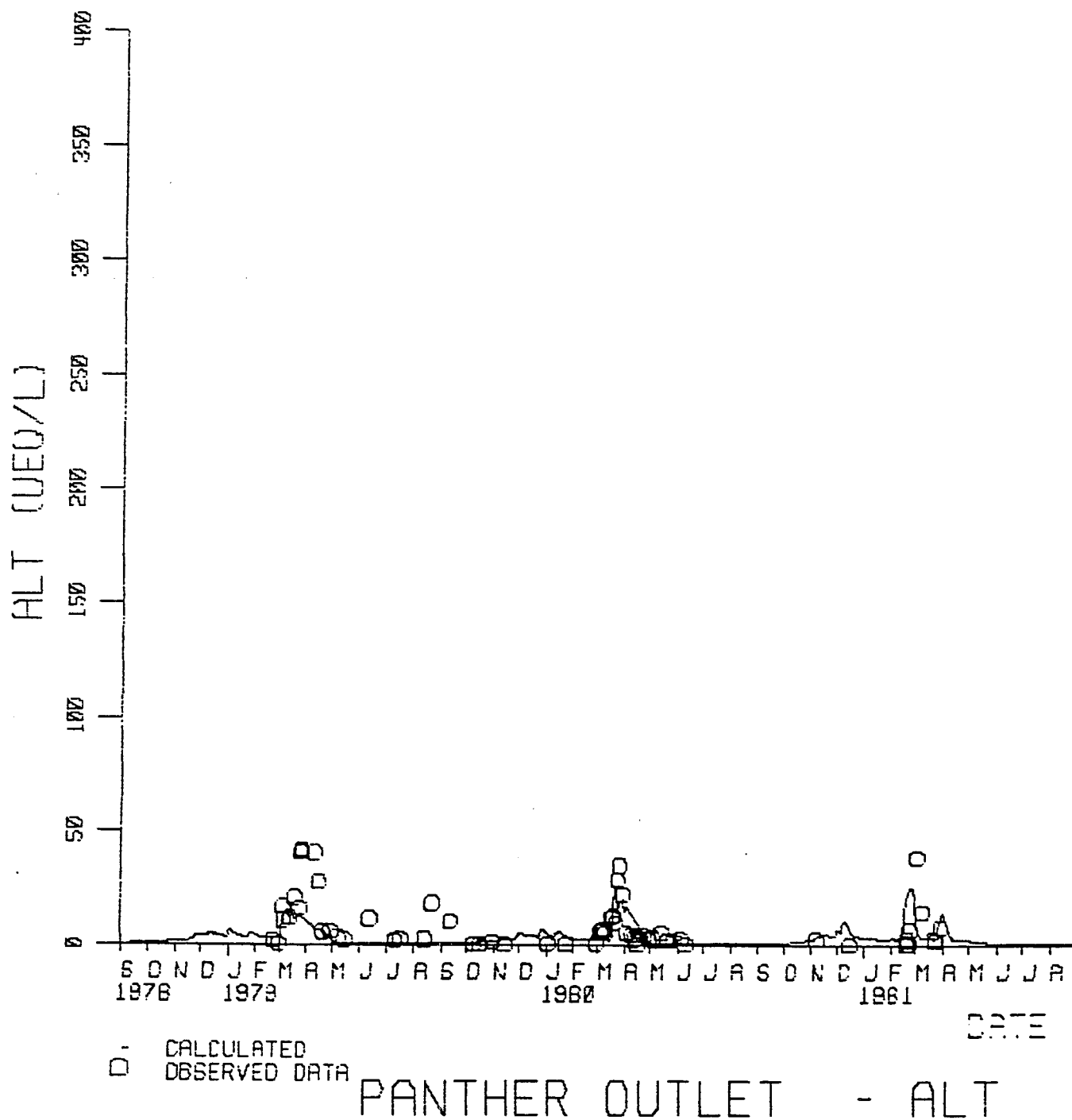


Figure 8. Simulated and observed total monomeric aluminum concentration for Panther Lake.

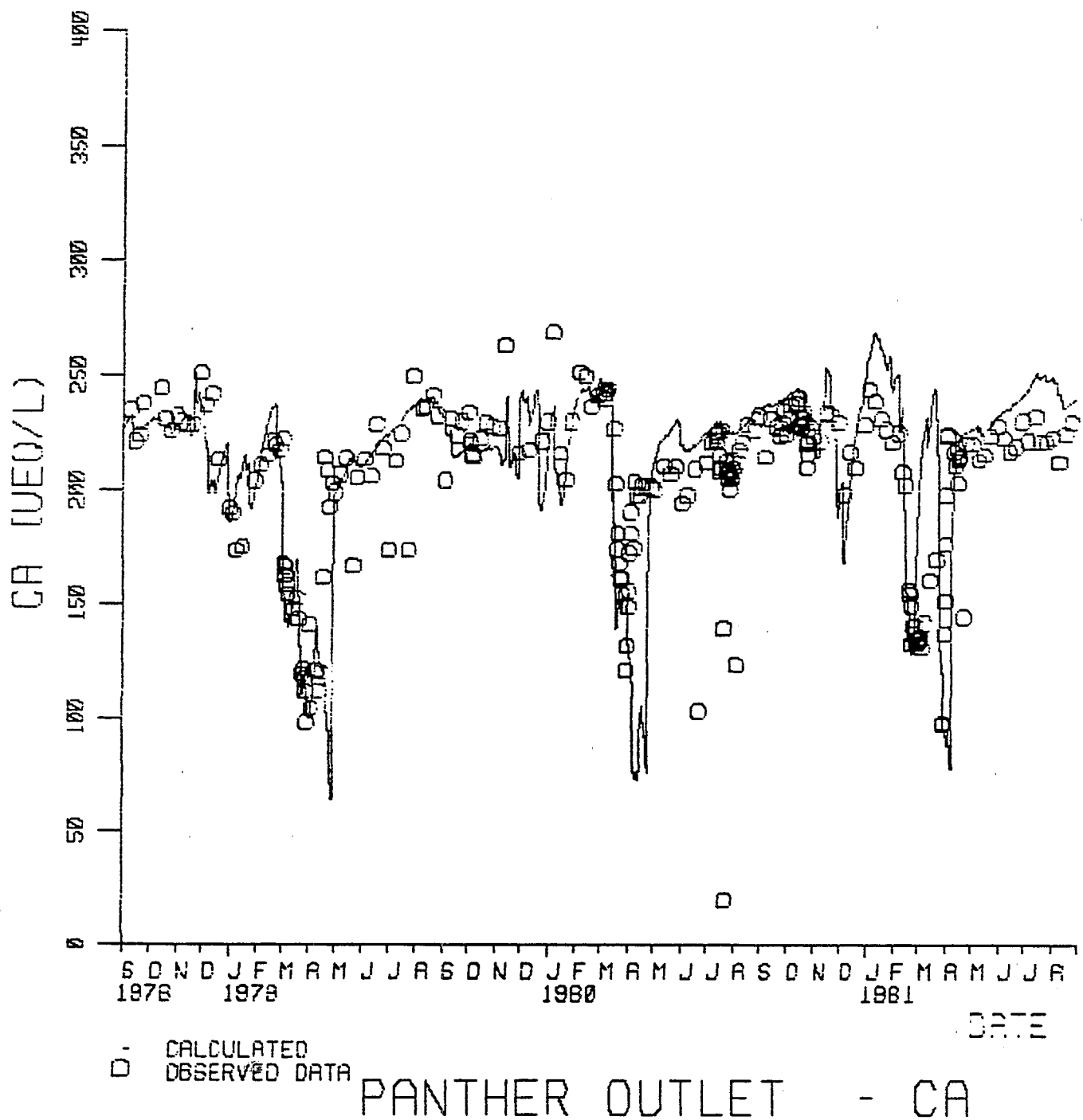


Figure 9. Simulated and observed calcium concentration for Panther Lake.

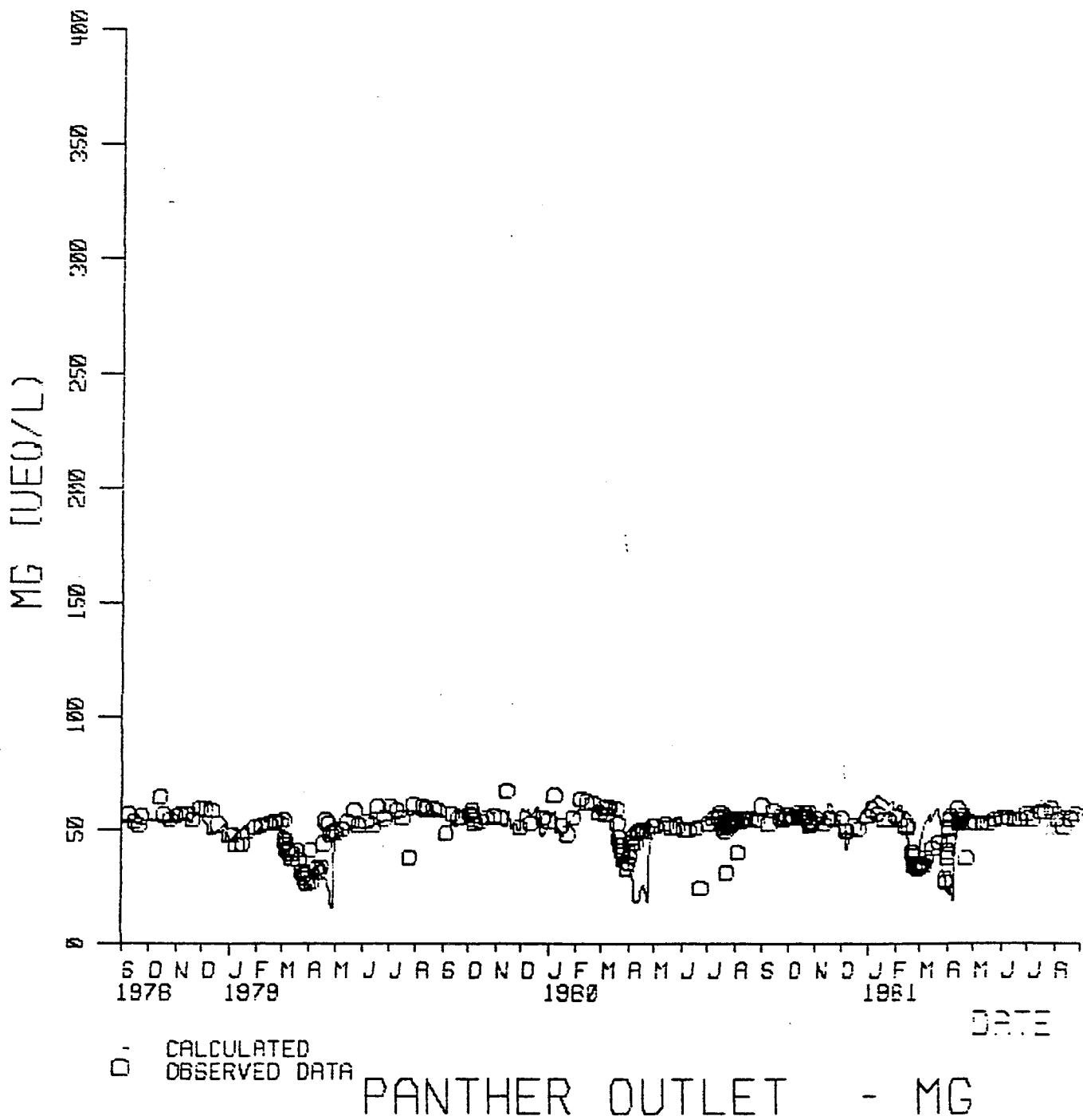


Figure 10. Simulated and observed magnesium concentration for Panther Lake.

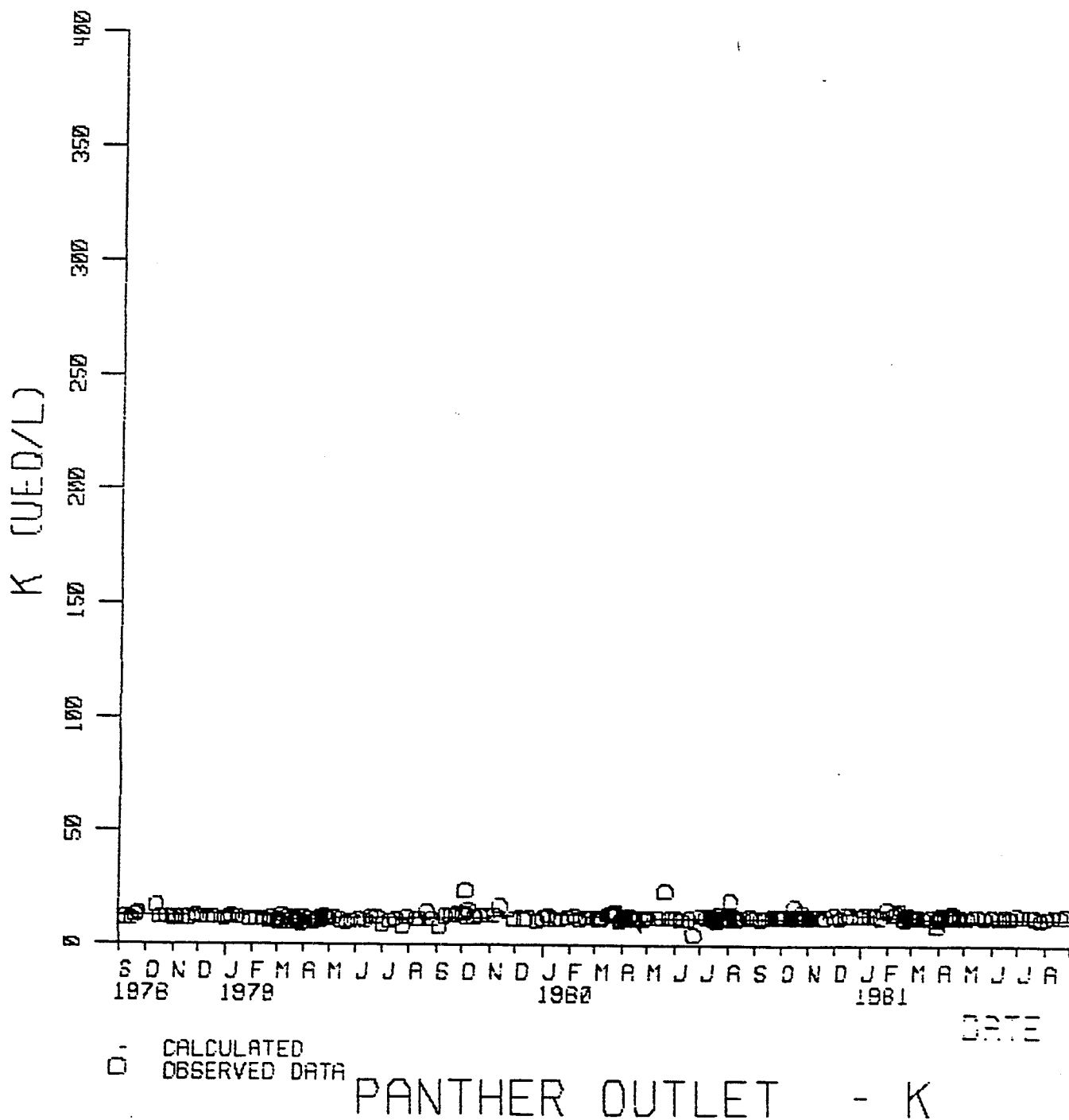


Figure 11. Simulated and observed potassium concentration for Panther Lake.

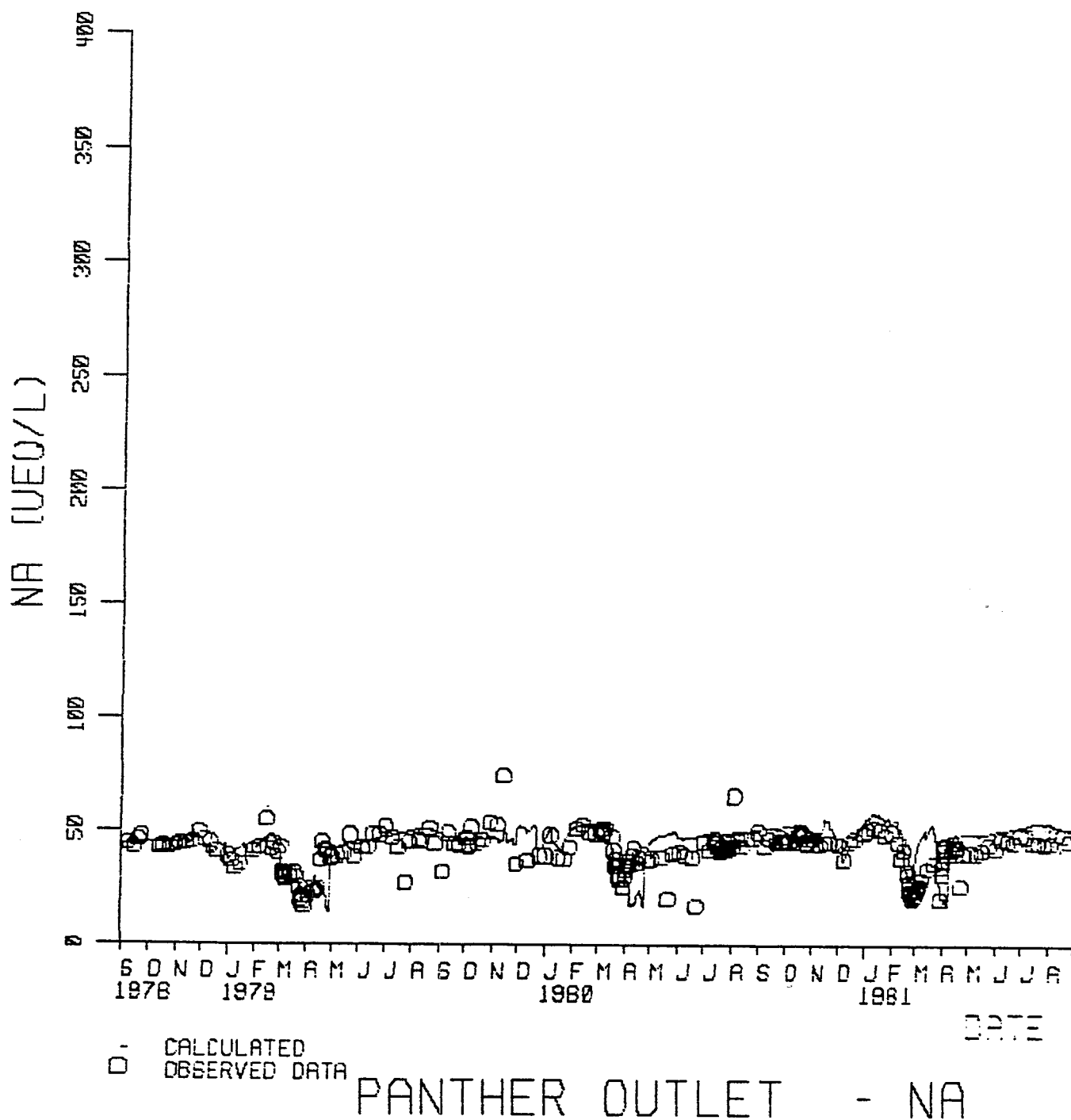


Figure 12. Simulated and observed sodium concentration for Panther Lake.

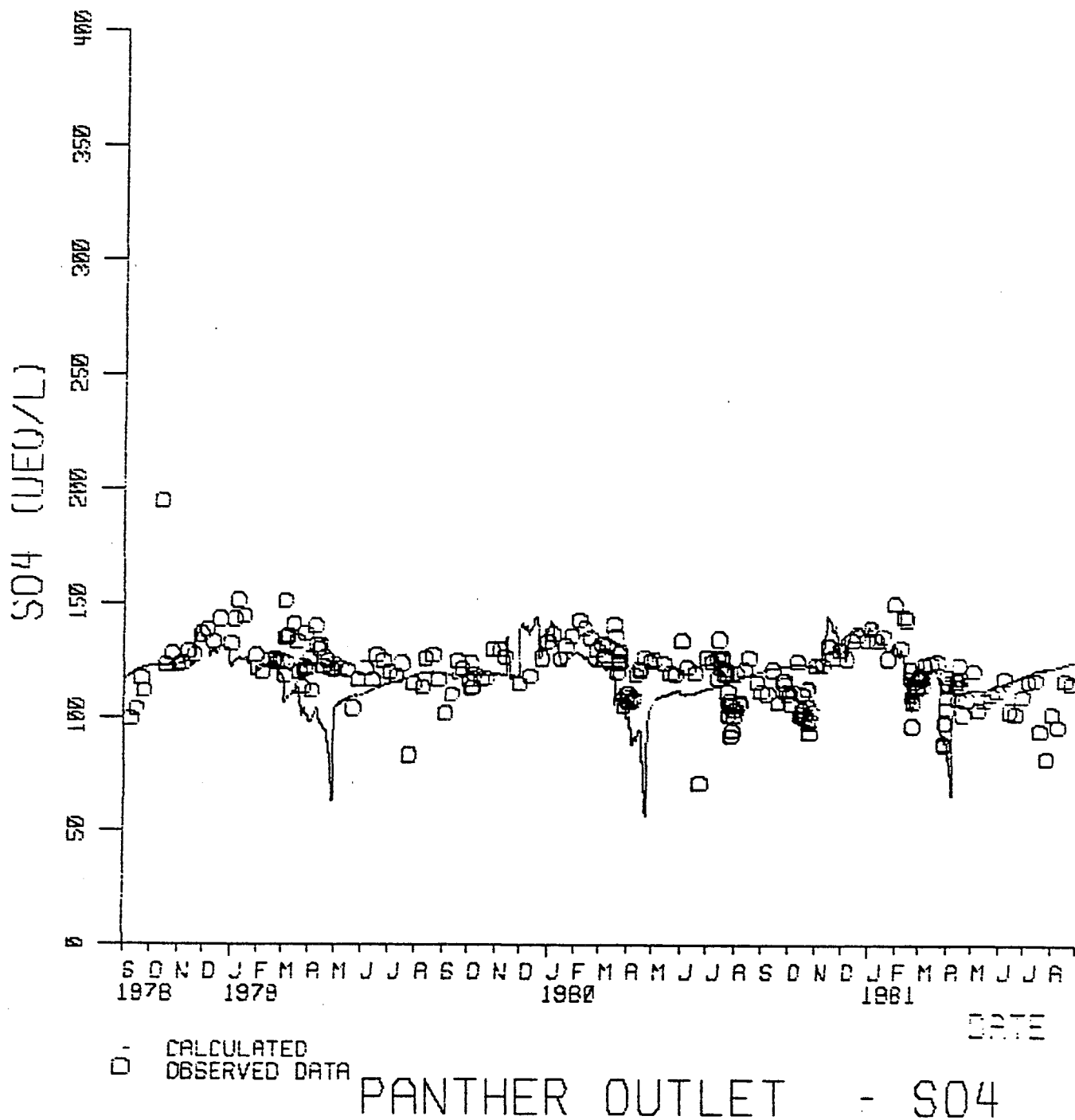


Figure 13. Simulated and observed sulfate concentration for Panther Lake.

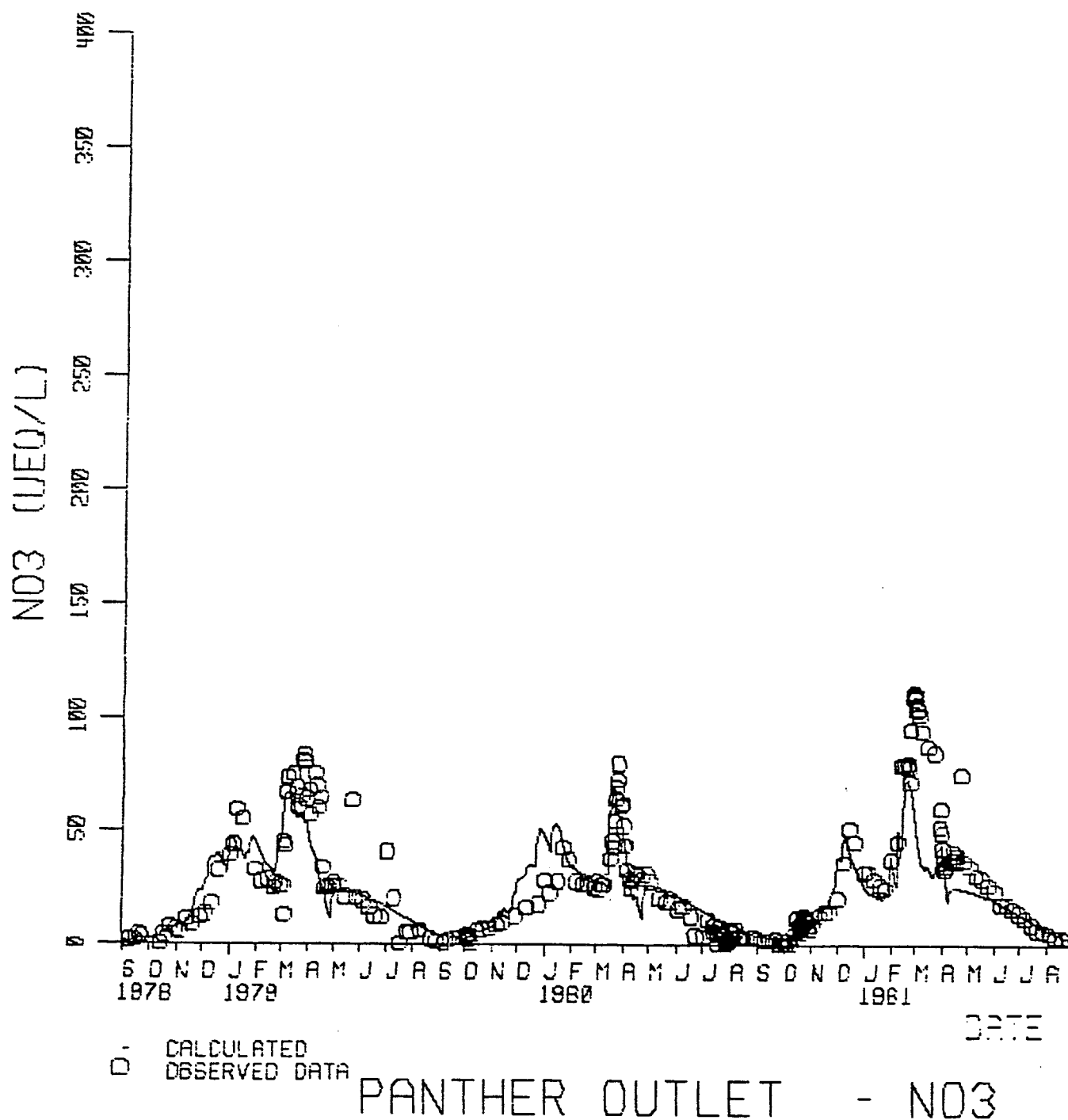


Figure 14. Simulated and observed nitrate concentration for Panther Lake.

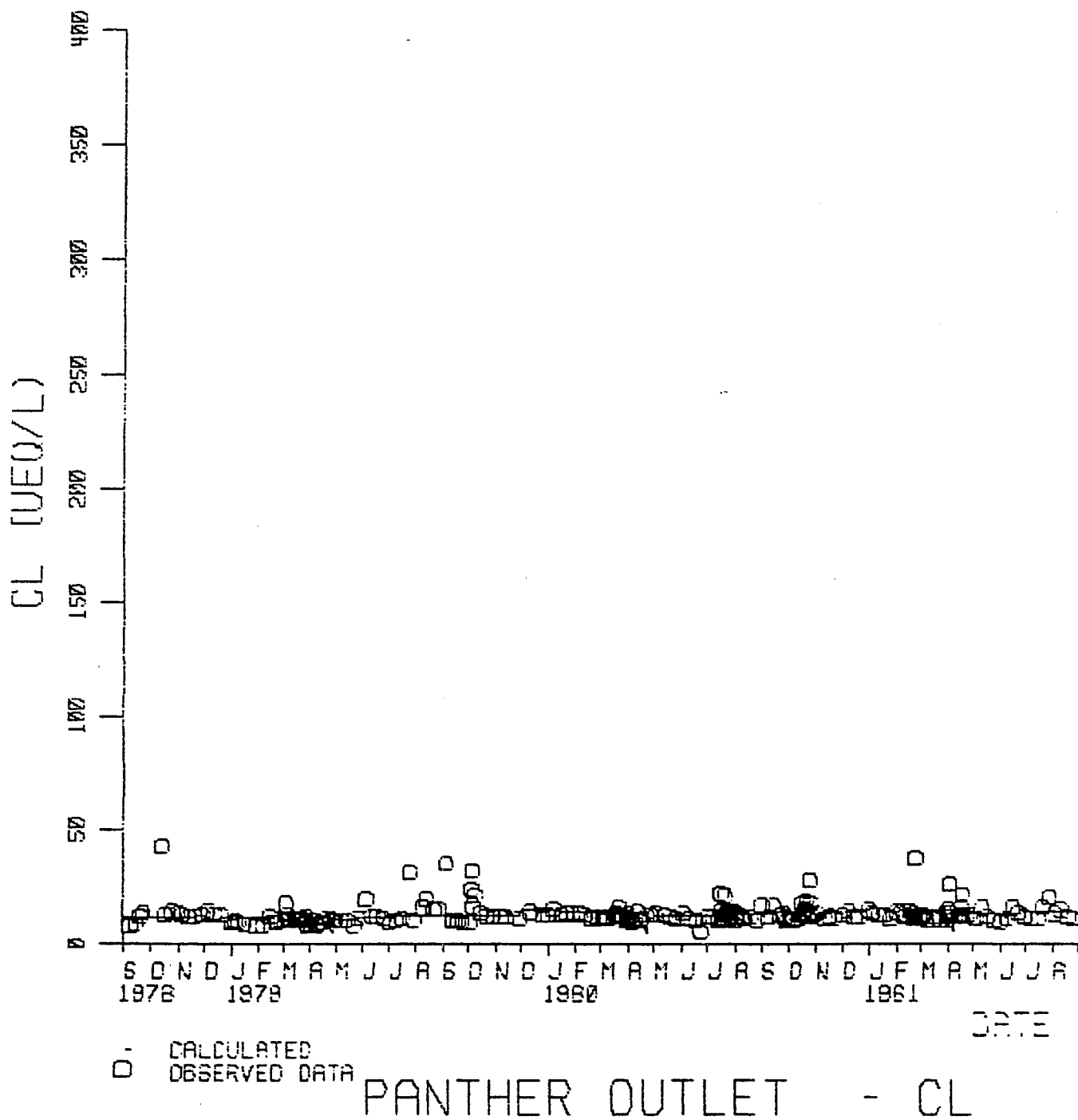


Figure 15. Simulated and observed chloride concentration for Panther Lake.

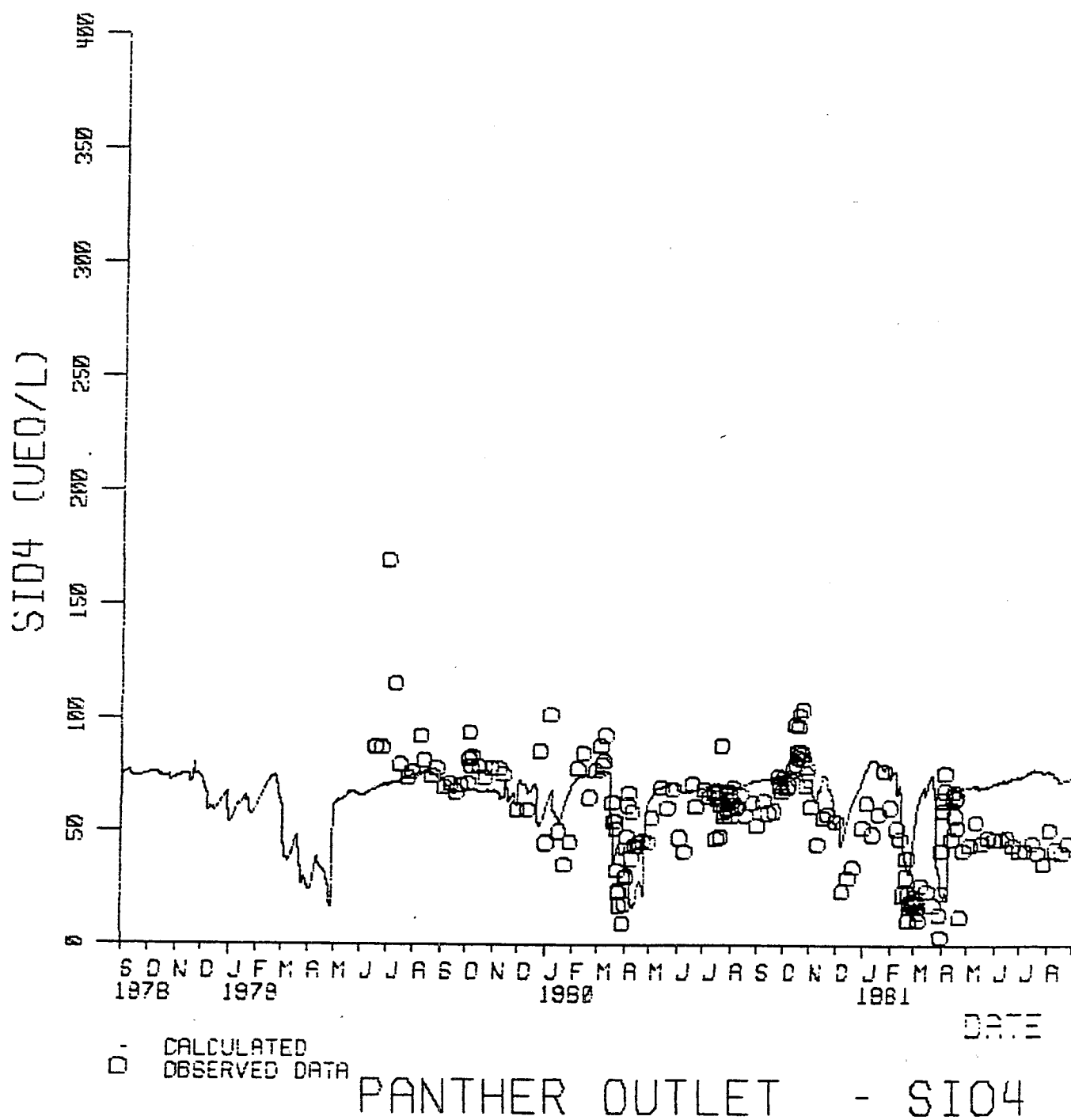


Figure 16. Simulated and observed silicic acid concentration for Panther Lake.

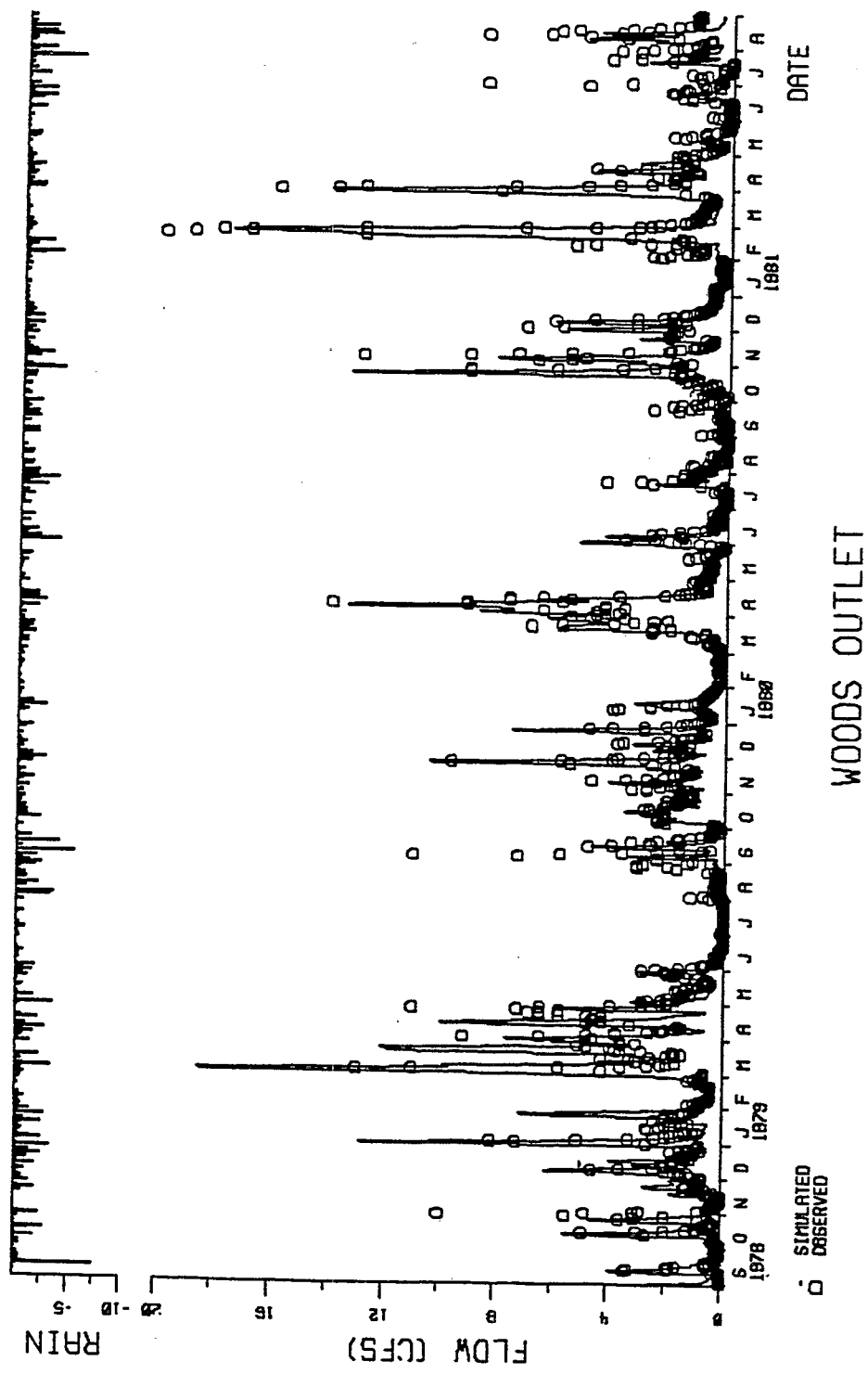


Figure 17. Simulated and observed instantaneous outflow for Woods Lake.

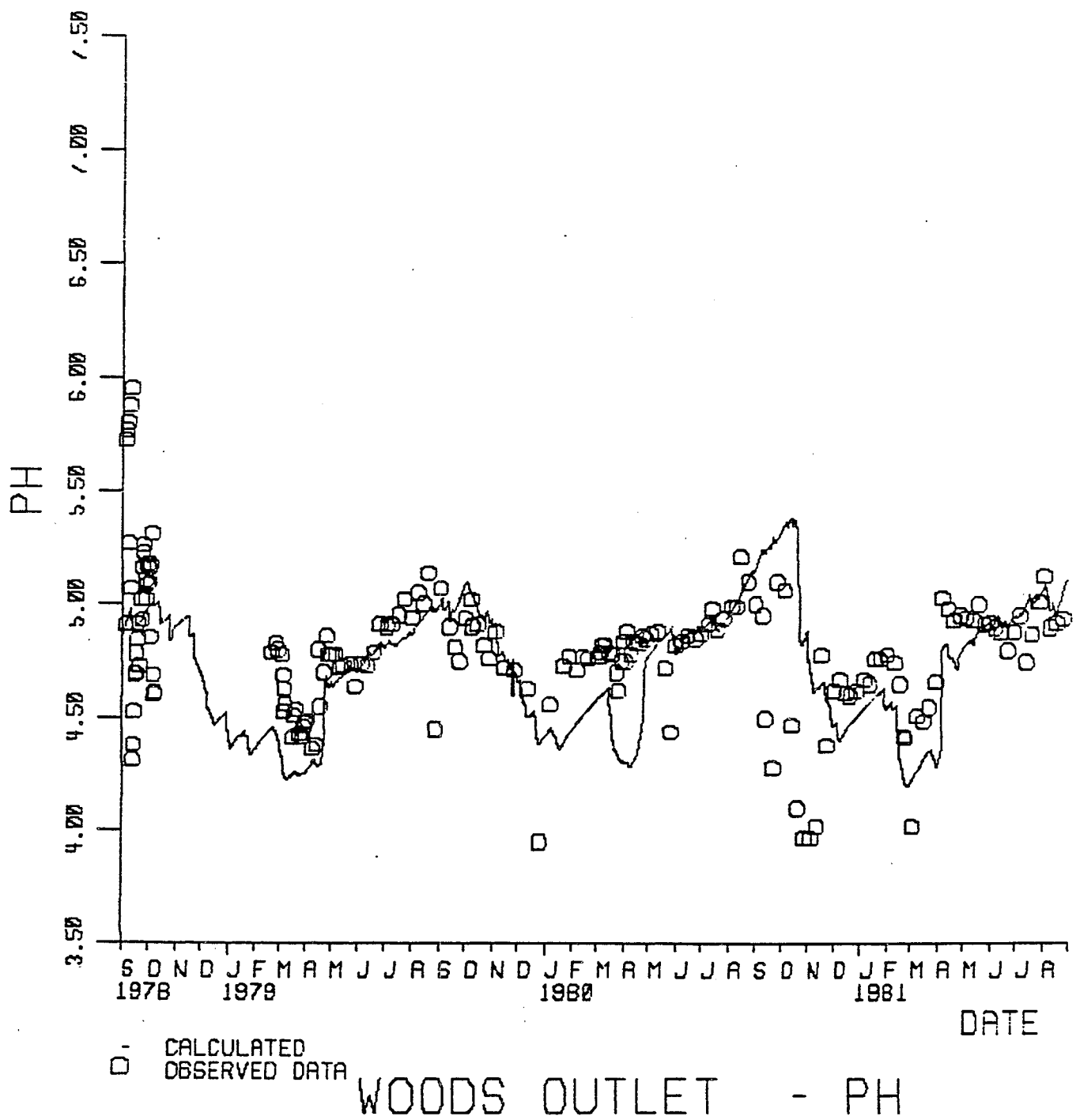


Figure 18. Simulated and observed pH for Woods Lake.

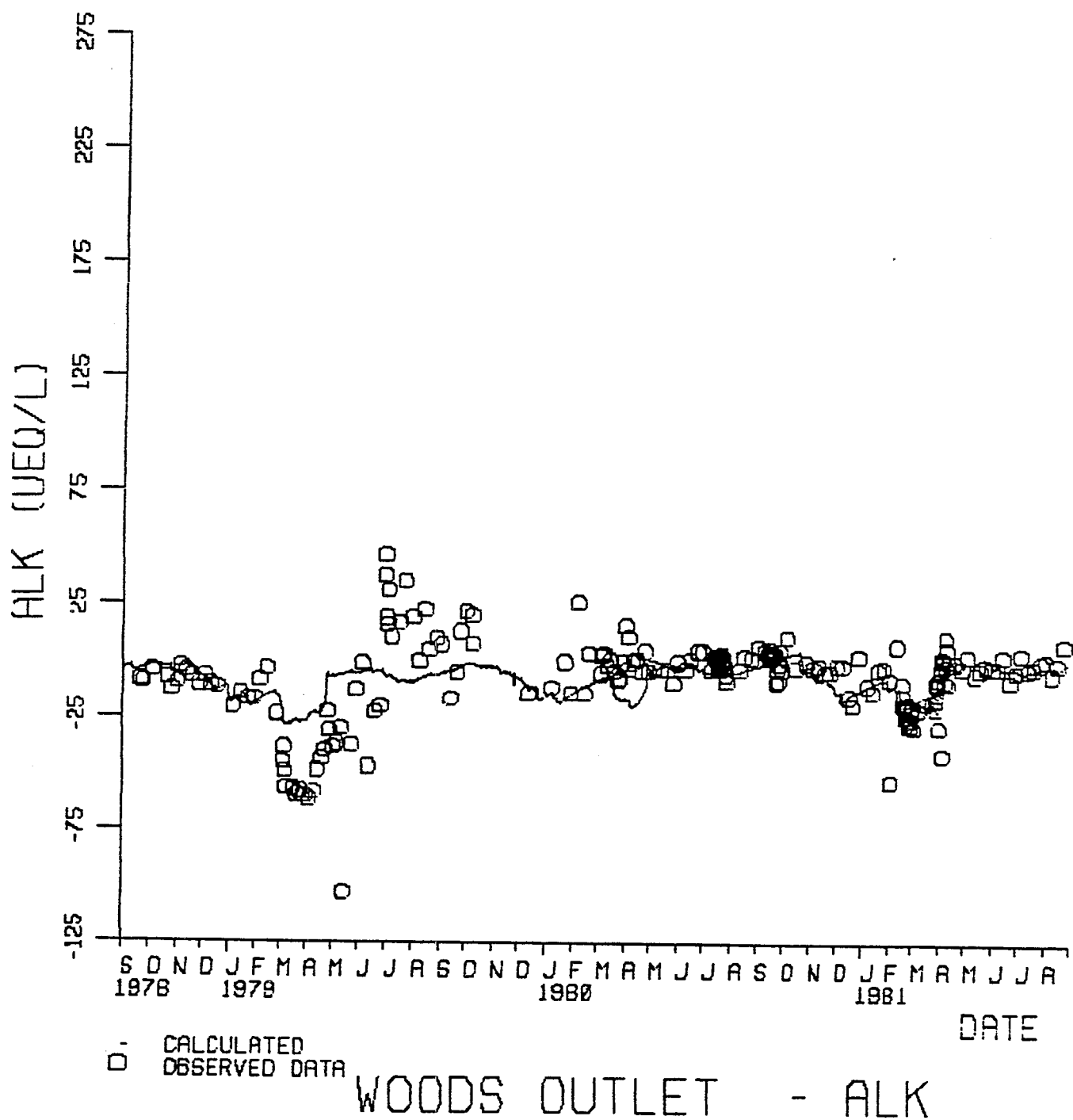


Figure 19. Simulated and observed alkalinity for Woods Lake.

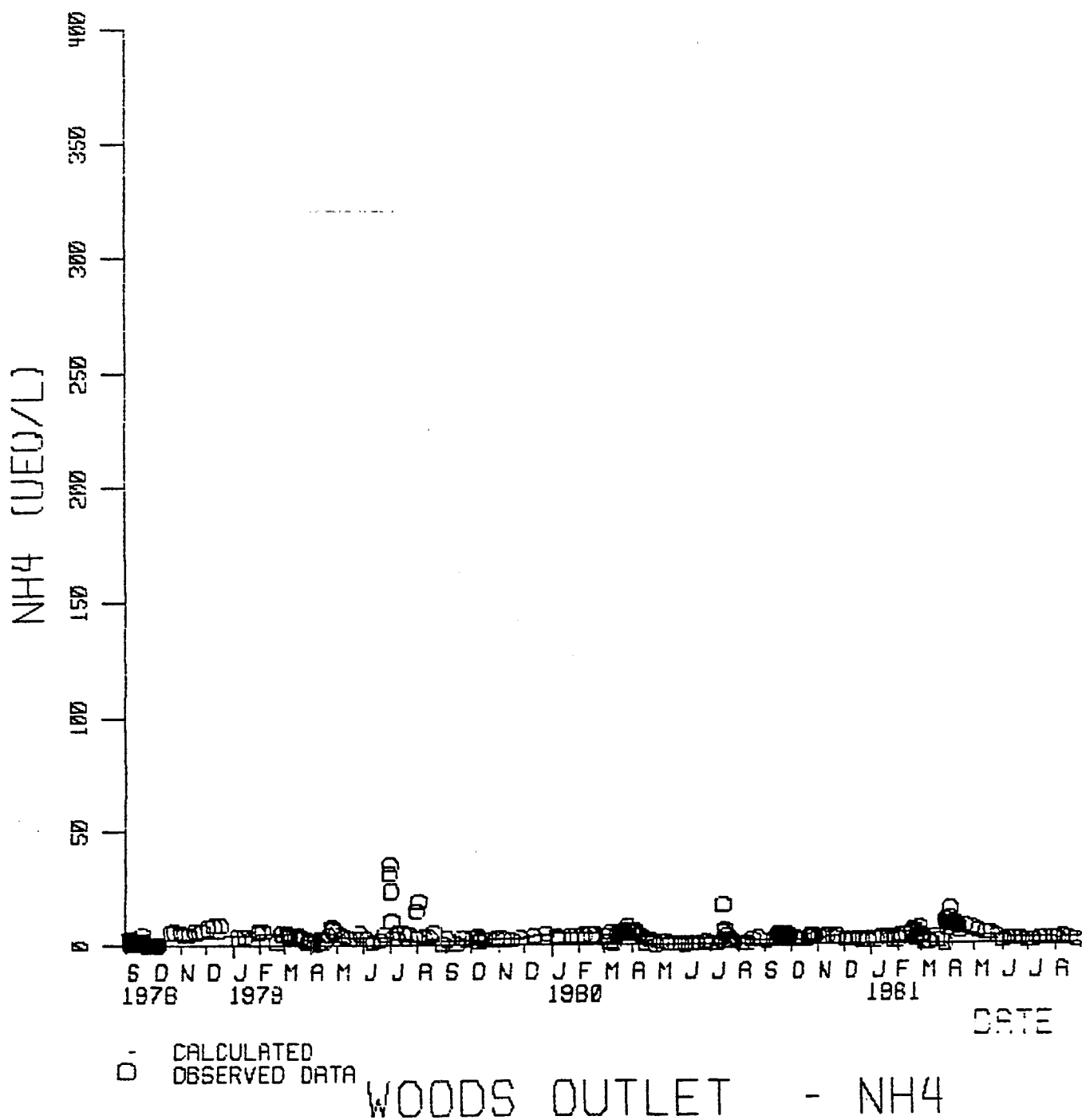


Figure 20. Simulated and observed ammonium concentration for Woods Lake.

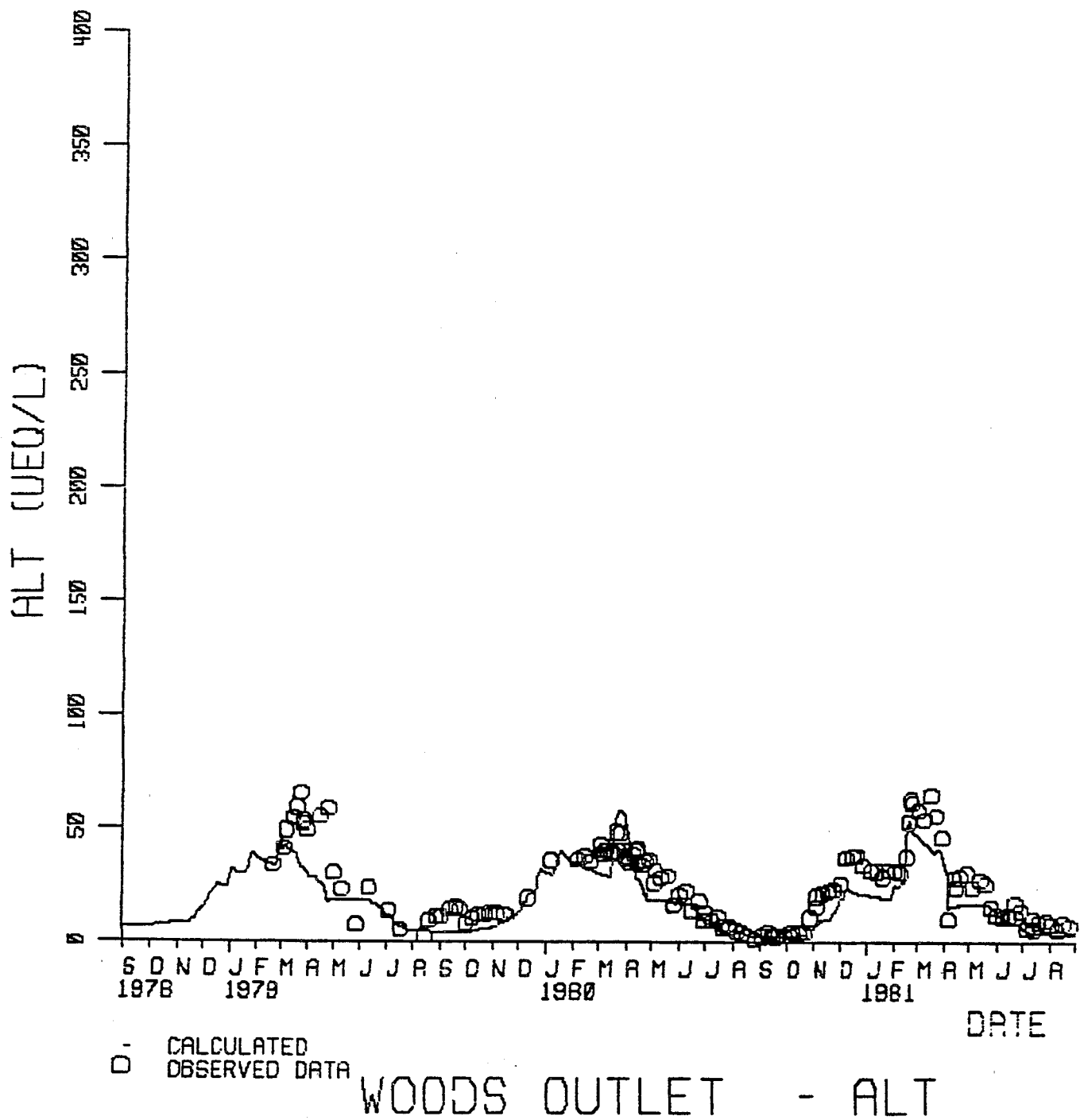


Figure 21. Simulated and observed total monomeric aluminum concentration for Woods Lake.

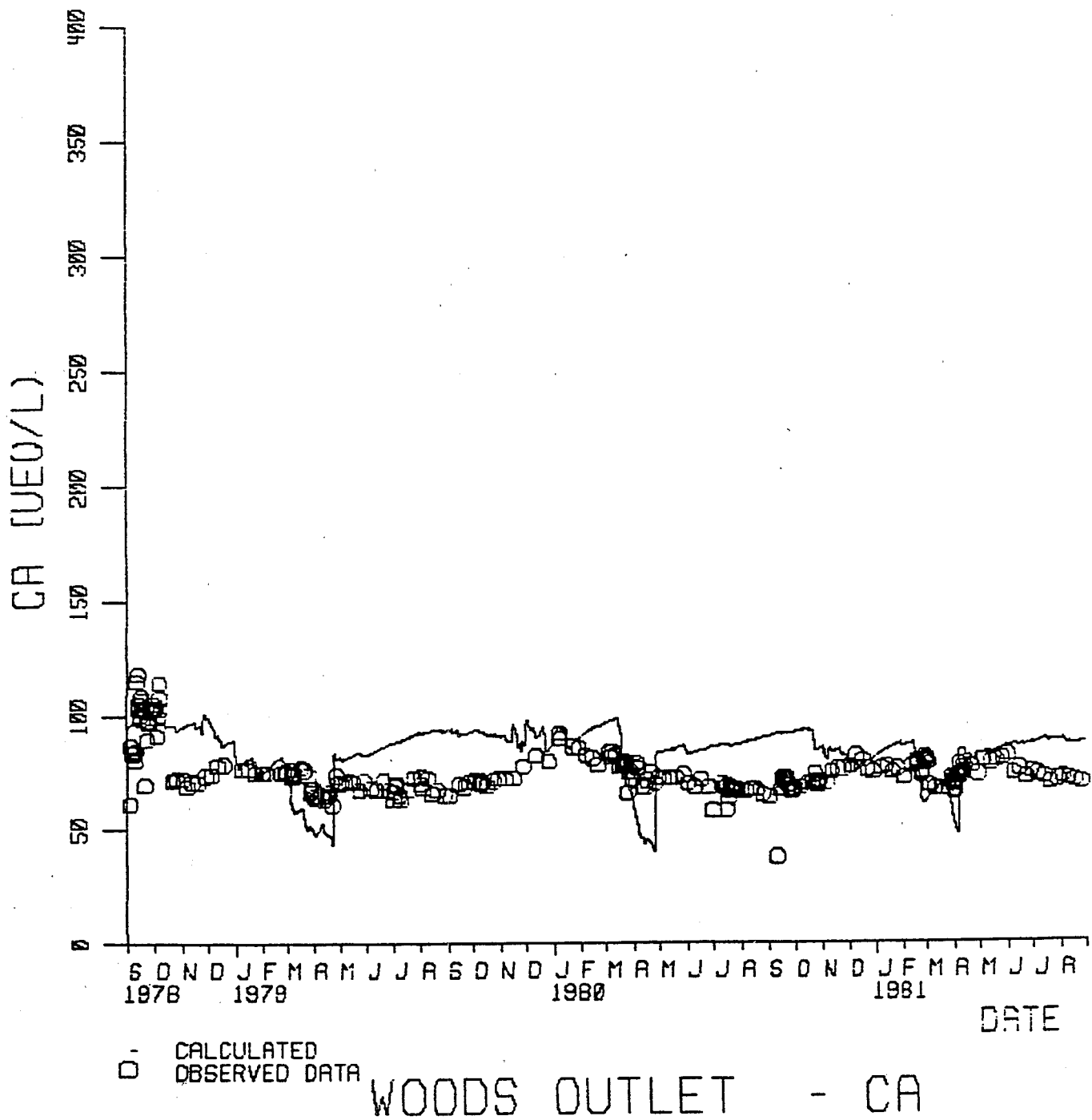


Figure 22. Simulated and observed calcium concentration for Woods Lake.

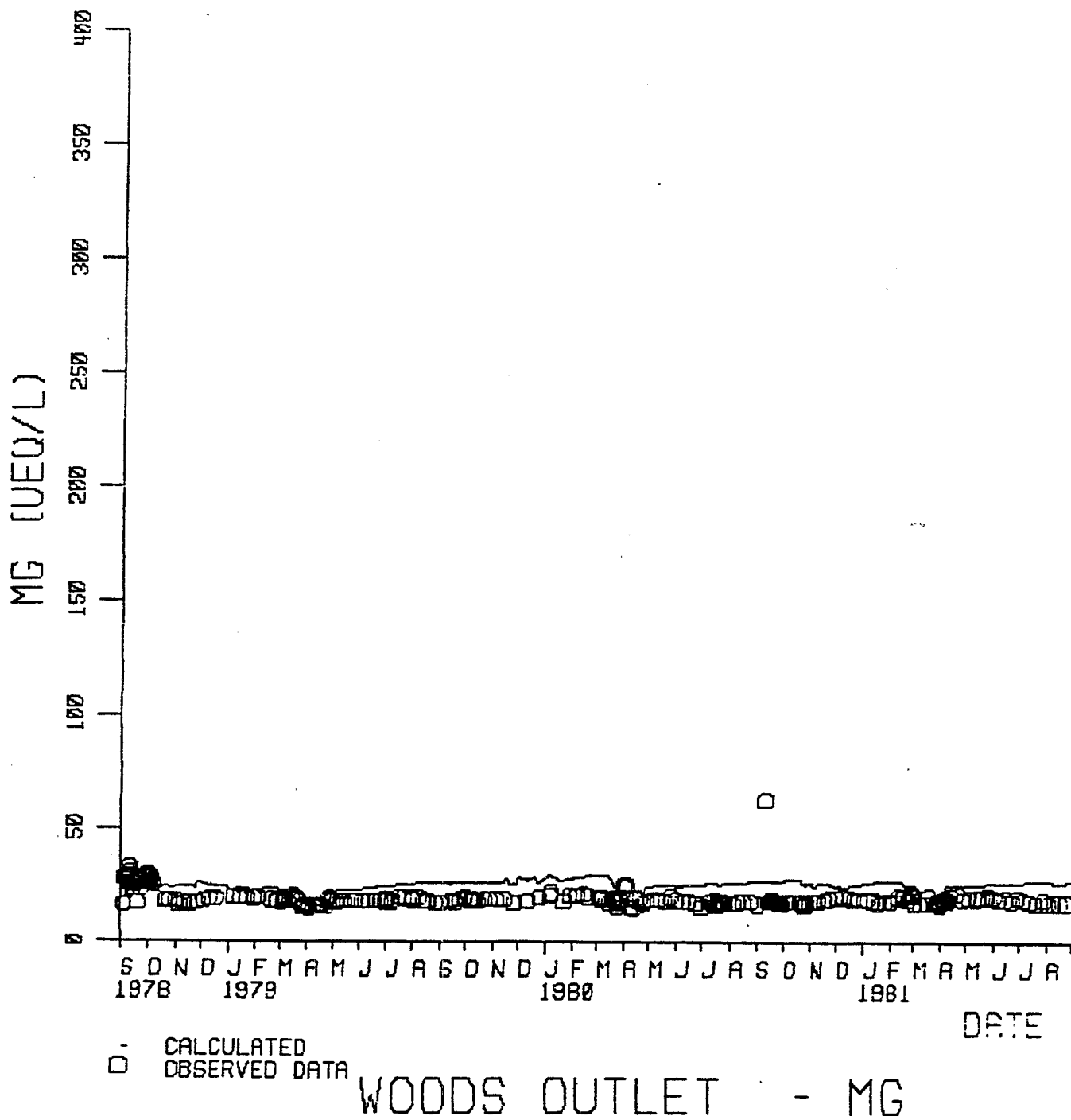


Figure 23. Simulated and observed magnesium concentration for Woods Lake.

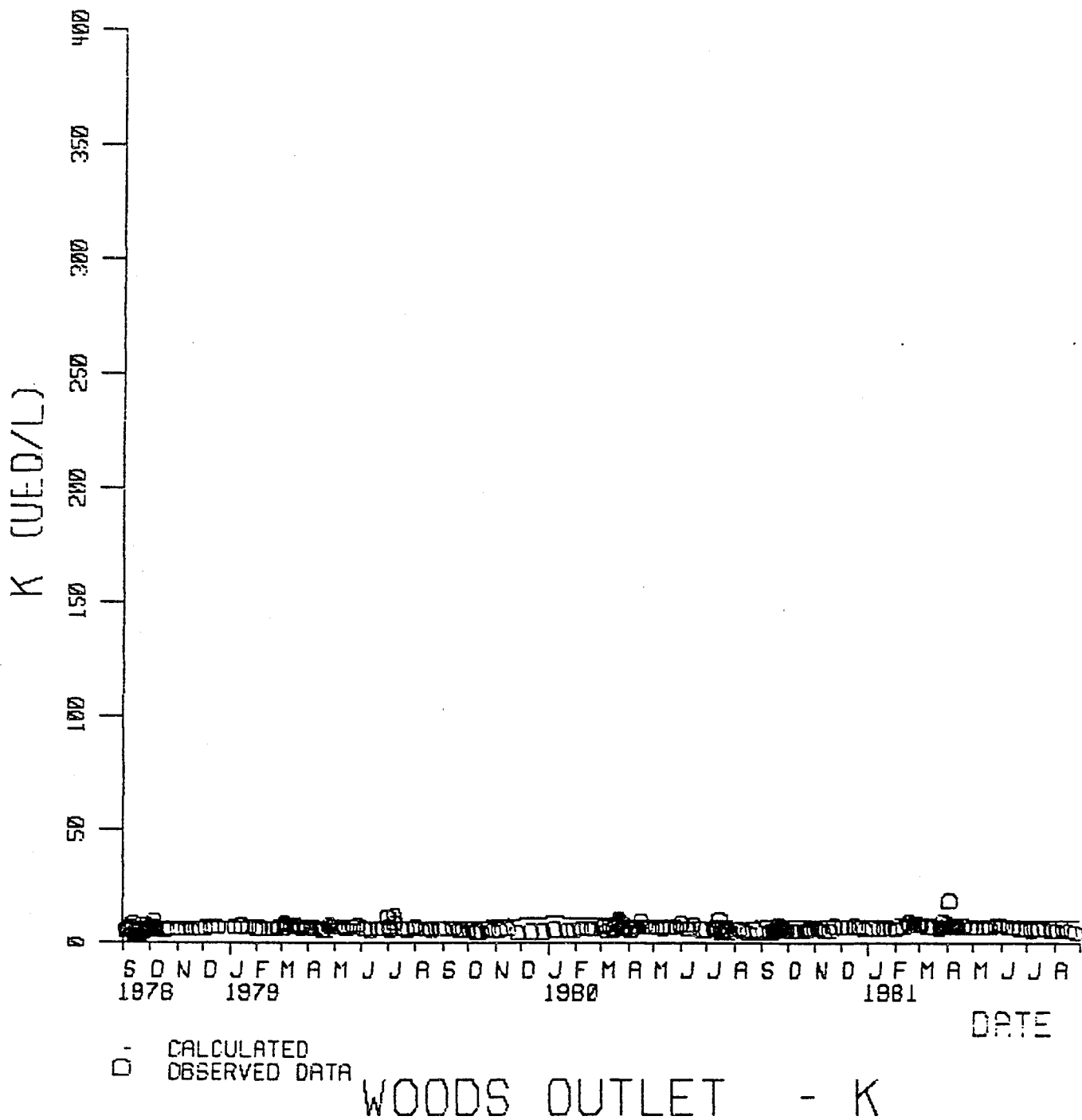


Figure 24. Simulated and observed potassium concentration for Woods Lake.

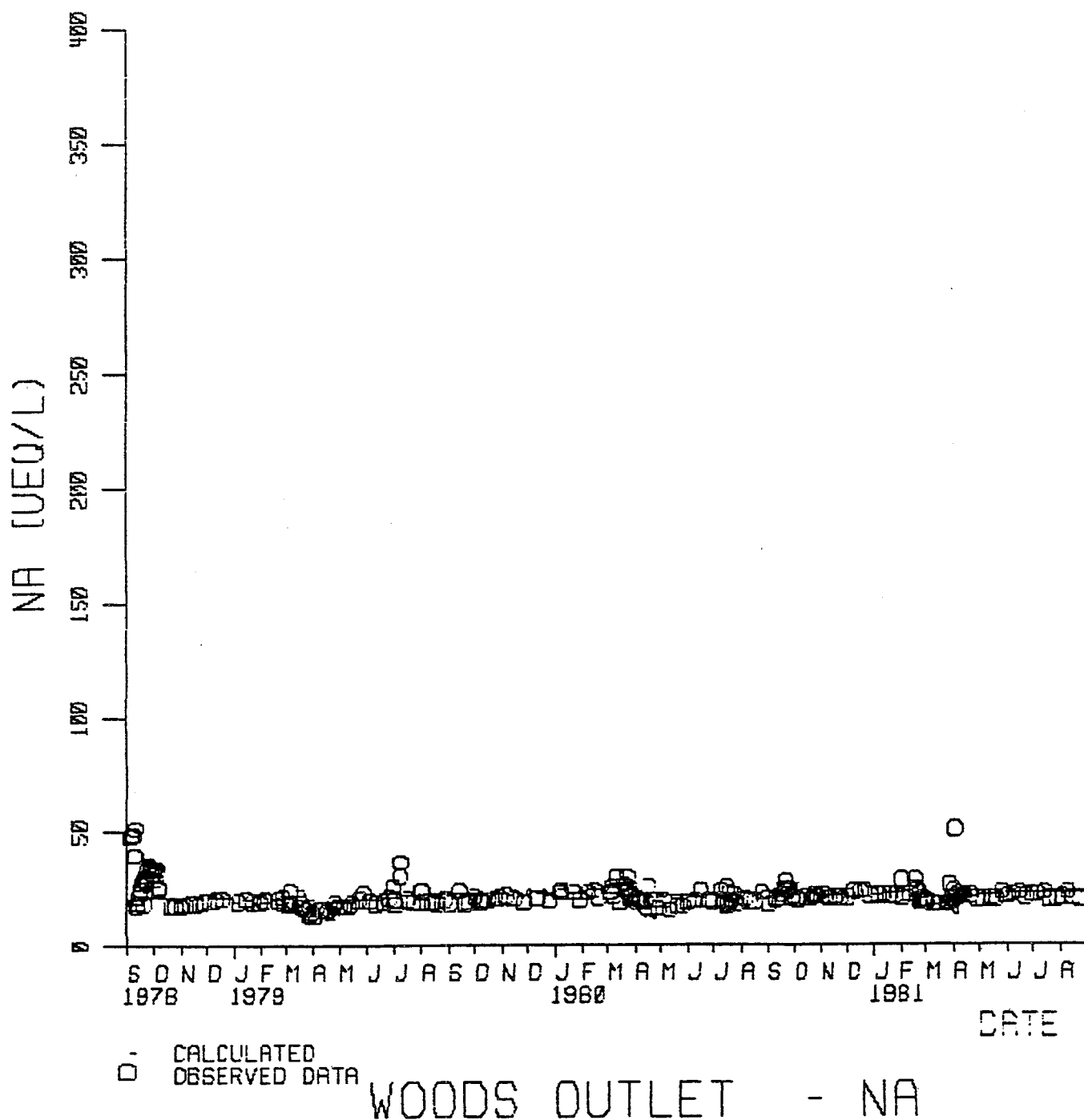


Figure 25. Simulated and observed sodium concentration for Woods Lake.

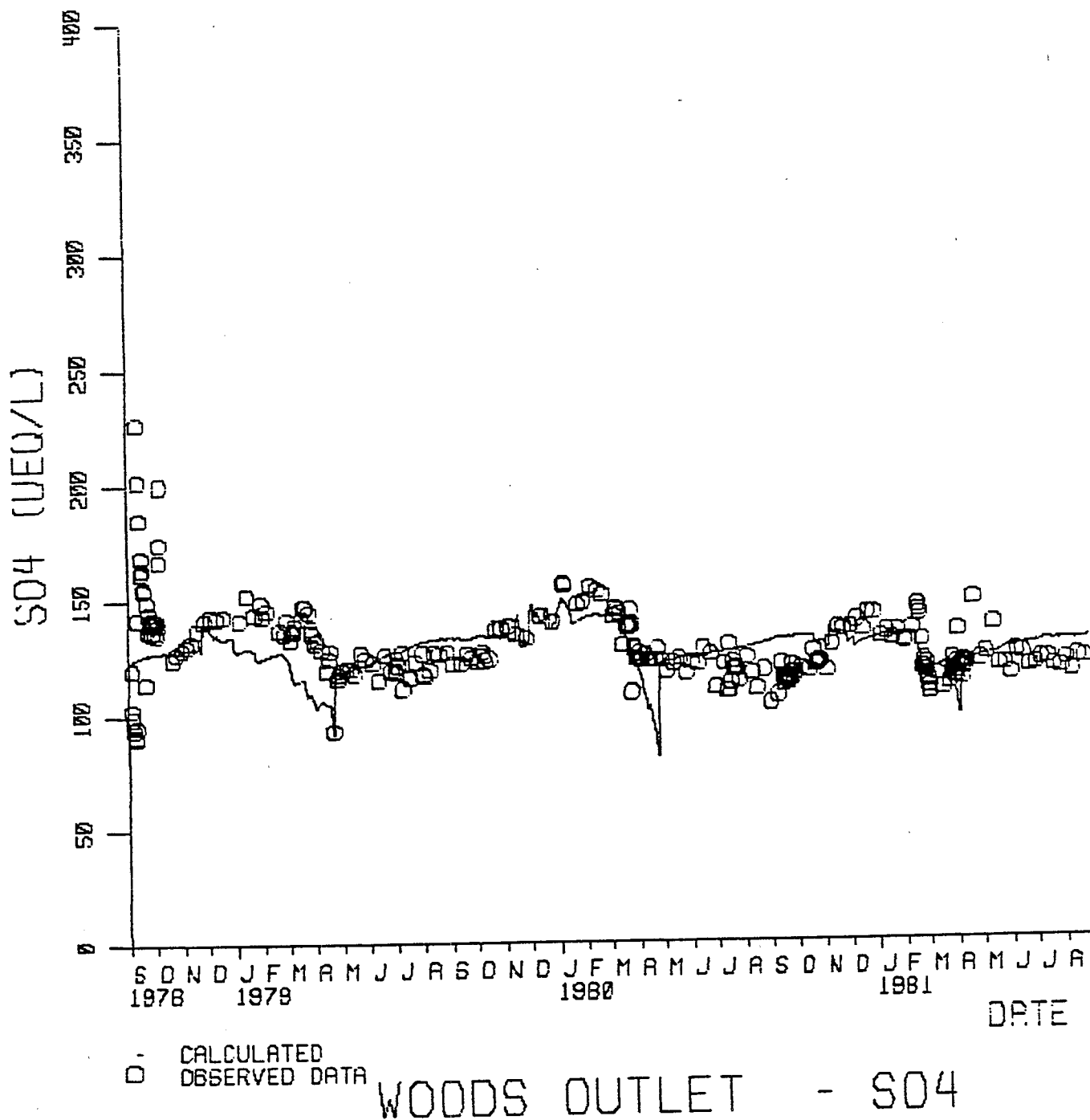


Figure 26. Simulated and observed sulfate concentration for Woods Lake.

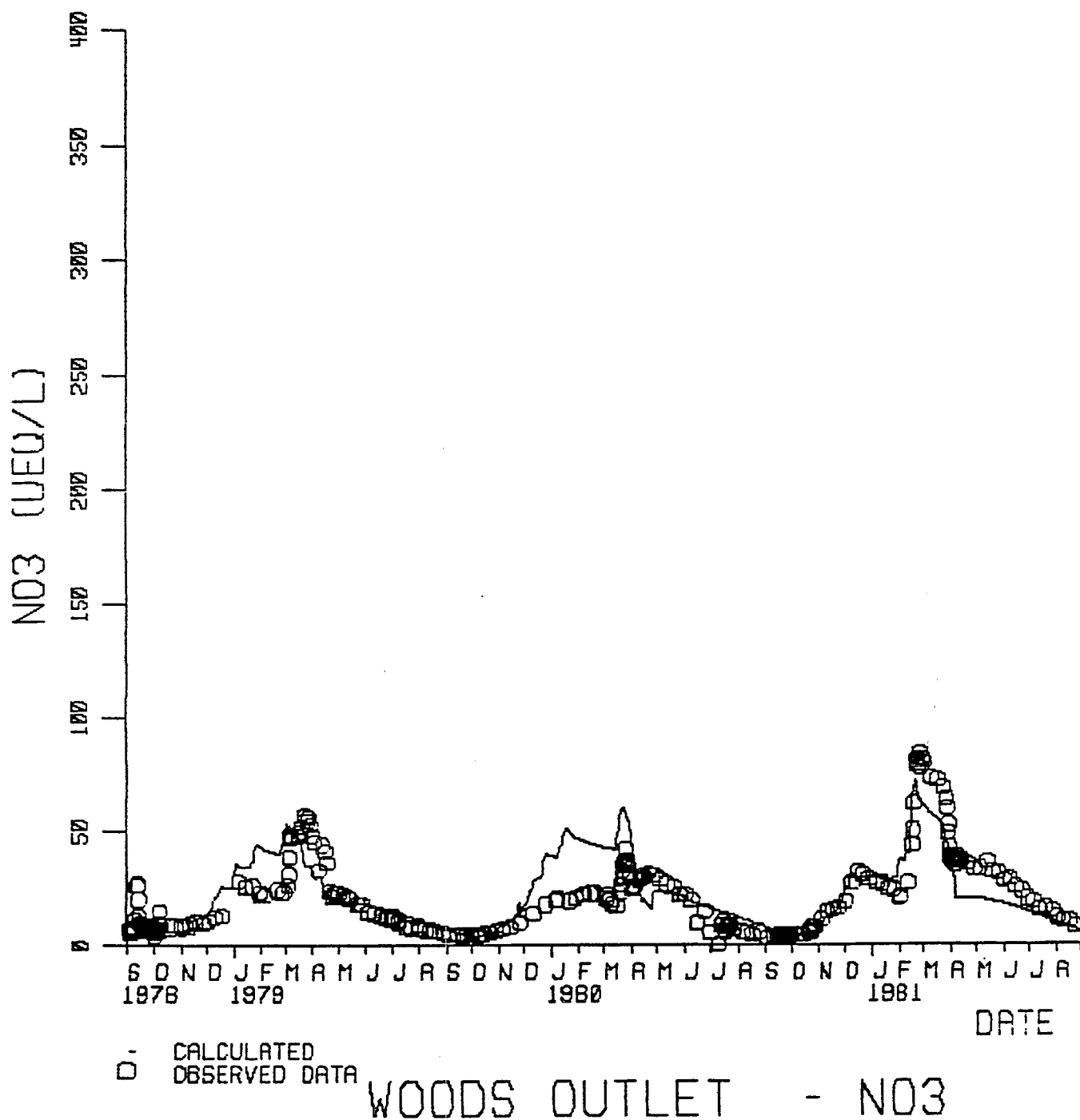


Figure 27. Simulated and observed nitrate concentration for Woods Lake.

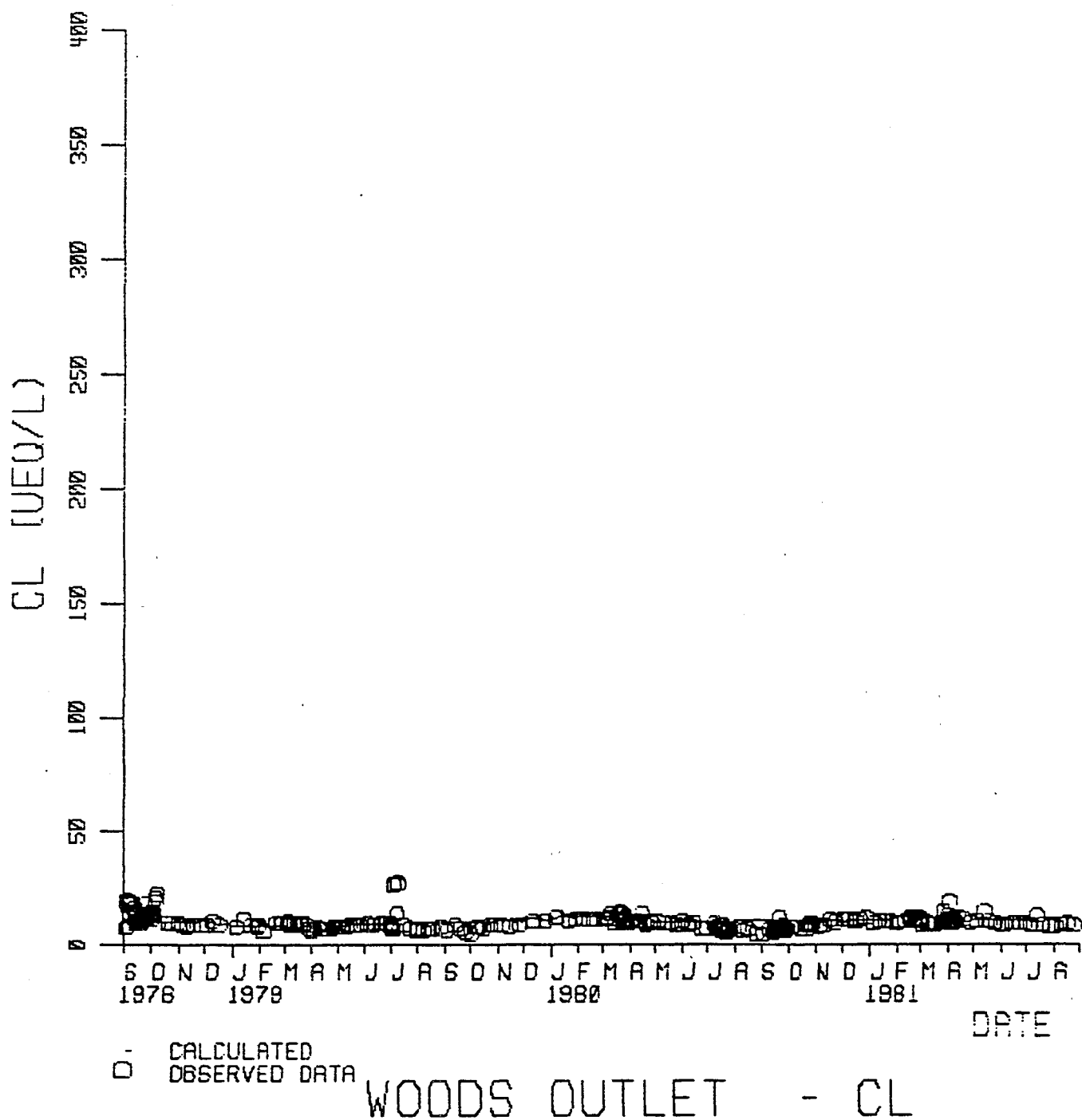


Figure 28. Simulated and observed chloride concentration for Woods Lake.

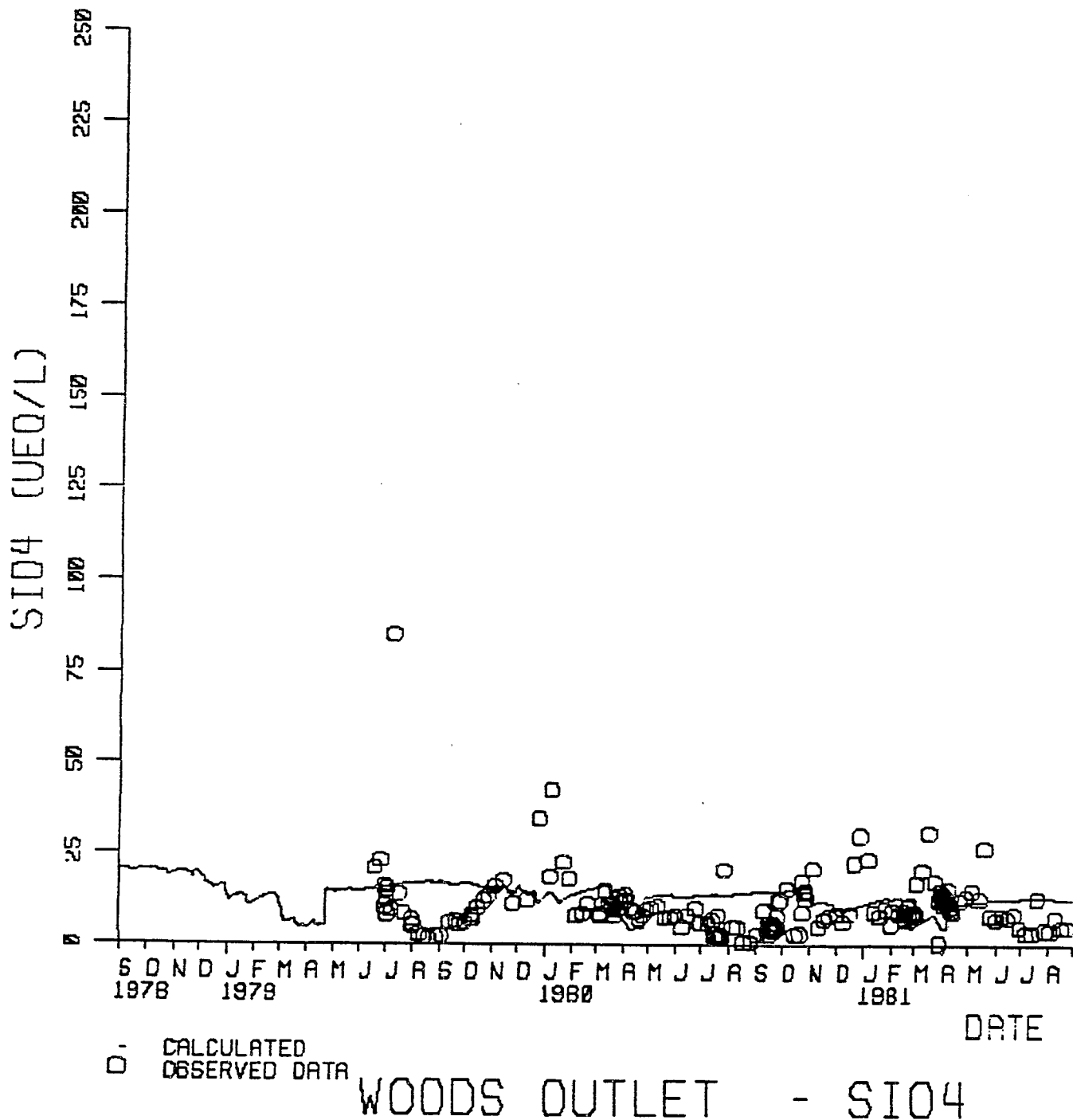


Figure 29. Simulated and observed silicic acid concentration for Woods Lake.

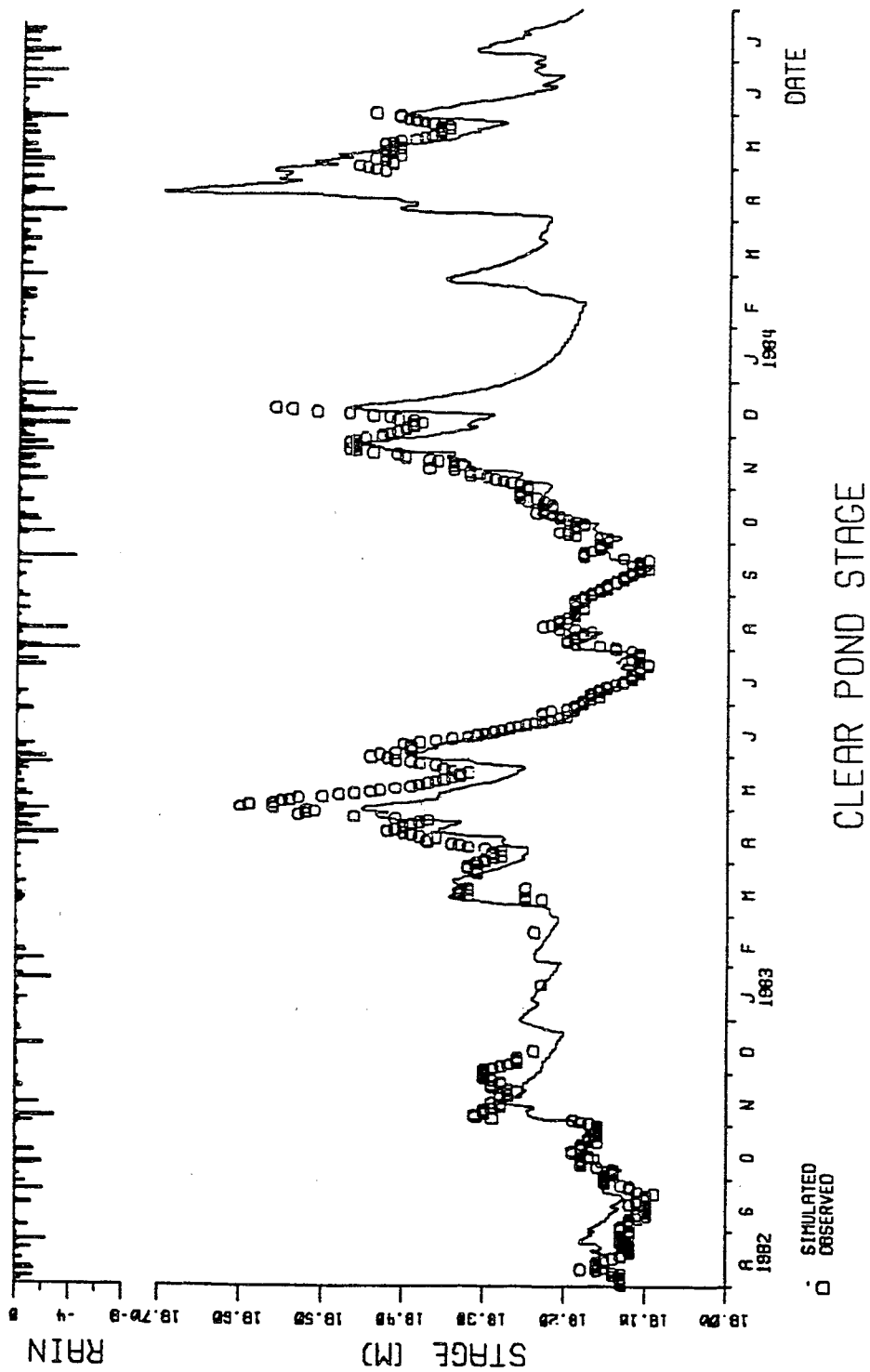


Figure 30. Simulated and observed lake stage for Clear Pond.

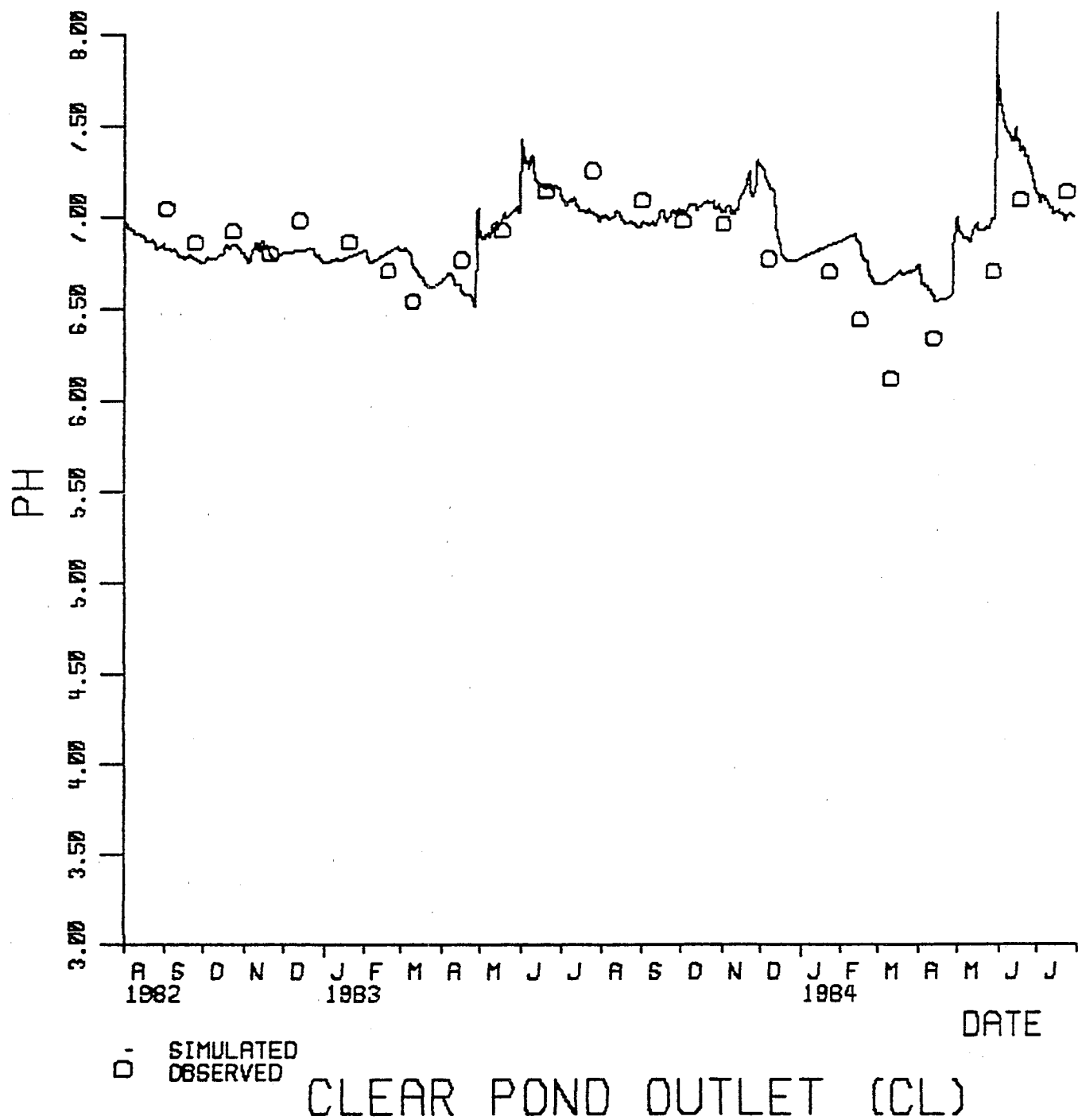


Figure 31. Simulated and observed pH for Clear Pond.

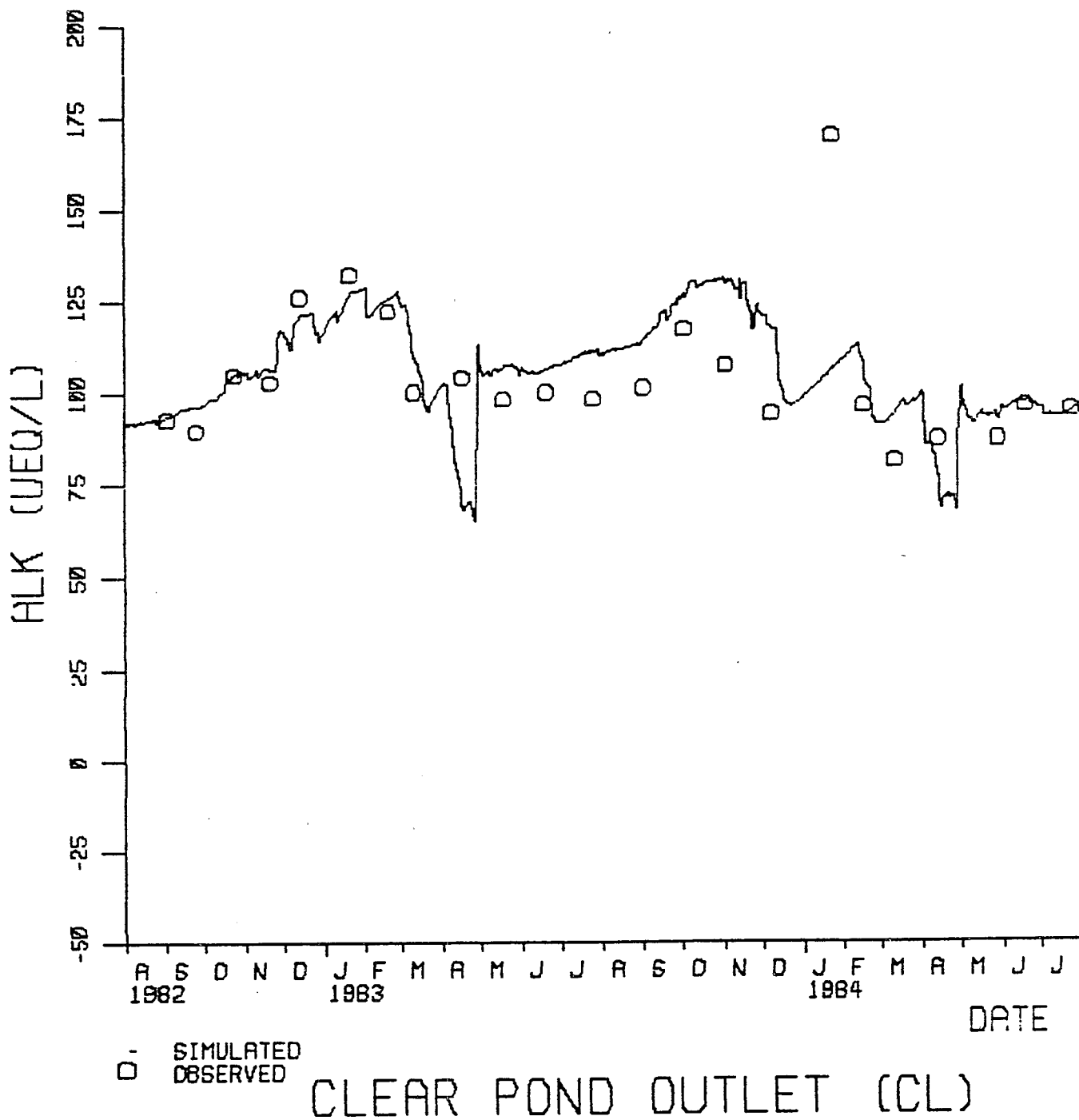


Figure 32. Simulated and observed alkalinity for Clear Pond.

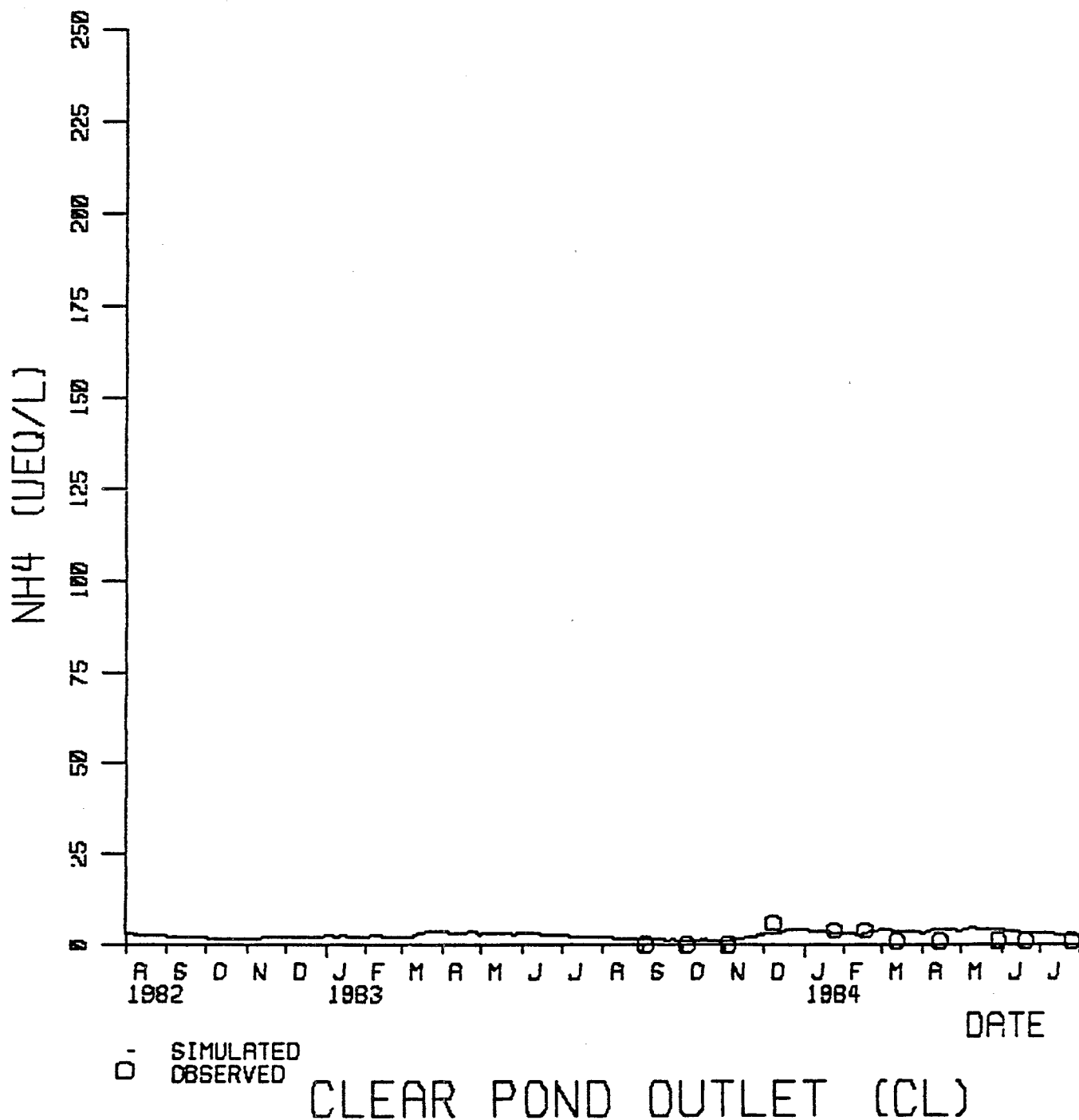


Figure 33. Simulated and observed ammonium concentration for Clear Pond.

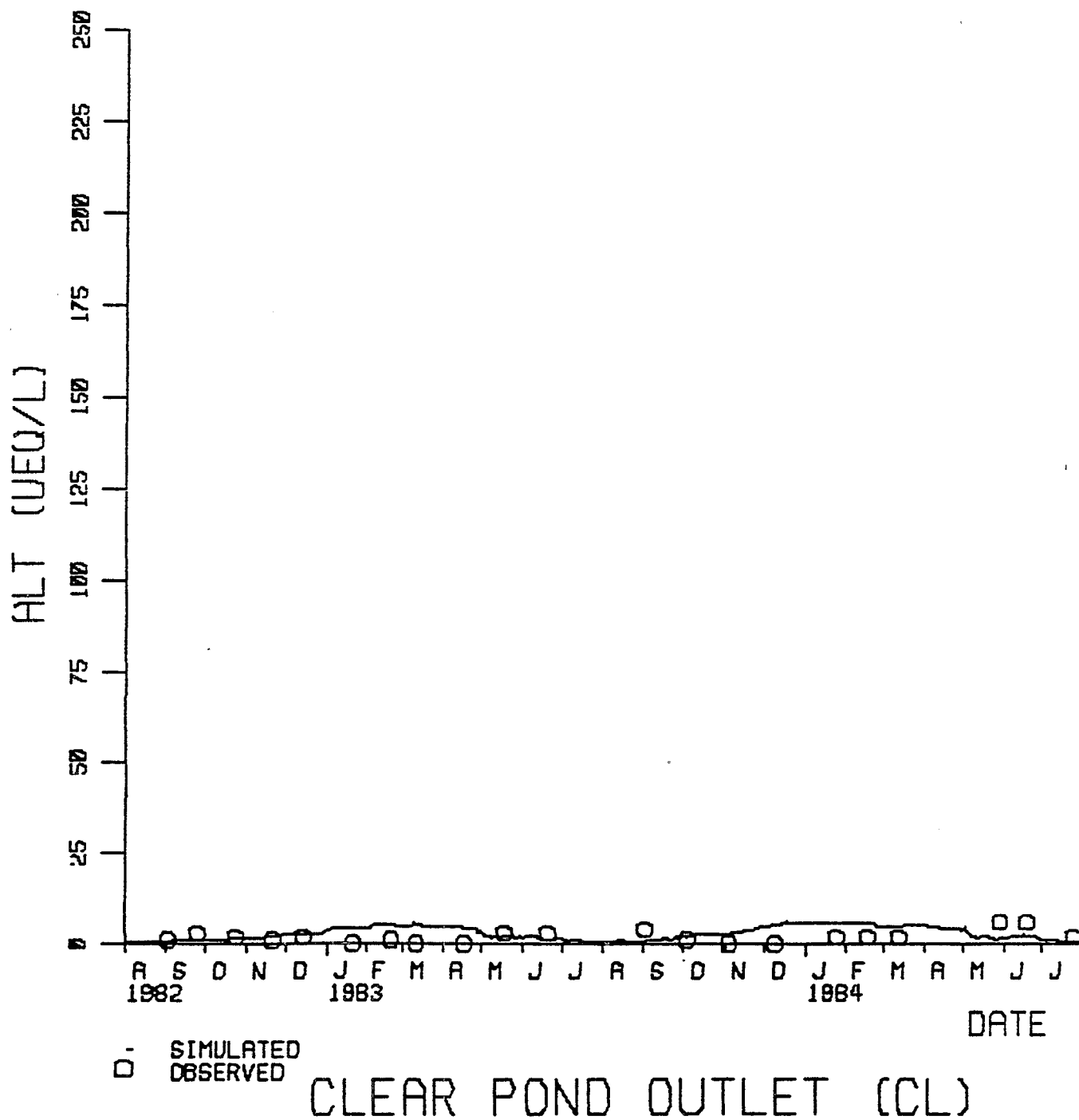


Figure 34. Simulated and observed total monomeric aluminum concentration for Clear Pond.

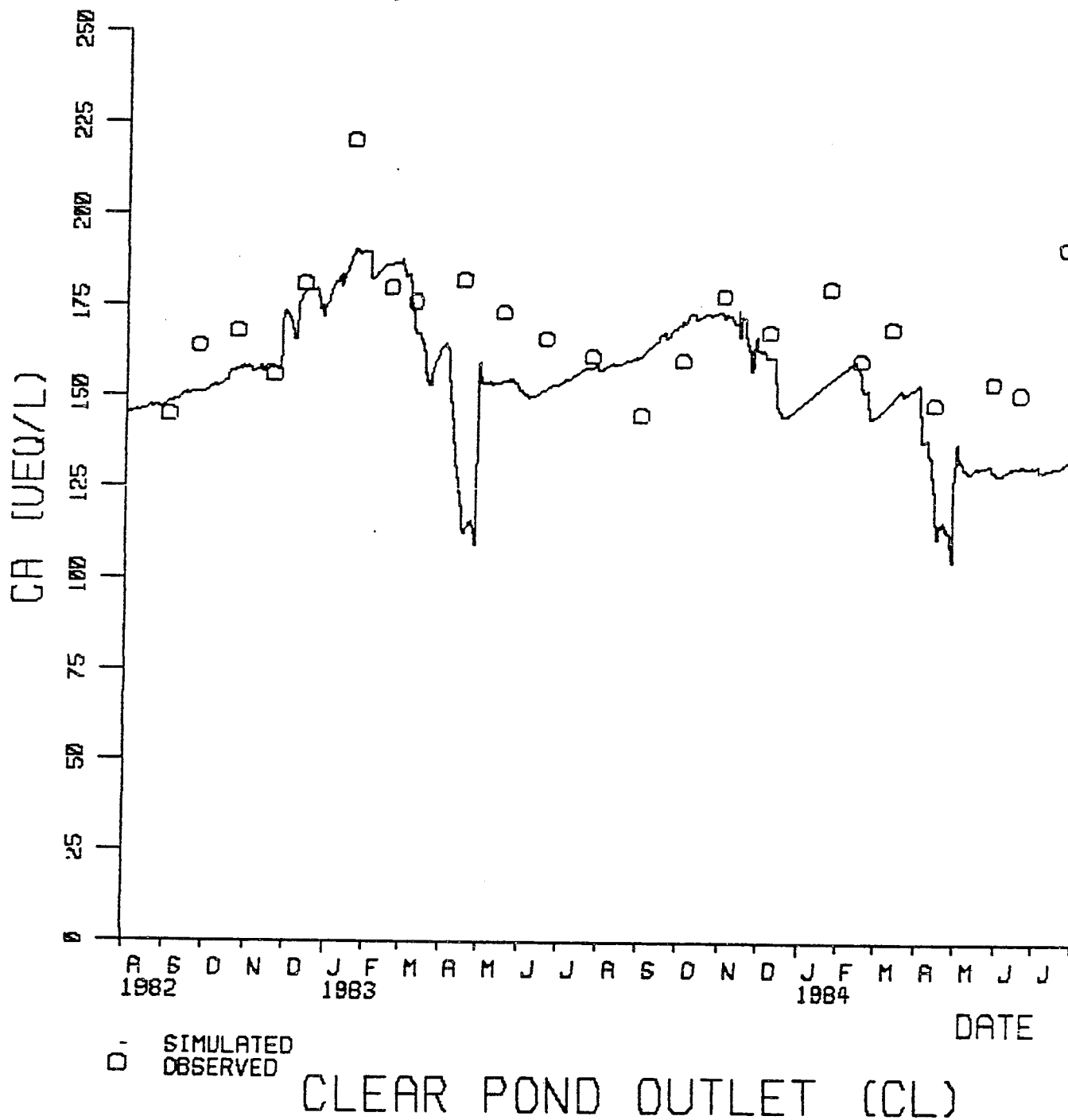


Figure 35. Simulated and observed calcium concentration for Clear Pond.

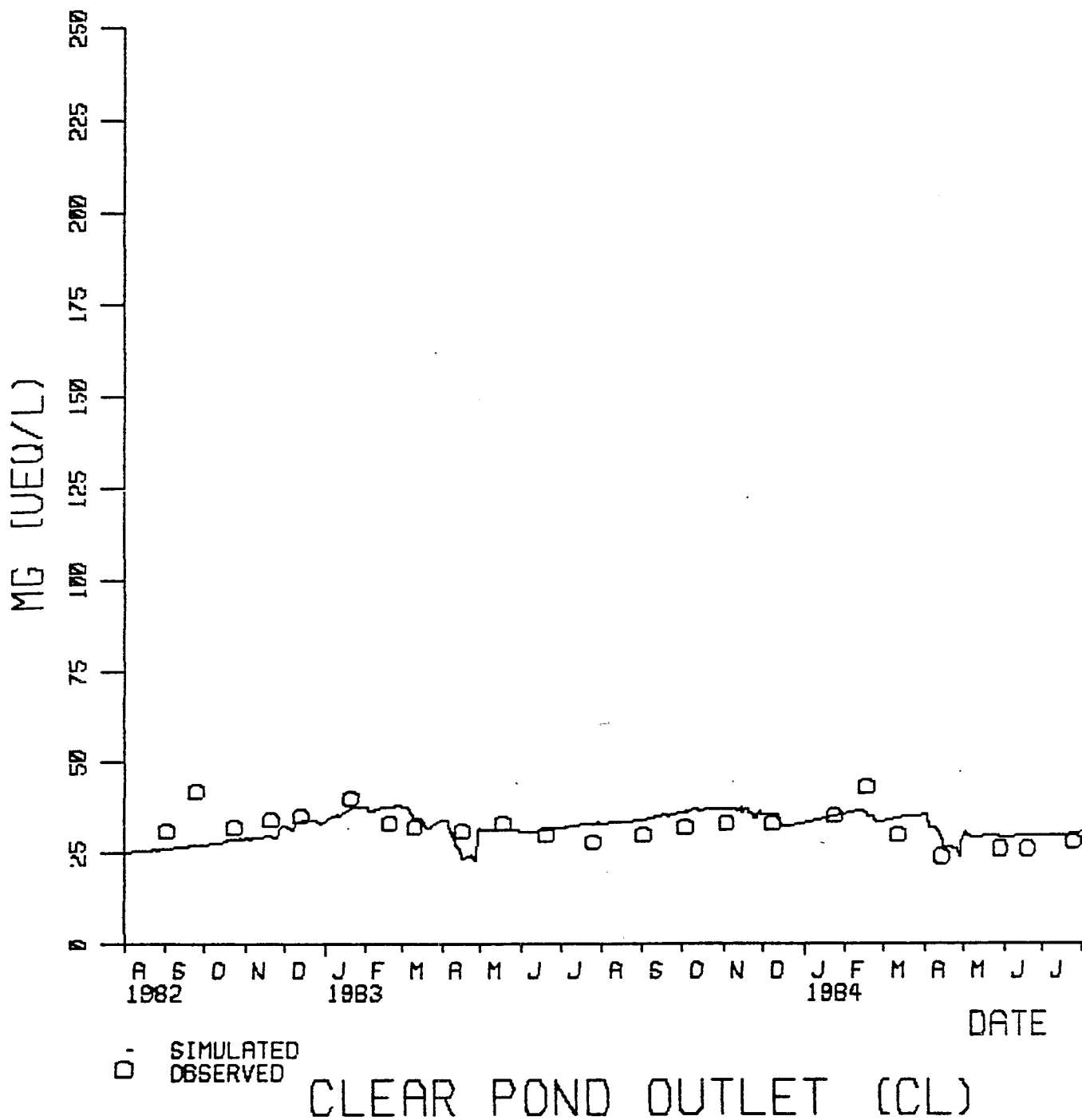


Figure 36. Simulated and observed magnesium concentration for Clear Pond.

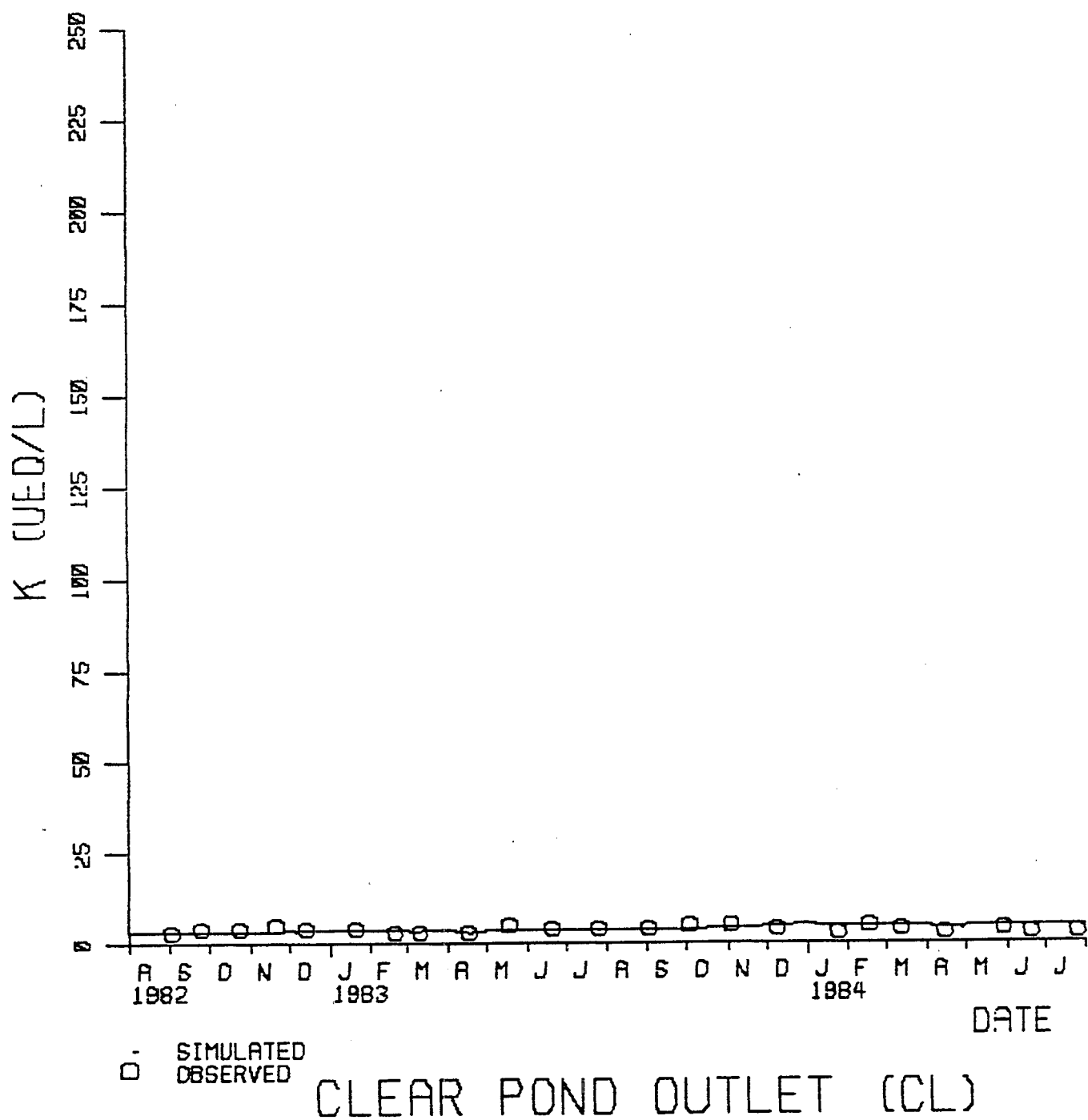


Figure 37. Simulated and observed potassium concentration for Clear Pond.

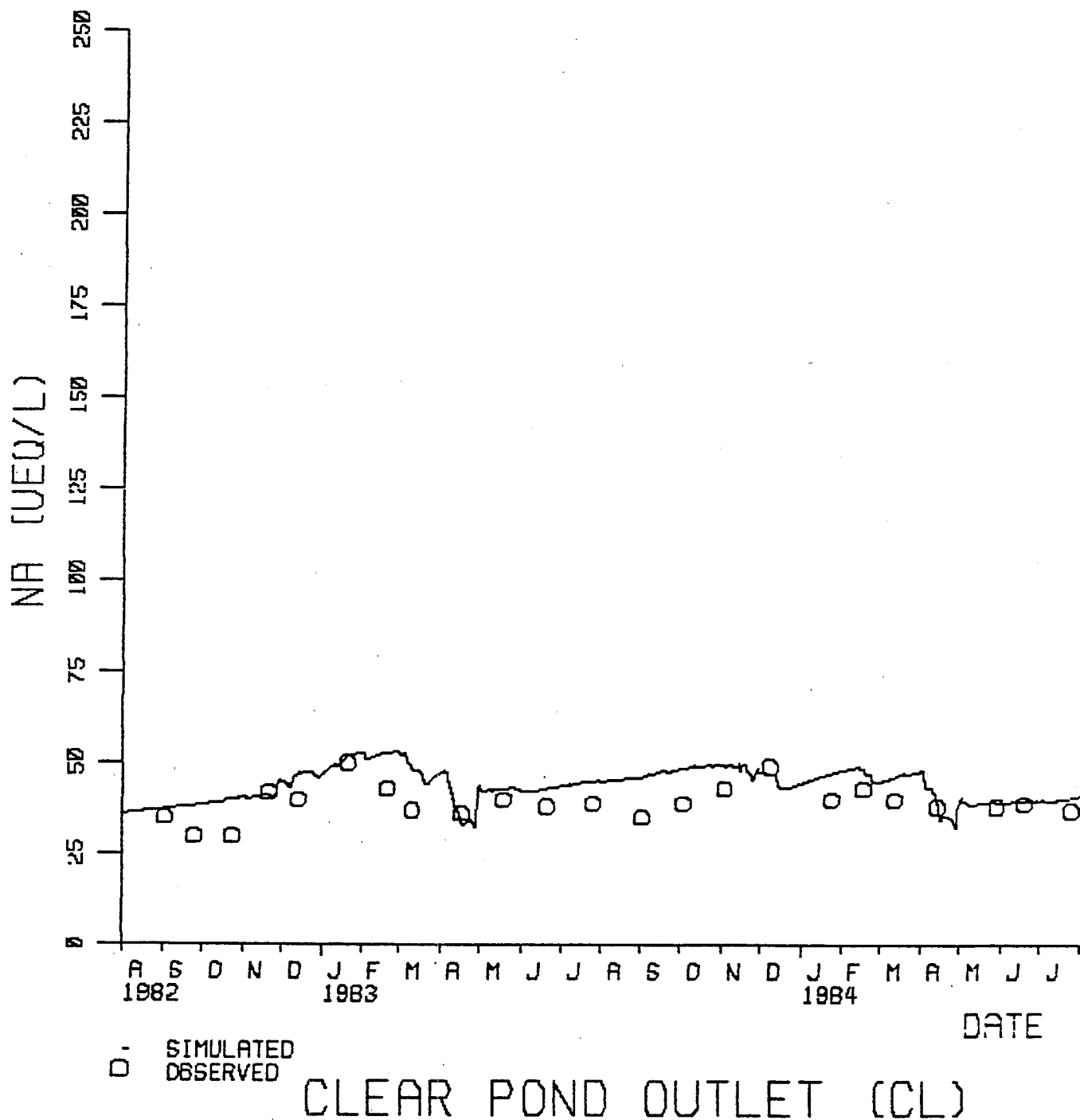


Figure 38. Simulated and observed sodium concentration for Clear Pond.

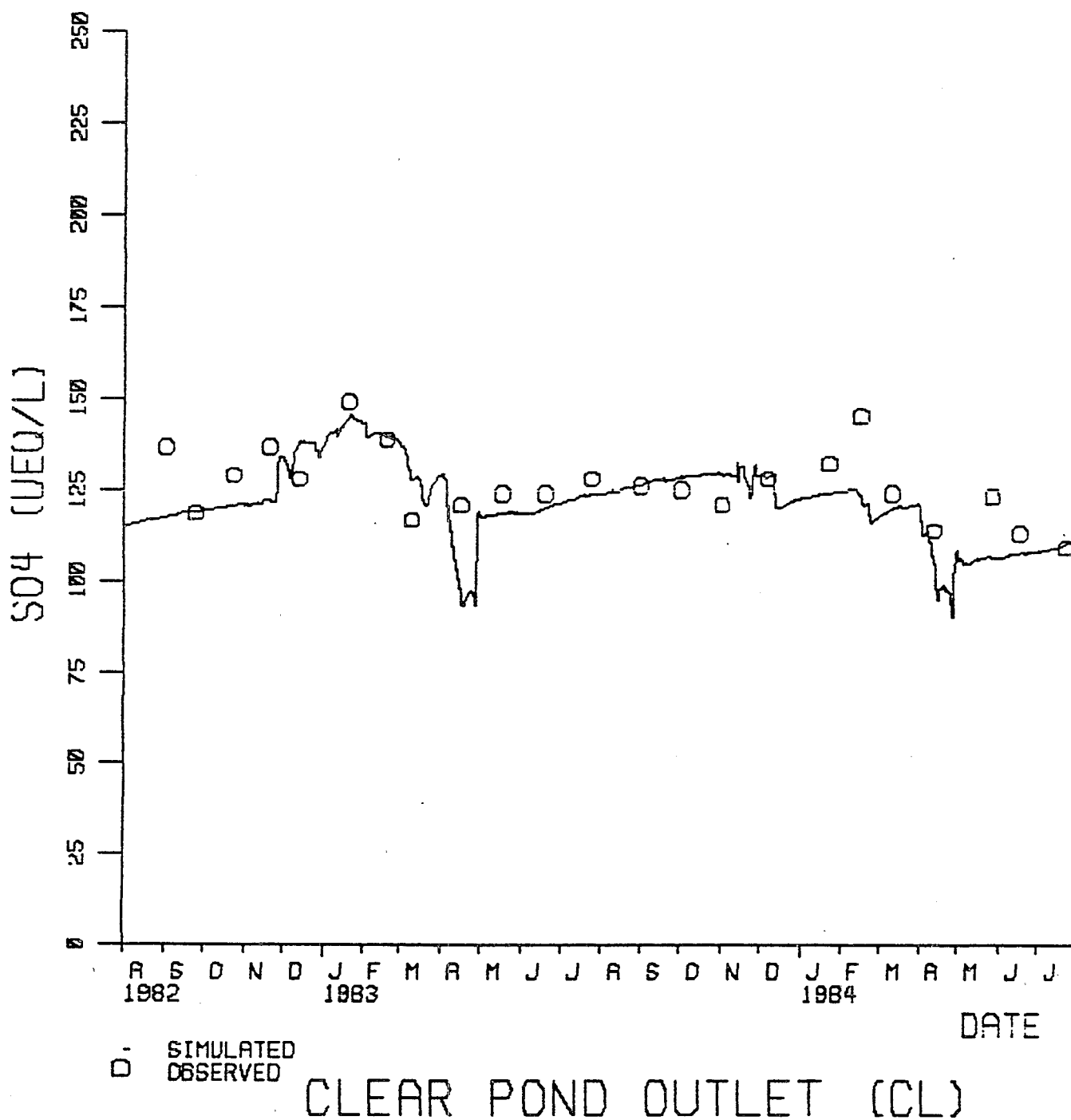


Figure 39. Simulated and observed sulfate concentration for Clear Pond.

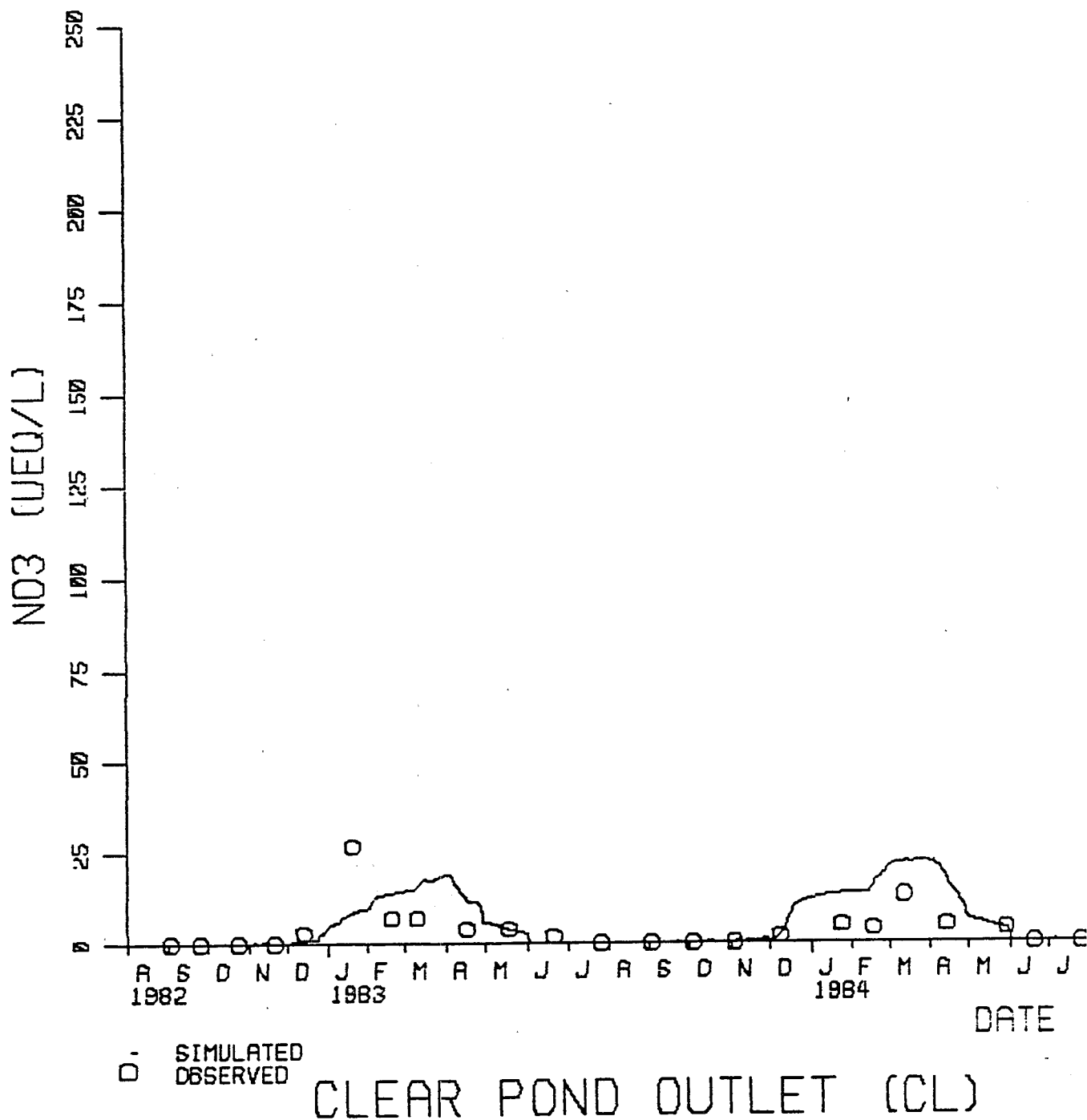


Figure 40. Simulated and observed nitrate concentration for Clear Pond.

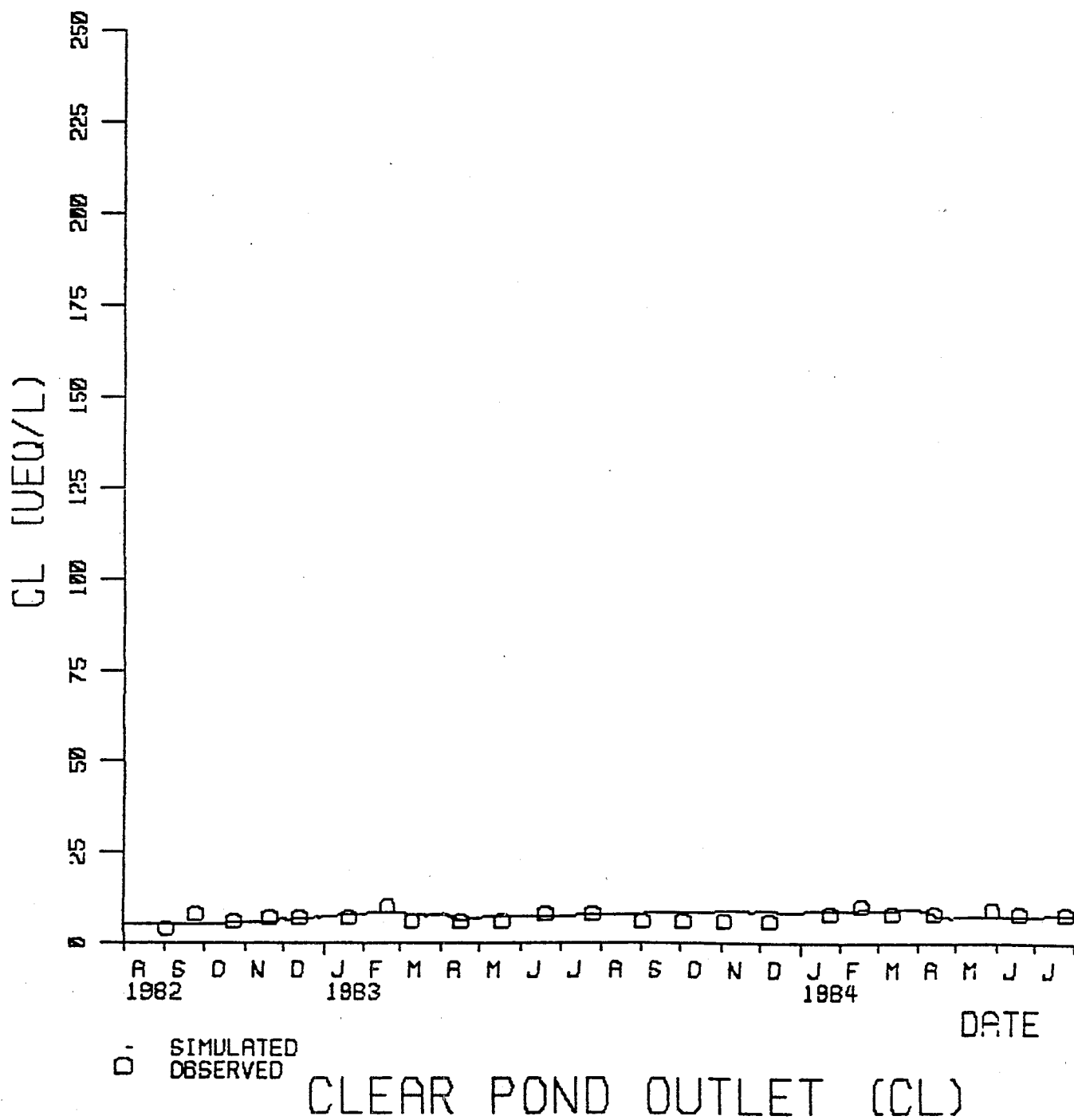


Figure 41. Simulated and observed chloride concentration for Clear Pond.

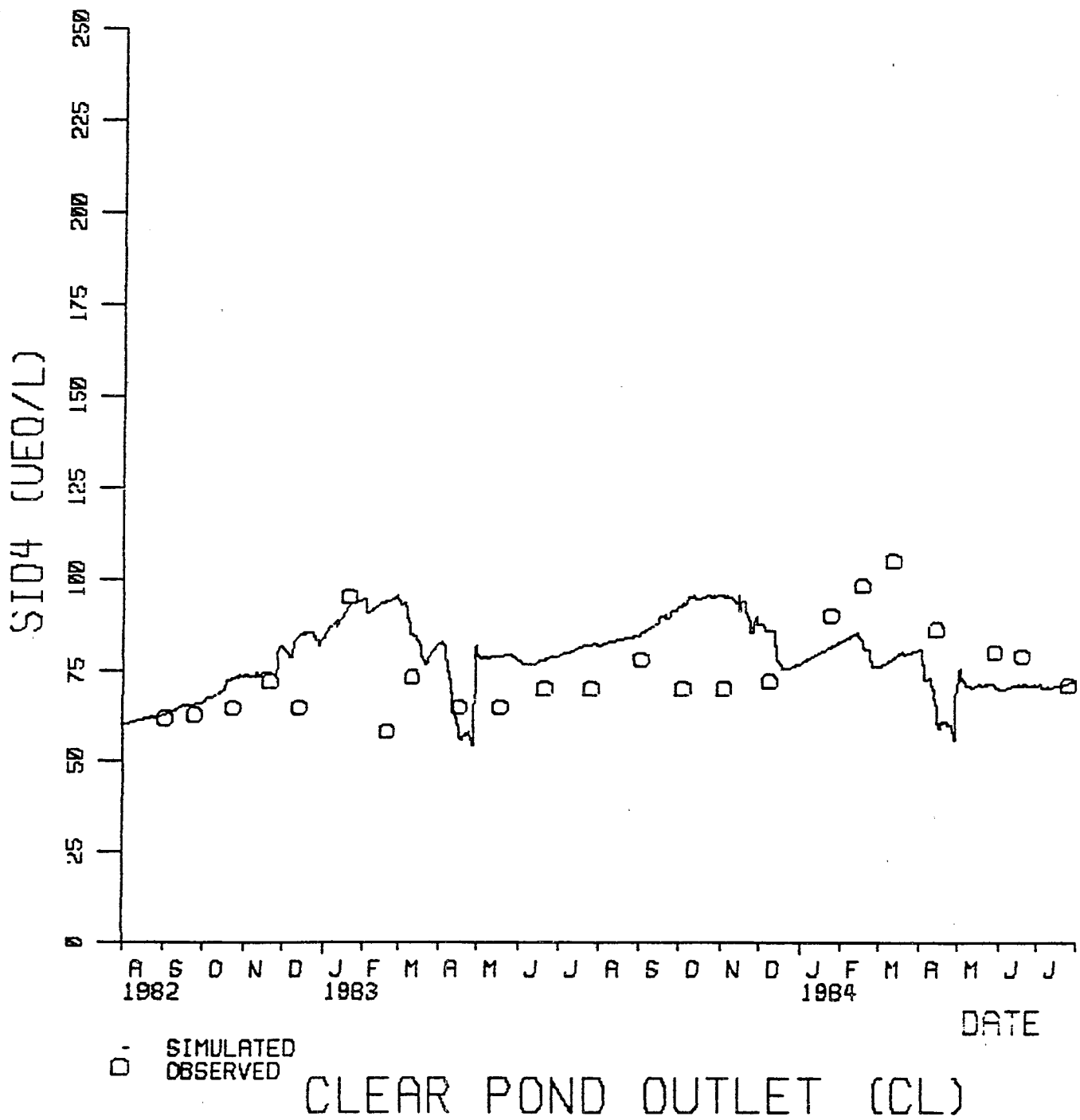


Figure 42. Simulated and observed silicic acid concentration for Clear Pond.

APPENDIX A.1-3

MODEL OF ACIDIFICATION OF GROUNDWATER IN CATCHMENTS (MAGIC)

PROTOCOL FOR CALIBRATION PHASE OF
DDRP MODELING

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INTRODUCTION

Four tasks must be completed in the calibration phase of our DDRP modeling project. 1) First, all inputs must be specified. Also, all "fixed" parameters must be set and an (objective) procedure for selecting these values must be specified. By "fixed" parameters we mean those that are not adjusted in calibration. 2) Second, the remaining ('adjustable') parameters are selected so that a loss function, in this case an unweighted sum of squared errors (SSE), is minimized. 3) Third, an analysis of how well the adjustable parameters have been estimated must be accomplished. This is, the sensitivity of the SSE to changes in the optimal values of the adjustable parameters must be determined. 4) Fourth, with the adjustable parameters fixed at their optimal values, a conventional, univariate sensitivity analysis for the 'fixed' parameters must be done. Again this will be a sensitivity with respect to the SSE.

The first task is relatively straightforward. Inputs will, in general, be specified using measured data. If data are unavailable, suitable extrapolations will be specified by objective procedures. In a similar vein, some model parameters will be fixed (i.e., have values specified) using observations in conjunction with well-defined objective procedures. These parameters will not be adjusted in the calibration.

The second task requires the minimization of the SSE between model predictions and observed data. In general terms the model can be written.

$$\underline{Y} = \underline{f}(\underline{x}, \underline{\Theta}) \quad (1)$$

where $\underline{Y}$ is a vector of 'outputs', $\underline{x}$ is a vector of 'inputs' (and fixed parameters), $\underline{\Theta}$ is a vector of adjustable parameters of order k , and $\underline{f}$ is a vector function relating the other quantities. We then seek to minimize

$$\Phi(\underline{\Theta}) = \sum_{a=1}^n \sum_{u=1}^m e_{ua}^2(\underline{\Theta}) \quad (2)$$

where e_{ua} Presents the error in the u^{th} component of the vector at the a^{th} temporal observation:

$$e_{ua} = [Y_{ua}(\text{obs}) - Y_{ua}(\text{model})]. \quad (3)$$

The order of the output vector is m and the number of observations is n .

There are any number of techniques for determining a value of $\underline{\Theta}$ that minimizes $\Phi(\underline{\Theta})$. (For example, see Bard, 1974). We propose to use the Rosenbrock (1960) method to optimize, although we may experiment with other methods (e.g., the Marquardt (1963) algorithm).

Once a parameter vector $\underline{\Theta}$ has been chosen such that the objective function is (approximately) a minimum for these values, questions about the reliability and precision of our estimates must be answered. This is the third task. Essentially we would like to know something of the sensitivity of the objective function to parameter changes, of the parameter estimation error covariance matrix, and of the goodness-of-fit of the model.

Useful approximations for nonlinear models with normally distributed errors using maximum likelihood estimation are given below.

1. The ϵ - indifference region is defined by the set of values of $\underline{\Theta}$ for which

$$\Phi(\underline{\Theta}) - \Phi^* \leq \epsilon,$$

where Φ^* is the estimated minimum value of the objective function. This region is defined approximately by

$$(\partial \underline{\Theta}^T) H^* (\partial \underline{\Theta}) \leq 2 \epsilon, \quad (4)$$

where $\delta \Theta = \Theta - \Theta^*$ and where H^* is an estimate of the Hessian matrix with elements $H_{\alpha\beta}(\Theta) = \partial^2 \Phi / \partial \Theta_\alpha \partial \Theta_\beta$ (α and β are indices of the $k \times k$ matrix). This equation defines ellipsoids about the estimated minimum in which the objective function does not vary greatly.

2. The covariance matrix of the estimates is defined by

$$V = E(\delta \Theta^* \delta \Theta^{*T})$$

where $\delta \Theta^*$ is the shift in the parameter estimates that would be caused by an error in the measured variables of δy . (That is, $\delta \Theta^*$ the estimation error in parameters that arises from measurement error in the variables.) For a wide class of maximum likelihood estimates with normally distributed errors,

$$V \approx H^{*-1}.$$

Generally speaking, the V computed from any given data sample can only be regarded as a rough estimate, correct to within an order of magnitude. Approximate confidence ellipsoids can be computed by

$$\delta \Theta^T H^* \delta \Theta \leq c \quad (5)$$

where c must be determined based on the sampling distribution. Thus confidence regions coincide with ϵ -indifference regions (compare equations 4 and 5). For a given confidence level, we choose c such that:

$$\text{Prob} [\delta \Theta^T V^{-1} \delta \Theta \leq c] = \alpha.$$

When the sampling distribution is normal, unbiased and with known covariance V , then the quantity $\delta \Theta^T V^{-1} \delta \Theta$ is distributed as χ^2 with 1 degree of freedom.

3. Two linear approximations for confidence limits are given in Conway et. al., 1970.

The fourth task is to determine the sensitivity of the SSE to changes in the fixed parameters in at least a crude fashion. Even though these parameters will be specified using an objective procedure and thus may be considered part of the model structure, they cannot be considered to be known with certainty and we think that it is prudent to determine how small changes in these parameters affect the SSSE. We cannot estimate the error covariances of these parameters and cannot comment on how well they have been estimated, but we believe that a simple sensitivity calculation is worthwhile nevertheless. In this task, we will individually perturb the fixed parameters a prescribed amount (in both the positive and negative directions) and record the change in SSE over the base case.

The DDRP modeling at the University of Virginia involves two models, the hydrological model TOPMODEL and the chemical flux model MAGIC. In the following sections each model is described and its inputs, fixed parameters, adjustable parameters, and outputs are specified.

Summary

The four tasks in the calibration phase of our DDRP modeling were outlined in the introduction. Each task will be performed on each model. The results will include the sensitivity of the SSE to changes in each fixed and adjustable parameter.

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SECTION A: SUMMARY

Table A.1	Values of MSE, RMSE and RMSE expressed as a percentage of the observed mean value of the DDRP variables for Woods Lake (calibration and corroboration periods)
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OTHER ASSORTED PRELIMINARIES:

Figure A.4	Conceptual basis of the hydrological model (TOPMODEL)
Figure A.5	Conceptual flux routing in the chemical flux model (MAGIC)
Figure A.6	Conceptual linking of TOPMODEL state variables to flow routing parameters in MAGIC

Table A.1. MSE summary for Woods Lake (based on DDRP variables of interest). MSE = Mean Squared Deviation, RMSE = Square Root of MSE, %MEAN = $100 \cdot \text{RMSE} / (\text{Mean of observed data})$.

Variable	Units	Calibration period (1)			Corrobration period (2)		
		<u>MSE</u>	<u>RMSE</u>	<u>%MEAN</u>	<u>MSE</u>	<u>RMSE</u>	<u>%MEAN</u>
Discharge	m3/s	.0029	.05	-	.0046	.07	-
Cum Disc.	m/yr	-	-	-	-	-	-
Chloride	meq/m3	22.8	4.8	50.5	19.2	4.4	48.4
Sulfate	meq/m3	368.2	19.2	14.7	173.0	13.2	10.7
Alk(grn)	meq/m3	617.0	24.8	-183.7	266.2	16.3	-429.0
Calcium	meq/m3	43.7	6.6	9.1	47.1	6.9	9.6
Magnesium	meq/m3	6.0	2.4	13.1	5.9	2.4	13.1
Sodium	meq/m3	17.6	4.2	21.5	8.9	3.0	14.5
Potassium	meq/m3	3.6	1.9	29.7	2.8	1.7	26.6
Alum(tot)	mol/m3	41.4	6.4	61.7	46.2	6.8	102.0
H+	meq/m3	49.5	7.0	36.5	64.8	8.0	52.6

(1) 1 September 1978 -- 31 May 1980

(2) 1 June 1980 -- 31 August 1981

Table A.2. MSE summary for Panther Lake (based on DDRP variables of interest). MSE = Mean Squared Deviation, RMSE = Square Root of MSE, %MEAN = $100 \cdot \text{RMSE} / (\text{Mean of observed data})$.

Variable	Units	Calibration period (1)			Corroboration period (2)		
		<u>MSE</u>	<u>RMSE</u>	<u>%MEAN</u>	<u>MSE</u>	<u>RMSE</u>	<u>%MEAN</u>
Discharge	m3/s	.0012	.03	-	.0025	.05	-
Cum Disc.	m/yr	-	-	-	-	-	-
Chloride	meq/m3	23.6	4.9	39.5	5.2	2.3	18.6
Sulfate	meq/m3	254.7	16.0	12.7	215.7	14.7	12.4
Alk(grn)	meq/m3	6194.2	78.6	61.9	3553.4	59.6	39.5
Calcium	meq/m3	1630.2	40.4	20.1	1597.6	40.0	19.2
Magnesium	meq/m3	83.6	9.1	18.0	69.5	8.3	15.9
Sodium	meq/m3	92.0	9.6	24.0	108.4	10.4	23.7
Potassium	meq/m3	4.0	2.0	17.0	7.8	2.8	21.9
Alum(tot)	mol/m3	13.8	3.7	133.7	3.5	1.9	560.0
H+	meq/m3	10.2	3.2	290.9	2.4	1.6	400.0

(1) 1 September 1978 -- 31 May 1980

(2) 1 June 1980 -- 31 August 1981

Table A.3. MSE summary for Clear Pond (based on DDRP variables of interest). MSE = Mean Squared Deviation, RMSE = Square Root of MSE, %MEAN = 100.*RMSE/(Mean of observed data).

Variable	Units	Period of Record (1)		
		<u>MSE</u>	<u>RMSE</u>	<u>%MEAN</u>
Discharge	m3/s	.0219	.15	-
Cum Disc.	m/yr	-	-	-
Chloride	meq/m3	21.7	4.7	63.5
Sulfate	meq/m3	90.2	9.5	7.5
Alk(grn)	meq/m3	347.4	18.6	17.9
Calcium	meq/m3	444.0	21.1	12.7
Magnesium	meq/m3	22.0	4.7	14.7
Sodium	meq/m3	25.0	5.0	12.8
Potassium	meq/m3	.5	.7	18.4
Alum(tot)	mol/m3	1.4	1.2	514.3
H+	meq/m3	.0	.2	28.6

(1) 27 July 1982 -- 24 May 1984

SECTION B: OPTIMIZATION PROTOCOL FOR TOPMODEL (HYDROLOGICAL MODEL)

	Description of optimization protocol
Table B.1	Values and sources of fixed parameter values
Table B.2	Ranges and optimal values of adjustable parameters (optimized using both the calibration period and the entire period of record for Woods and Panther)
Table B.3	Results of Hessian analysis on optimized parameters (Woods Lake, calibration period)
Table B.4	Results of Hessian analysis on optimized parameters (Panther Lake, calibration period)
Table B.5	Results of Hessian analysis on optimized parameters (Clear Pond, entire period of record)
Table B.6	Results of Hessian analysis on optimized parameters (Woods Lake, entire period of record)
Table B.7	Results of Hessian analysis on optimized parameter (Panther Lake, entire period of record)

Hydrological Model

The hydrological model, TOPMODEL (Beven and Kirkby, 1979), will be used to determine routing parameters for use in the chemistry model. TOPMODEL is a topography-based variable contributing area catchment model. The model has an upper and a lower storage zone, with precipitation input and evapotranspiration loss occurring only within the upper store. Flow paths within the model include overland flow directly into the stream, drainage from the upper zone to the lower zone, and baseflow from the lower zone into the stream. Precipitation can also bypass the upper zone and flow directly into the lower store.

A detailed description of TOPMODEL is given in Hornberger et. al. (1985). They also present the results of a sensitivity analysis which suggest a reduced TOPMODEL structure that captures the critical elements of catchment hydrological behavior. Based on their findings, a simplified version of the model is used for the DDRP. The inputs and parameters listed below correspond to those in Hornberger et. al. (1985).

A simple snow accumulation and melt model was added to the "front end" of TOPMODEL to be used for model applications where winter snowpack are significant. The optional TOPMODEL parameters are determined during the warm months when possible errors from a snow model need not be considered. The optimal TOPMODEL parameters are then taken as fixed and the optimal snow model parameters are determined using the entire period of record.

Since TOPMODEL simulates the hydrology of only the terrestrial portion of watersheds, it was necessary to include a simple reservoir routing routine on the "back-end" of TOPMODEL for those catchments with lakes. This routine utilizes hypsographic information to delay water entering the lake before it flows out through the outlet.

Inputs

- PPT - Measured precipitation [mm/day]. Snow accumulation and melt calculated using empirical formulas given in Chow (1964), and in Corps of Engineers (1956). The cutoff temperature for snow accumulation and the temperature-induced snowmelt parameter were optimized whereas the rain-induced snowmelt parameter was fixed to the value given in Chow (1964).
- PET - Potential evapotranspiration [mm/day]. Daily values calculated from mean temperature and daylength data using the equation of Hamon (1961).

TOPOGRAPHICAL INFORMATION. Includes A/TANB distribution, total blue line stream length and total catchment area. The constants A and TANB are the upslope area and the local slope respectively. All the information is derived from topographic maps.

- DISCH - Measured flow [mm/day] .

Fixed Parameters

- SUBV - Kinematic streamflow velocity [km/day]. Estimated from typical values given in the literature.
- RIP - Riparian area [fraction]. Calculated as:
$$RIP = WID * BLUE / CATCHAREA$$
where WID is the average stream width, BLUE is the total catchment blue line stream length and CATCHAREA is the total catchment area.
- ARLAK - Lake area [fraction].
- UO - Saturated hydraulic conductivity [mm/day]. Estimated from available data or literature sources.

- SZQ - Maximum baseflow rate [mm/day]. Calculated as:

$$SZQ = KMAX * DEPTH * (2 * BLUE + PERIMETER)$$
 TERRAREA where KMAX is the maximum saturated hydraulic conductivity, DEPTH is the average till depth, BLUE is the blue line stream length, PERIMETER is the stream perimeter and TERRAREA is the terrestrial area of the catchment.
- SRMAX - Maximum storage in upper layer [mm]. Calculated as $SRMAX = ROOTDEPTH * FIELD CAP$ where ROOTDEPTH is the rooting zone depth and FIELD CAP is the volumetric moisture proportion at field capacity.

Adjustable parameters:

- PMAC - Macropore flow parameter [fraction]. Optimum value determined from the range of 0 - 0.75.
- SZM - Baseflow recession parameter [mm]. Optimum value determined from the range 4-180.

Outputs

- QTOT - Total Streamflow per day [mm/day].
- QOF - Total Overland flow per day [mm/day].
- SMDEF - Average soil moisture deficit [mm].

Table B.1. Fixed parameter values.

Parameter	Woods	Panther	Clear Pond
RIP	1.326×10^{-4}	1.645×10^{-4}	1.519×10^{-3}
ARLAK	0.118	0.143	0.134
SRMAX (mm)	134.	206.	150.
SUBV ¹² (km/day)	5.	5.	5.
DMAX ³ (km)	0.9	0.91	4.21
UO ^{1,4} (mm/day)	3.197×10^2	4.579×10^3	4.493×10^2
SZQ (mm/day)	32.5	828.4	212.3
RAINPRO ⁸	0.007	0.007	0.007
total blue ³ (m)	296.	200.	8214.
width blue ⁹ (m)	0.9	0.9	0.9
total area ^{2,6} (km ²)	2.12	1.12	5.21
lake area ^{1,2,6} (km ²)	0.25	0.17	0.7
rooting depth ⁵ (m)	1.0	1.0	1.0
average till depth ^{2,7} (m)	2.3	24.5	55.0
max permeability ¹⁰ (mm/day)		1.12×10^4	1.9×10^4 9.5×10^2
field capacity ^{4,10}	0.134	0.206	0.150
lake perimeter ¹¹ (km)	1.76	1.45	2.95

RIP = total blue * width blue/total area

ARLAK = lake area/total area

SRMAX = rooting depth * field capacity

SYBV = approximate channel flow celerity

DMAX = maximum channel distance

UO = average permeability

SZQ = maximum baseflow rate

= max permeability * ave till depth

* (2 * total blue + lake perimeter)/terrestrial area

RAINPRO = empirical constant for snowmelt induced by rainfall

¹ Peters and Murdoch, 1975. WASP 26:387-402.

² Chen et al., 1982. ASCE J. Env. Eng. 108:455-472.

³ Digitization of 1:24000 scale topographic maps.

⁴ Smith College geology file.

⁵ Hank Shugart, U.Va., personal communication.

⁶ Robbins Church, personal communication.

⁷ Ron Munson, personal communication.

⁸ Chow, 1964. Handbook of Applied Hydrology.

⁹ Assumption.

¹⁰ April and Newton, 1985, WASP 26:373-386.

¹¹ Assumed a circular lake.

¹² Dunne and Leopold, 1978. Water in Environmental Planning.

Table B.2. Adjustable parameters.

Range for Optimization

Parameter	Minimum	Maximum
SZM (mm)	4.0	180.0
PMAC	0.0	0.75
TCUT (°F)	10.0	50.0
SNOPROP	0.0	0.5

Optimized Values

Catchment	Period of Optimization	SZM (mm)	PMAC	TCUT(°F)	SNOPROP
Woods	Calibration ¹	7.43	0.36	26.24	0.03
Woods	All Data ²	10.64	0.51	25.81	0.03
Panther	Calibration ¹	11.22	0.49	26.89	0.06
Panther	All data ²	14.82	0.53	26.46	0.04
Clear Pond	All data ³	12.19	0.30	32.62	0.04

¹ 4/14/78 to 5/31/80

² 4/14/78 to 12/19/81

³ 8/1/82 to 7/31/84

Table B.3. Hessian analysis.

Woods - Calibration Period

Topmodel Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
SZM	7.426	2.742	36.92
PMAC	.359	.095	26.32

Correlation matrix (R2*100) of parameter estimates

	SZM	PMAC
SZM	100.0	50.7
PMAC	50.7	100.0

Epsilon indifference region is: .19073E-01
(Based on Hessian Matrix with 2 parameters)

Snow Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
TCUT	26.244	1.406	5.36
SNOPROP	.030	.005	16.60

Correlation matrix (R2*100) of parameter estimates

	TCUT	SNOPROP
TCUT	100.0	-11.0
SNOPROP	-11.0	100.0

Epsilon indifference region is: .51813
(Based on Hessian Matrix with 2 parameters)

Table B.4. Hessian analysis.

Panther - Calibration Period

Topmodel Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
SZM	11.223	19.625	174.87
PMAC	.492	.457	92.79

Correlation matrix (R2*100) of parameter estimates

	SZM	PMAC
SZM	100.0	96.4
PMAC	96.4	100.0

Epsilon indifference region is: .53167E-02
(Based on Hessian Matrix with 2 parameters)

Snow Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
TCUT	26.888	.356	1.32
SNOPROP	.060	.003	5.80

Correlation matrix (R2*100) of parameter estimates

	TCUT	SNOPROP
TCUT	100.0	37.8
SNOPROP	37.8	100.0

Epsilon indifference region is: 7.3171
(Based on Hessian Matrix with 2 parameters)

Table B.5. Hessian analysis.

Clear - All Data

Topmodel Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
SZM	12.193	9.402	77.11
PMAC	.304	.393	129.15

Correlation matrix (R2*100) of parameter estimates

	SZM	PMAC
SZM	100.0	.5
PMAC	.5	100.0

Epsilon indifference region is: .28393E-02
(Based on Hessian Matrix with 2 parameters)

Snow Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
TCUT	32.619	.751	2.30
SNOPROP	.043	.005	11.16

Correlation matrix (R2*100) of parameter estimates

	TCUT	SNOPROP
TCUT	100.0	-1.2
SNOPROP	-1.2	100.0

Epsilon indifference region is: 2.4680
(Based on Hessian Matrix with 2 parameters)

Table B.6. Hessian analysis.

Woods - All Data

Topmodel Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
SZM	10.645	5.021	47.17
PMAC	.505	.064	12.75

Correlation matrix (R2*100) of parameter estimates

	SZM	PMAC
SZM	100.0	-38.2
PMAC	-38.2	100.0

Epsilon indifference region is: .11522
(Based on Hessian Matrix with 2 parameters)

Snow Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
TCUT	25.810	1.426	5.52
SNOPROP	.030	.006	19.75

Correlation matrix (R2*100) of parameter estimates

	TCUT	SNOPROP
TCUT	100.0	1.4
SNOPROP	1.4	100.0

Epsilon indifference region is: .43858
(Based on Hessian Matrix with 2 parameters)

Table B.7. Hessian analysis.

Panther - All Data

Topmodel Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
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SZM	14.818	***	***
PMAC	.533	***	***

Correlation matrix (R2*100) of parameter estimates

	SZM	PMAC
SZM	***	***
PMAC	***	***

Epsilon indifference region is: 1.0508
(Based on Hessian Matrix with 2 parameters)

Snow Parameters

Parameter	Estimated Optimum	Std Dev Estimate	% Std Err Estimate
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TCUT	26.463	.970	3.67
SNOPROP	.044	.005	10.39

Correlation matrix (R2*100) of parameter estimates

	TCUT	SNOPROP
TCUT	100.0	3.7
SNOPROP	3.7	100.0

Epsilon indifference region is: 1.0230
(Based on Hessian Matrix with 2 parameters)

SECTION C: EVALUATION OF MSE FOR THE HYDROLOGICAL MODEL

Table C.1	MSE of cumulative flow
Table C.2	MSE of daily flow (in units of m^3/s)
Table C.3	MSE of daily flow and efficiency (in units of mm/day)
Table C.4	MSE of average monthly discharge and efficiency (in units of mm/day)

In each table, entries are made for:

- a) Snowmodel vs. TOPMODEL contributions to MSE
- b) Calibration vs. corroboration period MSE values (for Woods and Panther)
- c) MSE values for the models calibrated to all available data (for Woods and Panther)

Table C.1. MSE of Cumulative Flow.

Watershed	Period of Optimization	Number of Time steps	MSE ([mm] ²)	MSE ([m ³] ²)
Woods	Calibration ¹	1287	5986.	2.69X10 ¹⁰
Woods	All data ²	1287	11975.	5.38X10 ¹⁰
Panther	Calibration ¹	1287	103788.	1.52X10 ¹¹
Panther	All data ²	1287	98726.	1.44X10 ¹¹
Clear Pond	All data ³	372	35664.	9.67X10 ¹¹

- ¹ 4/14/78 to 5/31/80
² 4/14/78 to 12/19/81
³ 8/01/82 to 7/31/84

Table C.2. MSE ($[m^3/s]^2$) of daily flow.

Watershed	Period	Model	MSE ($[m^3/s]^2$)
Woods Woods	Calibration ¹ Calibration	TOPMODEL ⁵ SNOW ⁶	69.X10 ⁻⁵ 288.X10 ⁻⁵
Woods Woods	Corroboration ² Corroboration	TOPMODEL SNOW	188.X10 ⁻⁵ 455.X10 ⁻⁵
Woods Woods	All data ³ All data ³	TOPMODEL SNOW	101.X10 ⁻⁵ 252.X10 ⁻⁵
Panther Panther	Calibration Calibration	TOPMODEL SNOW	7.X10 ⁻⁵ 124X10 ⁻⁵
Panther Panther	Corroboration Corroboration	TOPMODEL SNOW	214.X10 ⁻⁵ 429.X10 ⁻⁵
Panther Panther	All Data ³ All Data ³	TOPMODEL SNOW	7.X10 ⁻⁵ 45.X10 ⁻⁵
Clear Pond Clear Pond	All Data ⁴ All Data ⁴	TOPMODEL SNOW	120X10 ⁻⁵ 2190.X10 ⁻⁵

¹ 4/14/78 to 5/31/80

² 6/1/80 to 12/19/81

³ 4/14/78 to 12/19/81

⁴ 8/1/82 to 7/31/84

⁵ Optimizing TOPMODEL parameters from June to October.

⁶ Optimizing SNOW parameters during entire year.

Table C.3. MSE ($[\text{mm/day}]^2$) and efficiency of daily flow.

Watershed	Period	Model	MSE ($[\text{m}^3/\text{s}]^2$)	Number of time steps	Eff
Woods	Calibration ¹	TOPMODEL ⁵	1.15	296	0.54
Woods	Calibration	SNOW ⁶	4.78	721	0.01
Woods	Corroboration ²	TOPMODEL	3.12	306	0.50
Woods	Corroboration	SNOW	7.56	567	0.20
Woods	All data ³	TOPMODEL	1.67	602	0.63
Woods	All data ³	SNOW	4.19	1288	0.39
Panther	Calibration	TOPMODEL	0.38	295	0.63
Panther	Calibration	SNOW	6.31	720	-0.75
Panther	Corroboration	TOPMODEL	3.12	306	-6.73
Panther	Corroboration	SNOW	7.56	567	-5.38
Panther	All Data ³	TOPMODEL	0.38	601	0.70
Panther	All Data ³	SNOW	2.29	1287	0.21
Clear Pond	All Data ⁴	TOPMODEL	0.33	186	0.76
Clear Pond	All Data ⁴	SNOW	6.02	372	0.38

¹ 4/14/78 to 5/31/80

² 6/1/80 to 12/19/81

³ 4/14/78 to 12/19/81

⁴ 8/1/82 to 7/31/84

⁵ Optimizing TOPMODEL parameters from June to October.

⁶ Optimizing SNOW parameters during entire year.

Table C.4. $([\text{mm/day}]^2)$ and efficiency of monthly-averaged flow.

Watershed	Period	Model	MSE $([\text{mm/day}]^2)$	Number of time steps	Eff
Woods	Calibration ¹	TOPMODEL ⁵	0.18	9	0.78
Woods	Calibration	SNOW ⁶	0.30	23	0.86
Woods	Corroboration ²	TOPMODEL	0.31	10	0.76
Woods	Corroboration ²	SNOW	1.32	18	0.43
Woods	All data ³	TOPMODEL	0.30	19	0.76
Woods	All data ³	SNOW	1.32	18	0.64
Panther	Calibration	TOPMODEL	0.17	9	0.69
Panther	Calibration	SNOW	0.76	23	0.69
Panther	Corroboration	TOPMODEL	0.25	10	0.56
Panther	Corroboration	SNOW	0.72	18	0.24
Panther	All Data ³	TOPMODEL	0.16	19	0.72
Panther	All Data ³	SNOW	0.63	41	0.64
Clear Pond	All Data ⁴	TOPMODEL	0.22	6	0.70
Clear Pond	All Data ⁴	SNOW	3.08	11	0.48

¹ 4/14/78 to 5/31/80

² 6/1/80 to 12/19/81

³ 4/14/78 to 12/19/81

⁴ 8/1/82 to 7/31/84

⁵ Optimizing TOPMODEL parameters from June to October.

⁶ Optimizing SNOW parameters during entire year.

Table D.1. Woods calibration period (units of MSE are $(\text{m}^3/\text{s})^2$).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.1541E-04	.4999E-03	.1192E-04	.3867E-03
SZM	-.4130E-03	-.3066E-02	-.4865E-03	-.3613E-02
UO	0.	0.	0.	0.
SRMAX	-.6622E-06	-.8687E-04	.1806E-06	.2516E-04
SUBV	0.	0.	0.	0.
RIP	.5015E-03	.6020E-07	.5013E-03	.6020E-07
PMAC	.6110E-04	.2197E-04	-.4405E-03	-.1583E-03
TCUT	.5460E-04	.1433E-02	-.3499E-03	-.9182E-02
SNOPROP	.2866E-01	.8619E-03	-.8121E-02	-.2442E-03
RAINPRO	.3336E-01	.2335E-03	.2192E-01	.1534E-03
ARLAK	.5507E-03	.6502E-04	.4122E-03	.4864E-04

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.6501E+05	2000.	.8404E+05	2586.
SZM	-2422.	-326.1	-2055.	-276.7
SRMAX	-.1542E+07	-.1151E+05	.5331E+07	.3978E+05
RIP	1994.	.1504E+08	1995.	.1504E+08
PMAC	.1637E+05	.4553E+05	-2270.	-6316.
TCUT	.1831E+05	697.7	-2858.	-109.0
SNOPROP	34.88	1160.	-123.1	-4094.
RAINPRO	29.90	4282.	45.68	6517.
ARLAK	1816.	.1539E+05	2426.	.2056E+05

Table D.2. Woods corroboration period (units of MSE are $(\text{m}^3/\text{s})^2$).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.2101E-04	.6836E-03	.1944E-04	.6335E-03
SZM	-.3347E-03	-.2485E-02	-.3770E-03	-.2799E-02
U0	0.	0.	0.	0.
SRMAX	0.	0.	0.	0.
SUBV	0.	0.	0.	0.
RIP	-.4687E-03	-.6020E-07	-.4688E-03	-.6020E-07
PMAC	-.4250E-02	-.1528E-02	-.2237E-02	-.8042E-03
TCUT	.4006E-03	.1051E-01	.2275E-03	.5971E-02
SNOPROP	-.3483E-01	-.1047E-02	.4298E-01	.1293E-02
RAINPRO	-.2228E-01	-.1559E-03	.1232E-01	.8621E-04
ARLAK	-.3918E-03	-.4623E-04	-.4543E-03	-.5358E-04

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.4754E+05	1463.	.5139E+05	1581.
SZM	-2988.	-402.3	-2653.	-357.3
RIP	-2134.	-.1609E+08	-2133.	.1608E+08
PMAC	-235.4	-654.7	-447.0	-1244.
TCUT	2496.	95.18	4395.	167.4
SNOPROP	-28.74	-954.7	23.26	773.6
RAINPRO	-44.85	-6413.	81.23	.1160E+05
ARLAK	-2552.	-.2163E+05	-2201.	-.1866E+05

Table D.3. Panther calibration period (units of MSE are $(m^3/s)^2$).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.2548E-06	.2046E-03	.2548E-06	.2104E-03
SZM	-.1232E-03	.1383E-02	-.3489E-03	-.3915E-02
U0	0.	0.	0.	0.
SRMAX	-.3373E-04	-.6951E-02	-.1023E-03	-.2107E-01
SUBV	0.	0.	0.	0.
RIP	-.1213E-02	-.1960E-06	-.1214E-02	-.1960E-06
PMAC	-.1393E-01	-.6862E-02	-.4611E-01	-.2271E-01
TCUT	.5391E-03	.1450E-01	-.1886E-02	-.5071E-01
SNOPROP	.1336E-01	.1450E-01	-.4333E-01	-.2600E-02
RAINPRO	.1345	.9418E-03	.1227	.8588E-03
ARLAK	-.1161E-02	-.1660E-03	-.1260E-02	-.1801E-03

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.4049E+07	4888.	.3938E+07	4754.
SZM	8114.	723.0	-2866.	-255.6
SRMAX	-.2964E+05	-143.9	-9778.	-47.45
RIP	-824.0	-.5004E+07	-824.0	.5003E+07
PMAC	-71.94	-145.9	-21.94	-43.88
TCUT	1855.	68.88	-530.1	-19.90
SNOPROP	75.00	1248.	-22.96	-384.7
RAINPRO	7.653	1062.	8.163	1164.
ARLAK	-861.7	-6025.	-793.9	-5552.

Table D.4. Panther corroboration period (units of MSE are $(\text{m}^3/\text{s})^2$).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.8036E-06	.6605E-03	.8428E-06	.6908E-03
SZM	-.4813E-03	-.5402E-02	-.4926E-03	-.5529E-02
U0	0.	0.	0.	0.
SRMAX	0.	0.	0.	0.
SUBV	0.	0.	0.	0.
RIP	-.5364E-02	-.8820E-06	-.5364E-02	-.8820E-06
PMAC	-.2861E-01	-.1409E-01	-.1304E-01	-.6423E-02
TCUT	-.4085E-03	-.1099E-01	-.3724E-03	-.1001E-01
SNOPROP	.3067	.1840E-01	.2110	.1266E-01
RAINPRO	.7861E-01	.5502E-03	.7896E-01	.5527E-03
ARLAK	-.5277E-02	-.7546E-03	-.5451E-02	-.7795E-03

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.1254E+07	1514.	.1199E+07	1447.
SZM	-2078.	-185.2	-2030.	-181.1
RIP	-186.2	-.1132E+07	-186.2	-.1132E+07
PMAC	-34.69	-70.92	-76.53	-155.6
TCUT	-2447.	-90.82	-2685.	-100.0
SNOPROP	3.061	54.59	4.592	79.08
RAINPRO	12.76	1817.	12.76	1809.
ARLAK	-189.3	-1325.	-183.7	-1283.

Table D.5. Clear Pond all data (units of MSE are $(m^3/s)^2$).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.2184E-05	.4575E-03	.2912E-05	.6166E-03
SZM	-.2876E-03	-.3506E-02	-.4142E-03	-.5050E-02
U0	0.	0.	0.	0.
SRMAX	0.	0.	0.	0.
SUBV	0.	0.	0.	0.
RIP	-.9724E-02	-.1492E-04	-.9726E-02	-.1492E-04
PMAC	.1373E-01	.4178E-02	.1384E-01	-.4210E-02
TCUT	.8605E-02	.2807	-.1908E-02	-.6225E-01
SNOPROP	.1092	.4739E-02	-.2277	.9883E-02
RAINPRO	-.2618	-.1833E-02	-.2837	-.1986E-02
ARLAK	-.9713E-02	-.1301E-02	-.9835E-02	-.1318E-02

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.4640E+06	2185.	.3442E+06	1621.
SZM	-3478.	-285.2	-2415.	-198.0
RIP	-102.9	-.6770E+05	-102.8	-.6768E+05
PMAC	72.83	239.3	72.28	237.5
TCUT	116.2	3.571	-524.0	-16.07
SNOPROP	9.148	211.0	-4.396	-101.2
RAINPRO	-3.819	-545.7	-3.516	-503.6
ARLAK	-103.0	-768.4	-101.7	-758.8

Table D.6. Woods all data (units of MSE are $(m^3/s)^2$).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.1385E-05	.4461E-04	-.3612E-06	-.1156E-04
SZM	-.9734E-04	-.1036E-02	-.1286E-03	-.1369E-02
U0	0.	0.	0.	0.
SRMAX	-.3853E-05	-.5171E-03	-.5900E-05	-.7921E-03
SUBV	0.	0.	0.	0.
RIP	.1052E-02	.1204E-04	.1051E-02	.1204E-06
PMAC	-.2262E-03	-.1143E-03	-.3277E-02	-.1656E-02
TCUT	.2349E-03	.6062E-02	-.1474E-03	-.3805E-02
SNOPROP	.1380E-01	.4150E-03	-.1186E-01	-.3567E-03
RAINPRO	-.4933E-02	-.3455E-04	-.1630E-01	-.1141E-03
ARLAK	.1151E-02	.1359E-03	.9971E-03	.1153E-03

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.7282E+06	.2241E+05	-.2814E+07	-.8659E+05
SZM	-.1027E+05	-965.3	-7774.	-730.2
SRMAX	-.2592E+06	-1934.	-.1692E+06	-1262.
RIP	951.0	.7172E+07	951.2	.7173E+07
PMAC	-4421.	-8745.	-305.1	-603.7
TCUT	4258.	165.0	-6783.	-262.8
SNOPROP	72.43	2410.	-84.22	-2804.
RAINPRO	-202.7	-.2896E+05	-61.30	-8765.
ARLAK	868.4	7360.	1023.	8673.

Table D.7. Panther all data (units of MSE are $(\text{m}^3/\text{s})^2$).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.1960E-07	.2207E-04	.3920E-07	.2558E-04
SZM	-.8052E-04	-.1193E-02	-.1246E-03	-.1847E-02
U0	0.	0.	0.	0.
SRMAX	.2744E-06	.5517E-04	-.3332E-06	-.6819E-04
SUBV	0.	0.	0.	0.
RIP	-.9157E-04	-.1960E-07	-.9161E-04	-.1960E-07
PMAC	-.1767E-02	-.9421E-03	-.5374E-02	-.2865E-02
TCUT	.7648E-04	.2024E-02	-.1994E-03	-.5277E-02
SNOPROP	.1145E-01	.5033E-03	-.9211E-02	-.4050E-03
RAINPRO	.8317E-02	.5821E-04	-.1063E-02	-.7448E-05
ARLAK	-.7619E-04	-.1090E-04	-.1037E-03	-.1482E-04

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.3753E+08	.4531E+05	.3239E+08	.3910E+05
SZM	-.1242E+05	-838.3	-8024.	-541.3
SRMAX	.3734E+07	.1813E+05	-.3021E+07	-.1466E+05
PMAC	-565.8	-1062.	-186.2	-349.0
TCUT	.1308E+05	493.9	-5015.	-189.3
SNOPROP	87.24	1987.	-108.7	-2469.
RAINPRO	120.4	.1718E+05	-940.3	-.1343E+06
ARLAK	-.1313E+05	-.9180E+05	-9644.	-.6744E+05

Table D.8. Woods calibration period (units of MSE are (mm/day)²).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.0256	.8304	.0198	.6424
SZM	-.6860	-5.0937	-.8082	-6.0017
U0	.0000	.0000	.0000	.0000
SRMAX	-.0011	-.1443	.0003	.0418
SUBV	.0000	.0000	.0000	.0000
RIP	.8330	.0001	.8327	.0001
PMAC	.1015	.0365	-.7317	-.2630
TCUT	.0907	2.3808	-.5812	-15.2533
SNOPROP	47.6024	1.4317	-13.4899	-.4057
RAINPRO	55.4152	.3879	36.4135	.2549
ARLAK	.9148	.1080	.6847	.0808

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	39.1370	1.2042	50.5895	1.5566
SZM	-1.4578	-.1963	-.1.2373	-.1666
U0	***	***	***	***
SRMAX	-928.3128	-6.9277	3209.0907	23.9484
SUBV	***	***	***	***
RIP	1.2005	9053.7399	1.2010	9056.9471
PMAC	9.8520	27.4102	-1.3667	-3.8024
TCUT	11.0231	.4200	-1.7206	-.0656
SNOPROP	.0210	.6985	-.0741	-2.4647
RAINPRO	.0180	2.5779	.0275	3.9232
ARLAK	1.0931	9.2635	1.4604	12.3765

Table D.9. Woods corroboration period (units of MSE are (mm/day)²).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.0349	1.1356	.0323	1.0506
SZM	-.5560	-4.1286	-.6262	-4.6498
U0	.0000	.0000	.0000	.0000
SRMAX	.0000	.0000	.0000	.0000
SUBV	.0000	.0000	.0000	.0000
RIP	-.7785	-.0001	-.7788	-.0001
PMAC	-7.0594	-2.5374	-3.7165	-1.3358
TCUT	.6654	17.4641	.3779	9.9186
SNOPROP	-57.8502	-1.7400	71.3914	2.1472
RAINPRO	-37.0032	-.2590	20.4611	.1432
ARLAK	-.6509	-.0768	-.7546	-.0890

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	28.6199	.8806	30.9360	.9519
SZM	-1.7986	-.2422	-1.5970	-.2151
U0	***	***	***	***
SRMAX	***	***	***	***
SUBV	***	***	***	***
RIP	-1.2845	-9686.6915	-1.2840	-9683.0026
PMAC	-.1417	-.3941	-.2691	-.7486
TCUT	1.5028	.0573	2.6460	.1008
SNOPROP	-.0173	-.5747	.0140	.4657
RAINPRO	-.0270	-3.8607	.0489	6.9819
ARLAK	-1.5364	-13.0207	-1.3253	-11.2312

Table D.10. Panther calibration period (units of MSE are (mm/day)²).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.0013	1.0437	.0013	1.0733
SZM	.6288	7.0565	-1.7799	-19.9757
U0	.0000	.0000	.0000	.0000
SRMAX	-.1721	-35.4626	-.5218	-107.4959
SUBV	.0000	.0000	.0000	.0000
RIP	-6.1907	-.0010	-6.1914	-.0010
PMAC	-71.0944	-35.0101	-235.2789	-115.8622
TCUT	2.7505	73.9547	-9.6232	-258.7487
SNOPROP	68.1417	4.0885	-221.0526	-13.2632
RAINPRO	686.4570	4.8052	625.9177	4.3814
ARLAK	-5.9217	-.8468	-6.4268	-.9190

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	793.6812	.9581	771.7963	.9317
SZM	1.5904	.1417	-.5618	-.0501
U0	***	***	***	***
SRMAX	-5.8089	-.0282	-1.9164	-.0093
SUBV	***	***	***	***
RIP	-.1615	-980.7610	-.1615	-980.6621
PMAC	-.0141	-.0286	-.0043	-.0086
TCUT	.3636	.0135	-.1039	-.0039
SNOPROP	.0147	.2446	-.0045	-.0754
RAINPRO	.0015	.2081	.0016	.2282
ARLAK	-.1689	-1.1809	-.1556	-1.0881

Table D.11. Panther corroboration period (units of MSE are (mm/day)²).

Gradients				
Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.0041	3.3699	.0043	3.5247
SZM	-2.4558	-27.5609	-2.5134	-28.2079
U0	.0000	.0000	.0000	.0000
SRMAX	.0000	.0000	.0000	.0000
SUBV	.0000	.0000	.0000	.0000
RIP	-27.3687	-.0045	-27.3697	-.0045
PMAC	-145.9920	-71.8932	-66.5425	-32.7686
TCUT	-2.0844	-56.0466	-1.9002	-51.0923
SNOPROP	1564.8390	93.8903	1076.3864	64.5832
RAINPRO	401.0485	2.8073	402.8714	2.8201
ARLAK	-26.9225	-3.8499	-27.8124	-3.9772
Gradient Inverses				
Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	245.8209	.2967	235.0261	.2837
SZM	-.4072	-.0363	-.3979	-.0355
U0	***	***	***	***
SRMAX	***	***	***	***
SUBV	***	***	***	***
RIP	-.0365	-221.8466	-.0365	-221.8383
PMAC	-.0068	-.0139	-.0150	-.0305
TCUT	-.4797	-.0178	-.5263	-.0196
SNOPROP	.0006	.0107	.0009	.0155
RAINPRO	.0025	.3562	.0025	.3546
ARLAK	-.0371	-.2597	-.0360	-.2514

Table D.12. Clear Pond all data (units of MSE are (mm/day)²).

Gradients				
Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.0006	.1257	.0008	.1694
SZM	-.0790	-.9631	-.1138	-1.3874
U0	.0000	.0000	.0000	.0000
SRMAX	.0000	.0000	.0000	.0000
SUBV	.0000	.0000	.0000	.0000
RIP	-2.6713	-.0041	-2.6721	-.0041
PMAC	3.7721	1.1478	3.8011	1.1567
TCUT	2.3641	77.1153	-.5243	-17.1014
SNOPROP	29.9893	1.3018	-62.5493	-2.7152
RAINPRO	-71.9266	-.5035	-77.9372	-.5456
ARLAK	-2.6683	-.3575	-2.7018	-.3620
Gradient Inverses				
Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	1688.8323	7.9549	1252.9200	5.9016
SZM	-12.6600	-1.0383	-8.7888	-.7208
U0	***	***	***	***
SRMAX	***	***	***	***
SUBV	***	***	***	***
RIP	-.3744	-246.4454	-.3742	-246.3694
PMAC	.2651	.8712	.2631	.8646
TCUT	.4230	.0130	-1.9074	-.0585
SNOPROP	.0333	.7682	-.0160	-.3683
RAINPRO	-.0139	-1.9862	-.0128	-1.8330
ARLAK	-.3748	-2.7968	-.3701	-2.7621

Table D.13. Panther all data (units of MSE are (mm/day)²).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.0001	.1126	.0002	.1305
SZM	-.4108	-6.0868	-.6358	-9.4217
U0	.0000	.0000	.0000	.0000
SRMAX	.0014	.2815	-.0017	-.3479
SUBV	.0000	.0000	.0000	.0000
RIP	-.4672	-.0001	-.4674	-.0001
PMAC	-9.0147	-4.8065	-27.4182	-14.6189
TCUT	.3902	10.3257	-1.0174	-26.9230
SNOPROP	58.4028	2.5680	-46.9972	-2.0665
RAINPRO	42.4317	.2970	-5.4257	-.0380
ARLAK	-.3887	-.0556	-.5290	-.0756

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	7356.7523	8.8807	6348.0179	7.6630
SZM	-2.4344	-.1643	-1.5728	-.1061
U0	***	***	***	***
SRMAX	731.8991	3.5529	-592.0814	-2.8742
SUBV	***	***	***	***
RIP	-2.1404	***	-2.1396	***
PMAC	-.1109	-.2081	-.0365	-.0684
TCUT	2.5629	.0968	-.9829	-.0371
SNOPROP	.0171	.3894	-.0213	-.4839
RAINPRO	.0236	3.3668	-.1843	-26.3297
ARLAK	-2.5729	-17.9922	-1.8903	-13.2191

Table D.14. Woods all data (units of MSE are (mm/day)²).

Gradients

Parameter	Del(MSE)/Del(Par+)		Del(MSE)/Del(Par-)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	.0023	.0741	-.0006	-.0192
SZM	-.1617	-1.7210	-.2137	-2.2746
U0	.0000	.0000	.0000	.0000
SRMAX	-.0064	-.8589	-.0098	-1.3157
SUBV	.0000	.0000	.0000	.0000
RIP	1.7468	.0002	1.7464	.0002
PMAC	-.3758	-.1899	-5.4433	-2.7515
TCUT	.3902	10.0697	-.2449	-6.3207
SNOPROP	22.9272	.6893	-19.7071	-.5925
RAINPRO	-8.1943	-.0574	-27.0751	-.1895
ARLAK	1.9127	.2257	1.6231	.1915

Gradient Inverses

Parameter	Del(Par+)/Del(MSE)		Del(Par-)/Del(MSE)	
	Unnormalized	Normalized	Unnormalized	Normalized
SZQ	438.3686	13.4883	-1694.0493	-52.1246
SZM	-6.1853	-.5811	-4.6798	-.4396
U0	***	***	***	***
SRMAX	-156.0121	-1.1643	-101.8441	-.7600
SUBV	***	***	***	***
RIP	.5725	4317.3967	.5726	4318.1945
PMAC	-2.6612	-5.2646	-.1837	-.3634
TCUT	2.5631	.0993	-4.0833	-.1582
SNOPROP	.0436	1.4508	-.0507	-1.6879
RAINPRO	-.1220	-17.4338	-.0369	-5.2763
ARLAK	.5228	4.4307	.6161	5.2214

SECTION E: OPTIMIZATION PROTOCOL FOR MAGIC (CHEMICAL FLUX MODEL)

Description of optimization protocol

Table E.1	Values and sources of fixed parameter values
Table E.2	Ranges adjustable parameters for optimization
Table E.3	Optimal values of adjustable parameters (Woods Lake, calibration period and entire record)
Table E.4	Optimal values of adjustable parameters (Panther Lake, calibration period and entire record)
Table E.5	Optimal values of adjustable parameters (Clear Pond, entire record)
Table E.6	Results of Hessian analysis on optimized parameters (Woods Lake, calibration period)
Table E.7	Results of Hessian analysis on optimized parameters (Panther Lake, calibration period)
Table E.8	Results of Hessian analysis on optimized parameters (Clear Pond, entire period of record)

Table E.1. Fixed parameter values for MAGIC - DDRP northeast special interest watersheds.

Parameter	Woods	Panther	Clear
Soil Depth (m) ¹			
A+B	0.62	0.68	0.55
C	1.68	23.82	54.45
Bulk Density (kg/m ³) ²			
A+B	1009.	1283.	1140.
C	1620.	1549.	1590.
Porosity (frac) ³			
A+B	0.62	0.52	0.57
C	0.39	0.42	0.40
CEC (meq/kg) ⁴			
A+B	121.1	94.7	33.8
C	20.9	11.4	9.0
KAL(OH) ₃ ⁵			
A+B	7.9	7.9	7.9
C	9.6	9.6	9.6
Lake	8.9	8.9	8.9
SO ₄ Halfsat. (meq/m ³) ⁶			
A+B	150	150	150
C	150	150	150
Lake Area/Basin Area ⁷	0.12	0.14	0.14
Lake Residence Time(y) ⁸	0.54	0.68	1.98

¹ The average start depth of the "C" horizon for all available samples in the ILWAS file SMIGEOL on card 85 was used as the depth of the A+B horizons. The sample sizes and standard deviations were 12 and 0.14 m for Woods and 17 and 0.16 m for Panther. The Clear Pond catchment value was based on one sample in RILWAS file COLX. The C horizon thickness was the difference between the average depth to bedrock and the A+B depth. The average depths to bedrock were those cited by Peters and Murdoch (1985) for Woods and Panther and a value of 55 m for Clear Pond was a preliminary value for the deep till region determined by Robert Newton (Ron Munson, personal communication).

² Bulk density = (1-porosity)*2.65*1000, where 2.65 g/cc is an assumed specific gravity of the soil solids.

³ Porosity was assumed to be equal to the percent soil moisture by volume at saturation. The values used are the depth-weighted averages of one profile each from the Woods and Panther catchments found on card 93 of the SMIGEOL file. Since no data were available for the Clear Pond catchment, the averages of Woods and Panther were used.

⁴ CEC data for Woods and Panther were obtained from the ILWAS file UMACEC. Depth-weighted averages were used. For Woods 7 profiles were averaged for the A+B value and 6 for the C. The

Panther averages were based on 9 profiles of the A+B and 6 of the C. The values for Clear Pond were based on one profile from the COLX RILWAS file.

Table E.1. Continued.

⁵ KALOH3 values were based on concentrations of total monomeric aluminum and hydrogen ion found in the ILWAS file CORAL and from the analysis by Schofield (1983).

⁶ SO4 half-saturation constant. Assumed.

⁷ ILWAS values are from Peters and Murdoch (1985). Clear Pond lake and catchment areas supplied by EPA (M. R. Church, pers. com.).

⁸ Lake residence time was calculated as lake volume divided by mean annual discharge. Lake volumes for Woods and Panther are from Peters and Murdoch (1985). Mean annual discharges were calculated from the ILWAS file USGFLOW. Clear Pond volume was estimated from the hypsographic curve supplied by Tetra Tech and discharge from RILWAS file USGSTAGE and the observed yield.

Table E.2. Adjustable parameters for MAGIC.

-----Ranges for Optimization-----			
Parameter	Units	Minimum	Maximum
UP(NH4L)	%	0.0	100.0
UP(NO3L)	%	0.0	100.0
UP(NH4A+B)	%	0.0	100.0
UP(NO3A+B)	%	0.0	100.0
EMX	meq/kg	0.0	15.0
WE(Ca)	meq/m2/yr	1.0	150.0
WE(Mg)	meq/m2/yr	1.0	150.0
WE(Na)	meq/m2/yr	1.0	100.0
WE(K)	meq/m2/yr	1.0	100.0
log(SA1Ca)	-	-5.00	5.00
log(SA1Mg)	-	-5.00	5.00
log(SA1Na)	-	-5.00	5.00
log(SA1K)	-	-5.00	5.00
COZ(A+B)	%	.30	10.00
COZ(C)	%	.30	10.00

Table E.3. Adjustable parameters for MAGIC.

Parameter	Units	-----Optimized Values-----	
		Woods Lake calibration period	Woods Lake entire period of record
UP(NH4L)	%	86.3	87.3
UP(NO3L)	%	59.8	57.1
UP(NH4A+B)	%	92.2	91.8
UP(NO3A+B)	%	73.9	68.2
EMX	meq/kg	8.30	7.14
WE(Ca)	meq/m2/yr	13.4	13.5
WE(Mg)	meq/m2/yr	1.3	1.5
WE(Na)	meq/m2/yr	1.0	1.0
WE(K)	meq/m2/yr	1.2	1.0
log(SA1Ca)	-	2.62	3.45
log(SA1Mg)	-	1.70	.21
log(SA1Na)	-	-3.67	-2.96
log(SA1K)	-	-4.99	-4.99
COZ(A+B)	%	10.00	5.35
COZ(C)	%	1.55	1.32

Table E.4. Adjustable parameters for MAGIC.

Parameter	Units	-----Optimized Values-----	
		Panther Lake calibration period	Panther Lake entire period of record
UP(NH4L)	%	91.2	93.0
UP(NO3L)	%	55.0	56.5
UP(NH4A+B)	%	93.8	94.9
UP(NO3A+B)	%	60.8	60.9
EMX	meq/kg	.67	.67
WE(Ca)	meq/m2/yr	112.7	118.2
WE(Mg)	meq/m2/yr	22.8	28.3
WE(Na)	meq/m2/yr	24.5	20.0
WE(K)	meq/m2/yr	7.6	1.0
log(SA1Ca)	-	3.63	4.50
log(SA1Mg)	-	4.44	2.78
log(SA1Na)	-	3.76	-2.46
log(SA1K)	-	-4.01	2.22
COZ(A+B)	%	.33	2.94
COZ(C)	%	4.68	4.36

Table E.5. Adjustable parameters for MAGIC.

-----Optimized Values-----		
Parameter	Units	Clear Pond entire period of record
UP(NH4L)	%	93.1
UP(NO3L)	%	90.9
UP(NH4A+B)	%	96.6
UP(NO3A+B)	%	95.4
EMX	meq/kg	.05
WE(Ca)	meq/m2/yr	74.3
WE(Mg)	meq/m2/yr	12.0
WE(Na)	meq/m2/yr	16.6
WE(K)	meq/m2/yr	1.0
log(SA1Ca)	-	1.69
log(SA1Mg)	-	1.18
log(SA1Na)	-	-2.30
log(SA1K)	-	-1.72
COZ(A+B)	%	.30
COZ(C)	%	3.39

Table E.6. Hessian Analysis: Woods Lake.

Parameter	Estimated Optimum	Std Dev Estimate	%Std Error Estimate
UNH%L	86.260	2.955	3.43
UNO%L	59.770	1.163	1.95
UNH%B	92.220	1.790	1.94
UNO%B	73.880	0.742	1.00
EMX	8.302	1.113	1.36

Correlation Matrix (R²*100) of parameter estimates.

	UNH%L	UNO%L	UNH%B	UNO%B	EMX
UNH%L	100.0	0.0	-6.6	0.0	-2.4
UNO%L	0.0	100.0	0.0	-18.8	3.1
UNH%B	-6.6	0.0	100.0	0.0	1.2
UNO%B	0.0	-18.8	0.0	100.0	-0.9
EMX	-2.4	3.1	1.2	-0.9	100.0

The epsilon indifference region is: 119.74
(Based on Hessian Matrix with 5 parameters)

Table E.7. Hessian Analysis: Panther Lake.

Parameter	Estimated Optimum	Std Dev Estimate	%Std Error Estimate
UNH%L	91.200	3.032	3.32
UNO%L	54.970	1.062	1.93
UNH%B	98.800	2.440	2.60
UNO%B	60.790	0.901	1.48
EMX	0.674	0.006	0.89

Correlation Matrix (R2*100) of parameter estimates.

	UNH%L	UNO%L	UNH%B	UNO%B	EMX
UNH%L	100.0	0.0	-4.9	0.0	-2.7
UNO%L	0.0	100.0	0.0	-23.5	2.8
UNH%B	-4.9	0.0	100.0	0.0	0.7
UNO%B	0.0	-23.5	0.0	100.0	-1.1
EMX	-2.7	2.8	0.7	-1.1	100.0

The epsilon indifference region is: 121.95
(Based on Hessian Matrix with 5 parameters)

Table E.8. Hessian Analysis: Clear Pond.

Parameter	Estimated Optimum	Std Dev Estimate	%Std Error Estimate
UNH%L	93.060	6.969	7.49
UNO%L	90.880	2.488	2.74
UNH%B	96.630	4.066	4.21
UNO%B	95.430	1.593	1.67
EMX	0.052	0.002	4.03

Correlation Matrix (R2*100) of parameter estimates.

	UNH%L	UNO%L	UNH%B	UNO%B	EMX
UNH%L	100.0	-0.1	-6.2	0.1	-3.9
UNO%L	-0.1	100.0	0.0	-6.2	2.9
UNH%B	-6.2	0.0	100.0	0.0	1.4
UNO%B	0.1	-6.2	0.0	100.0	-1.1
EMX	-3.9	2.9	1.4	-1.1	100.0

The epsilon indifference region is: 32.928
(Based on Hessian Matrix with 5 parameters)

Chemical flux model

The chemical flux model is MAGIC (Cosby et al., 1985 a,b,c). Details of MAGIC and examples of its use have been given elsewhere (Cosby et al., 1986b, Wright et al., 1986, Neal et al., 1986), including a sensitivity analysis (Cosby et al., 1986a). MAGIC has been modified for this work in the following ways: the model now contains two soil layers; atmospheric inputs can be measured values when available (rather than inferred annual means); atmospheric inputs can bypass the upper soil layer (macropore flow); atmospheric inputs can be accumulated and released from a snowpack. Several outputs from TOPMODEL are used to set routing parameters and to control the snow accumulation and melt in MAGIC. The basic chemical reactions modeled in MAGIC are unchanged. The inputs and parameters listed below correspond to those in Cosby et al., (1985b) with the exception of the routing parameters (identified with a*) which were introduced for this two layer version of MAGIC.

Inputs

- Q-M measured streamflow [mm/day].
- F_{xx} (xx = Ca, Mg, Na, K, SO_4 , Cl, NO_3 , F) - Measured atmospheric deposition of ions [meq/m²/day]. The rate at which the measured deposition is added to the soil is controlled in the case of snow accumulation and melt by the outputs of TOPMODEL.
- W_{xx} (xx = Ca, Mg, Na, K) - Weathering inputs of base cations [meq/m²/yr]. Measurements of these rates are not available. These inputs will be treated as adjustable parameters that must be optimized (see below).
- W_{xx} (xx = SO_4 , Cl, NO_3 , F) - Net Uptake rates of anions [meq/m²/yr]. These net uptake rates simulate biological utilization of the anions. The annual rates of these net uptakes will be calculated from measured net fluxes of the anions.
- PCO_2 Partial pressure of CO_2 in the two soils [atm]. These partial are linearly scaled to temperature (a measured input). The scaling factor (St) is an adjustable parameter that is optimized (see below).
- T Temperature of the two soil layers and the surface water [deg. C]. Taken from measurements or literature.

Fixed parameters:

- CEC Cation exchange capacities for the two soil layers [meg/kg]. Taken from appropriately weighted measurements.
- C Sulfate adsorption parameters (C = half-saturation constant [meq/m³]), for the two soil layers. Taken from appropriately weighted measurements.
- D Average depth of the two soil layers [m]. Taken from appropriately weighted measurements.
- BD Bulk density of the two soils [kg/m³]. Taken from appropriately weighted measurements or the literature.
- P Porosity of the two soils [fraction]. Taken from measurements or literature.
- K_{als} Equilibrium constant for $Al(OH)_3$ solubility in the stream. Calculated from observed pH-Al relationships.
- K_{al} Lumped equilibrium constant for the solubility of $Al(OH)_3$ in each soil layer.
- OF* Fraction of deposition (or snow melt) that bypasses the soils and enters surface waters directly [fraction]. Derived from the calibration of TOPMODEL.
- PMAC* Fraction of deposition (or snowmelt) that bypasses the upper soil layer and enters the lower soil layer directly [fraction]. Derived from the calibration of TOPMODEL.
- IF* Fraction of water leaving the upper soil layer and flowing directly to the surface waters [fraction]. Derived from the calibration of TOPMODEL.
- K_{yy} Thermodynamic equilibrium constants for the yy aqueous chemical yy reactions that occur in the soil and surface waters (see Cosby et al., 1985b). Derived from the literature.

Adjustable parameters

- St_{*} Scaling parameter that relates PCO in the two soil layers and the surface waters to the temperature [atm/deg] .
- W_{xx} (xx = Ca, Mg, Na, K) - Mineral weathering inputs of base cations for the soil layers [meq/m²/yr].
- S_{A11:xx} (xx = Ca, Mg, Na, K) - Selectivity coefficients for exchange of Al and base cations on the two soil types.
- Emx Maximum sulfate adsorption capacity for each soil (meq/kg).

Outputs:

The output variables of MAGIC are summarized in Cosby et al. (1985b).

SECTION F: EVALUATION OF MSE FOR CHEMICAL FLUX MODEL

Model driven by observed inputs

Table F.1	MSE values of the DDRP variables for Woods Lake (calibration and corroboration periods)
Table F.2	MSE values of the DDRP variables for Panther Lake (calibration and corroboration periods)
Table F.3	MSE values of the DDRP variables for Clear Pond (entire period of record)

Model driven by average hydrological and chemical fluxes

Table F.4	MSE values of the DDRP variables for Woods Lake (calibration and corroboration periods)
Table F.5	MSE values of the DDRP variables for Panther Lake (calibration and corroboration periods)
Table F.6	MSE values of the DDRP variables for Clear Pond (entire period of record)

Table F.1. MSE values of the DDRP variables for Woods Lake (calibration and corroboration periods). Model driven by observed inputs.

Calibration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	109	43.7	33.8	-0.3	72.6	6.6
MG	109	6.0	3.1	-0.9	18.3	2.4
NA	108	17.6	17.4	0.0	19.5	4.2
K	108	3.6	0.9	-2.9	6.4	1.9
NH4	109	4.2	3.7	-0.2	3.6	2.1
SO4	109	368.2	152.0	-1.4	130.7	19.2
CL	109	22.8	18.3	-0.2	9.5	4.8
NO3	109	210.9	191.8	-0.1	21.3	14.5
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	88	617.0	604.0	0.0	-13.5	24.8
H	106	49.5	38.9	-0.3	19.2	7.0
TOT AL	61	372.8	250.3	-0.5	31.3	19.3
Corroboration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	66	47.1	24.7	-0.9	72.2	6.9
MG	66	5.9	1.3	-3.7	18.3	2.4
NA	66	8.9	3.5	-1.5	20.7	3.0
K	66	2.8	0.9	-2.1	6.4	1.7
NH4	66	3.5	3.5	0.0	2.4	1.9
SO4	66	183.0	86.9	-1.0	123.5	13.2
CL	66	19.2	3.7	-4.3	9.1	4.4
NO3	66	451.8	411.9	-0.1	23.5	21.3
TOT F	7	0.5	0.1	-3.1	2.7	0.7
ALK	62	266.2	113.6	-1.3	-3.8	16.3
H	65	64.8	57.2	-0.1	15.2	8.0
TOT AL	75	415.4	271.2	-0.5	20.0	20.4

Table F.2. MSE values of the DDRP variables for Panther Lake (calibration and corroboration periods). Model driven by observed inputs.

Calibration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	112	1630.2	1621.0	0.0	201.4	40.4
MG	112	83.6	83.8	0.0	50.6	9.1
NA	112	92.0	90.5	0.0	40.0	9.6
K	112	4.0	3.3	-0.2	11.8	2.0
NH4	112	1.8	1.4	-0.3	1.4	1.4
SO4	112	254.7	156.6	-0.6	125.9	16.0
CL	112	23.6	21.9	-0.1	12.4	4.9
NO3	112	546.8	535.0	0.0	29.2	23.4
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	96	6194.2	5984.1	0.0	127.2	78.7
H	113	10.2	9.3	-0.1	1.1	3.2
TOT AL	59	124.3	120.4	0.0	8.3	11.1
Corroboration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	66	1597.6	1492.2	-0.1	208.7	40.0
MG	66	69.5	63.7	-0.1	52.1	8.3
NA	66	108.4	79.2	-0.4	43.8	10.4
K	66	6.8	4.7	-0.7	12.8	2.8
NH4	66	2.2	1.3	-0.7	1.0	1.5
SO4	66	215.7	203.2	-0.1	118.4	14.7
CL	66	5.2	4.4	-0.2	12.4	2.3
NO3	66	671.7	638.1	-0.1	24.5	25.9
TOT F	5	3.0	1.9	-0.6	7.1	1.7
ALK	66	3553.3	2980.7	-0.2	150.9	59.6
H	71	2.4	2.4	0.0	0.4	1.6
TOT AL	82	31.1	22.2	-0.4	1.0	5.6

Table F.3. MSE values of the DDRP variables for Clear Pond (entire period of record). Model driven by observed inputs.

Variable	N	Calibration Period				
		MSE	VAR	EFF	MEAN	RMSE
CA	24	444.0	466.3	0.0	165.7	21.1
MG	24	22.0	22.5	0.0	32.0	4.7
NA	24	25.0	24.6	0.0	39.0	5.0
K	24	0.5	0.5	0.0	3.8	0.7
NH4	12	4.5	3.9	-0.2	1.8	2.1
SO4	24	90.2	95.2	0.1	126.6	9.5
CL	24	21.7	2.6	-7.4	7.4	4.7
NO3	24	35.0	35.4	0.0	3.6	5.9
TOT F	14	0.1	0.1	0.1	0.7	0.3
ALK	24	347.4	345.1	0.0	104.0	18.6
H	24	0.0	0.0	-0.1	0.2	0.2
TOT AL	22	12.5	0.3	-35.0	0.7	3.5

Table F.4. MSE values of the DDRP variables for Woods Lake (calibration and corroboration periods). Model driven by average hydrological and chemical fluxes.

Calibration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	109	35.2	33.8	0.0	72.6	5.9
MG	109	4.2	3.1	-0.4	18.3	2.1
NA	108	17.7	17.4	0.0	19.5	4.2
K	108	2.8	0.9	-2.1	6.4	1.7
NH4	109	3.7	3.7	0.0	3.6	1.9
SO4	109	202.3	152.0	-0.3	130.7	14.2
CL	109	23.7	18.3	-0.3	9.5	4.9
NO3	109	213.7	191.8	-0.1	21.3	14.6
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	88	617.8	604.0	0.0	-13.5	24.9
H	106	42.5	38.9	-0.1	19.2	6.5
TOT AL	61	290.9	250.3	-0.2	31.3	17.1
Corroboration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	66	29.8	24.7	-0.2	72.2	5.5
MG	66	2.5	1.3	-1.0	18.3	1.6
NA	66	7.1	3.5	-1.0	20.7	2.7
K	66	2.7	0.9	-2.0	6.4	1.6
NH4	66	4.1	3.5	-0.2	2.4	2.0
SO4	66	92.1	86.9	-0.1	123.5	9.6
CL	66	11.0	3.7	-2.0	9.1	3.3
NO3	66	417.6	411.9	0.0	23.5	20.4
TOT F	7	0.5	0.1	-3.1	2.7	0.7
ALK	62	293.7	113.6	-1.6	-3.8	17.1
H	65	63.0	57.2	-0.1	15.2	7.9
TOT AL	75	455.9	271.2	-0.7	20.0	21.4

Table F.5. MSE values of the DDRP variables for Woods Lake (calibration and corroboration periods). Model driven by average hydrological and chemical fluxes.

Variable	N	MSE	Calibration Period			
			VAR	EFF	MEAN	RMSE
CA	112	1634.8	1621.0	0.0	201.4	40.4
MG	112	84.2	83.8	0.0	50.6	9.2
NA	112	91.8	90.5	0.0	40.0	9.6
K	112	4.1	3.3	-0.2	11.8	2.0
NH4	112	1.9	1.4	-0.4	1.4	1.4
SO4	112	211.5	156.6	-0.4	125.9	14.5
CL	112	23.3	21.9	-0.1	12.4	4.8
NO3	112	545.9	535.0	0.0	29.2	23.4
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	96	6049.8	5984.1	0.0	127.2	77.8
H	113	10.2	9.3	-0.1	1.1	3.2
TOT AL	59	124.9	120.4	0.0	8.3	11.2

Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	66	1629.4	1492.2	-0.1	208.7	40.4
MG	66	70.2	63.7	-0.1	52.1	8.4
NA	66	109.9	79.2	-0.4	43.8	10.5
K	66	8.0	4.7	-0.7	12.8	2.8
NH4	66	2.5	1.3	-0.9	1.0	1.6
SO4	66	189.8	203.2	0.1	118.4	13.8
CL	66	6.1	4.4	-0.4	12.4	2.5
NO3	66	676.5	638.1	-0.1	24.5	26.0
TOT F	5	3.0	1.9	-0.6	7.1	1.7
ALK	66	3511.6	2980.7	-0.2	150.9	59.3
H	71	2.4	2.4	0.0	0.4	1.6
TOT AL	82	30.7	22.2	-0.4	1.0	5.5

Table F.6. MSE values of the DDRP variables for Clear Pond (entire period of record). Model driven by average hydrological and chemical fluxes.

Variable	N	MSE	Calibration Period		MEAN	RMSE
			VAR	EFF		
CA	24	444.8	466.3	0.0	165.7	21.1
MG	24	22.3	22.5	0.0	32.0	4.7
NA	24	24.9	24.6	0.0	39.0	5.0
K	24	0.5	0.5	0.1	3.8	0.7
NH4	12	4.5	3.9	-0.2	1.8	2.1
SO4	24	98.4	95.2	0.0	126.6	9.9
CL	24	21.2	2.6	-7.2	7.4	4.6
NO3	24	35.0	35.4	0.0	3.6	5.9
TOT F	14	0.1	0.1	0.1	0.7	0.3
ALK	24	331.1	345.1	0.0	104.0	18.2
H	24	0.0	0.0	-0.1	0.2	0.2
TOT AL	22	12.5	0.3	-35.0	0.7	3.5

Table G.1. Sensitivity Analysis: Woods Lake.

DDRP Evaluations of MSE (Weathering at optimal values)

Variable	N	MSE	Calibration Period			
			VAR	EFF	MEAN	RMSE
CA	109	43.7	33.8	-0.3	72.6	6.6
MG	109	6.0	3.1	-0.9	18.3	2.4
NA	108	17.6	17.4	0.0	19.5	4.2
K	108	3.6	0.9	-2.9	6.4	1.9
NH4	109	4.2	3.7	-0.2	3.6	2.1
SO4	109	368.2	152.0	-1.4	130.7	19.2
CL	109	22.8	18.3	-0.2	90.5	4.8
NO3	109	210.9	191.8	-0.1	21.3	14.5
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	88	617.0	604.0	0.0	-13.5	24.8
H	106	49.5	38.9	-0.3	19.2	7.0
TOT AL	61	372.8	250.3	-0.5	31.3	19.3

Variable	N	MSE	VAR	EFF	Corroboration Period	
					MEAN	RMSE
CA	66	47.1	24.7	-0.9	72.2	6.9
MG	66	5.9	1.3	-3.7	18.3	2.4
NA	66	8.9	3.5	-1.5	20.7	3.0
K	66	2.8	0.9	-2.1	6.4	1.7
NH4	66	3.5	3.5	0.0	2.4	1.9
SO4	66	173.0	86.9	-1.0	123.5	13.2
CL	66	19.2	3.7	-4.3	9.1	4.4
NO3	66	451.8	411.9	-0.1	23.5	21.3
TOT F	7	0.5	0.1	-3.1	2.7	0.7
ALK	62	266.2	133.6	-1.3	-3.8	16.3
H	65	64.8	57.2	-0.1	15.2	8.0
TOT AL	75	415.4	271.2	-0.5	20.0	20.4

Table G.1. Continued.

DDRP Evaluations of MSE (Weathering increased by 10%)

Variable	N	MSE	Calibration Period			RMSE
			VAR	EFF	MEAN	
CA	109	39.0	33.8	-0.2	72.6	6.2
MG	109	5.1	3.1	-0.7	18.3	2.3
NA	108	17.4	17.4	0.0	19.5	4.2
K	108	2.9	0.9	-2.2	6.4	1.7
NH4	109	4.2	3.7	-0.2	3.6	2.1
SO4	109	366.9	152.0	-1.4	130.7	19.2
CL	109	22.8	18.3	-0.2	9.5	4.8
NO3	109	210.9	191.8	-0.1	21.3	14.5
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	88	612.9	604.0	0.0	-13.5	24.8
H	106	54.1	38.9	-0.4	19.2	7.4
TOT AL	61	394.2	250.3	-0.6	31.3	19.9

Corroboration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	66	43.3	24.7	-0.8	72.2	6.6
MG	66	4.8	1.3	-2.9	18.3	2.2
NA	66	8.4	3.5	-1.4	20.7	2.9
K	66	2.2	0.9	-1.5	6.4	1.5
NH4	66	3.5	3.5	0.0	2.4	1.9
SO4	66	172.6	786.9	-1.0	123.5	13.1
CL	66	19.2	3.7	-4.3	9.1	4.4
NO3	66	451.8	411.9	-0.1	23.5	21.3
TOT F	7	0.5	0.1	-3.1	2.7	0.7
ALK	62	246.3	113.6	-1.2	-3.8	15.7
H	65	64.4	57.2	-0.1	15.2	8.0
TOT AL	75	376.0	271.2	-0.4	20.0	19.4

Table G.1. Continued.

DDRP Evaluations of MSE (Weathering decreased by 10%)

Variable	N	MSE	Calibration Period			MEAN	RMSE
			VAR	EFF			
CA	109	63.7	33.8	-0.9	72.6	8.0	
MG	109	7.1	3.1	-1.3	18.3	2.7	
NA	108	17.8	17.4	0.0	19.5	4.2	
K	108	4.4	0.9	-3.8	6.4	2.1	
NH4	109	4.2	3.7	-0.2	3.6	2.1	
SO4	109	369.3	152.0	-1.4	130.7	19.2	
CL	109	22.8	18.3	-0.2	9.5	4.8	
NO3	109	210.9	191.8	-0.1	21.3	14.5	
TOT F	0	0.0	0.0	0.0	0.0	0.0	
ALK	88	620.4	604.0	0.0	-13.5	24.9	
H	106	46.4	38.9	-0.2	19.2	6.8	
TOT AL	61	370.2	250.3	-0.5	31.3	19.2	

Variable	N	MSE	VAR	Corroboration Period			MEAN	RMSE
				EFF				
CA	66	63.7	24.7	-1.6	72.2	8.0		
MG	66	7.0	1.3	-4.5	18.3	2.6		
NA	66	9.4	3.5	-1.7	20.7	3.1		
K	66	3.4	0.9	-2.9	6.4	1.9		
NH4	66	3.5	3.5	0.0	2.4	1.9		
SO4	66	173.4	86.9	-1.0	123.5	13.2		
CL	66	19.2	3.7	-4.3	9.1	4.4		
NO3	66	451.8	411.9	-0.1	23.5	21.3		
TOT F	7	0.5	0.1	-3.1	2.7	0.7		
ALK	62	287.1	113.6	-1.5	-3.8	16.9		
H	65	67.7	57.2	-0.2	15.2	8.2		
TOT AL	75	473.2	271.2	-0.7	20.0	21.8		

Table G.2. Sensitivity Analysis: Panther Lake.

DDRP Evaluations of MSE (Weathering at optimal values)

Variable	N	MSE	Calibration Period			MEAN	RMSE
			VAR	EFF			
CA	112	1630.2	1621.0	0.0		201.4	40.4
MG	112	83.6	83.8	0.0		50.6	9.1
NA	112	92.0	90.5	0.0		40.0	9.6
K	112	4.0	3.3	-0.2		11.8	2.0
NH4	112	1.8	1.4	-0.3		1.4	1.4
SO4	112	254.7	156.6	-0.6		125.9	16.0
CL	112	23.6	21.9	-0.1		12.4	4.9
NO3	112	546.8	535.0	0.0		29.2	23.4
TOT F	0	0.0	0.0	0.0		0.0	0.0
ALK	96	6194.2	5984.1	0.0		127.2	78.7
H	113	10.2	9.3	-0.1		1.1	3.2
TOT AL	59	124.3	120.4	0.0		8.3	11.1

Variable	N	MSE	VAR	Corroboration Period			MEAN	RMSE
				EFF				
CA	66	1597.6	1492.2	-0.1		208.7	40.0	
MG	66	69.5	63.7	-0.1		52.1	8.3	
NA	66	108.4	79.2	-0.4		43.8	10.4	
K	66	7.8	4.7	-0.7		12.8	2.8	
NH4	66	2.2	1.3	-0.7		1.0	1.5	
SO4	66	215.7	203.2	-0.1		118.4	14.7	
CL	66	5.2	4.4	-0.2		12.4	2.3	
NO3	66	671.7	638.1	-0.1		24.5	25.9	
TOT F	5	3.0	1.9	-0.6		7.1	1.7	
ALK	66	3553.3	2980.7	-0.2		150.9	59.6	
H	71	2.4	2.4	0.0		0.4	1.6	
TOT AL	82	31.1	22.2	-0.4		1.0	5.6	

Table G.2. Continued.

DDRP Evaluations of MSE (Weathering increased by 10%)

Variable	N	MSE	Calibration Period			RMSE
			VAR	EFF	MEAN	
CA	112	1641.2	1621.0	0.0	201.4	40.5
MG	112	82.7	83.8	0.0	50.6	9.1
NA	112	88.4	90.5	0.0	40.0	9.4
K	112	3.1	3.3	0.0	11.8	1.8
NH4	112	1.8	1.4	-0.3	1.4	1.4
SO4	112	254.8	156.6	-0.6	125.9	16.0
CL	112	23.6	21.9	-0.1	12.4	4.9
NO3	112	546.8	535.0	0.0	29.2	23.4
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	96	6607.7	5984.1	-0.1	127.2	81.3
H	113	10.3	9.3	-0.1	1.1	3.2
TOT AL	59	120.2	120.4	0.0	8.3	11.0

Corroboration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	66	1454.0	1492.2	0.0	208.7	38.1
MG	66	62.6	63.7	0.0	52.1	7.9
NA	66	86.90	79.2	-0.1	43.8	9.3
K	66	5.6	4.7	-0.2	12.8	2.4
NH4	66	2.2	1.3	-0.7	1.0	1.5
SO4	66	215.7	203.2	-0.1	118.4	14.7
CL	66	5.2	4.4	-0.2	12.4	2.3
NO3	66	671.7	638.1	-0.1	24.5	25.9
TOT F	5	3.0	1.9	-0.6	7.1	1.7
ALK	66	3083.7	2980.7	0.0	150.9	55.5
H	71	2.5	2.4	0.0	0.4	1.6
TOT AL	82	35.5	22.2	-0.6	1.0	6.0

Table G.2. Continued.

DDRP Evaluations of MSE (Weathering decreased by 10%)

Variable	N	MSE	Calibration Period			RMSE
			VAR	EFF	MEAN	
CA	112	1924.3	1621.0	-0.2	201.4	43.9
MG	112	96.4	83.8	-0.2	50.6	9.8
NA	112	107.8	90.5	-0.2	40.0	10.4
K	112	6.2	3.3	-0.9	11.8	2.5
NH4	112	1.8	1.4	-0.3	1.4	1.4
SO4	112	254.5	156.6	-0.6	125.9	16.0
CL	112	23.6	21.9	-0.1	12.4	4.9
NO3	112	546.8	535.0	0.0	29.2	23.4
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	96	6450.5	5984.1	-0.1	127.2	80.3
H	113	10.2	9.3	-0.1	1.1	3.2
TOT AL	59	129.2	120.4	-0.1	8.3	11.4

Corroboration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	66	2051.5	1492.2	-0.4	208.7	45.3
MG	66	88.6	63.7	-0.4	52.1	9.4
NA	66	142.3	79.2	-0.8	43.8	11.9
K	66	11.3	4.7	-1.4	12.8	3.4
NH4	66	2.2	1.3	-0.7	1.0	1.5
SO4	66	215.7	203.2	-0.1	118.4	14.7
CL	66	5.2	4.4	-0.2	12.4	2.3
NO3	66	671.7	638.1	-0.1	24.5	25.9
TOT F	5	3.0	1.9	-0.6	7.1	1.7
ALK	66	4667.0	2980.7	-0.6	150.90	68.3
H	71	2.4	2.4	0.0	0.4	1.6
TOT AL	82	27.5	22.2	-0.2	1.0	5.2

Table G.3. Sensitivity Analysis: Clear Pond. Modified values of MSE resulting from 10% increase (top) and 10% decrease (bottom) of weathering.

DDRP Evaluations of MSE

Variable	N	MSE	Calibration Period			RMSE
			VAR	EFF	MEAN	
CA	24	593.0	466.3	-0.3	165.7	24.4
MG	24	21.4	22.5	0.0	32.0	4.6
NA	24	36.0	24.6	-0.5	39.0	6.0
K	24	0.5	0.5	0.0	3.8	0.7
NH4	12	4.5	3.9	-0.2	1.8	2.1
SO4	24	90.2	95.2	0.1	126.6	9.5
CL	24	21.7	2.6	-7.4	7.4	4.7
NO3	24	35.0	35.4	0.0	3.6	5.9
TOT F	14	0.1	0.1	0.1	0.7	0.3
ALK	24	533.6	345.1	-0.5	104.0	23.1
H	24	0.0	0.0	-0.2	0.2	0.2
TOT AL	22	16.5	0.3	-46.6	0.7	4.1

Corroboration Period						
Variable	N	MSE	VAR	EFF	MEAN	RMSE
CA	24	522.3	466.3	-0.1	165.7	22.9
MG	24	27.2	22.5	-0.2	32.0	5.2
NA	24	23.9	24.6	0.0	39.0	4.9
K	24	0.5	0.5	0.0	3.8	0.7
NH4	12	4.5	3.9	-0.2	1.8	2.1
SO4	24	50.1	95.2	0.1	126.6	9.5
CL	24	21.7	2.6	-7.4	7.4	4.7
NO3	24	35.0	35.4	0.0	3.6	5.9
TOT F	14	0.1	0.1	0.1	0.7	0.3
ALK	24	564.7	345.1	-0.6	104.0	23.8
H	24	0.0	0.0	0.0	0.2	0.2
TOT AL	22	9.0	0.3	-25.0	0.7	3.0

Table G.2. Continued.

DDRP Evaluations of MSE (Weathering decreased by 10%)

Variable	N	Calibration Period				
		MSE	VAR	EFF	MEAN	RMSE
CA	112	1924.3	1621.0	-0.2	201.4	43.9
MG	112	96.4	83.8	-0.2	50.6	9.8
NA	112	107.8	90.5	-0.2	40.0	10.4
K	112	6.2	3.3	-0.9	11.8	2.5
NH4	112	1.8	1.4	-0.3	1.4	1.4
SO4	112	254.5	156.6	-0.6	125.9	16.0
CL	112	23.6	21.9	-0.1	12.4	4.9
NO3	112	546.8	535.0	0.0	29.2	23.4
TOT F	0	0.0	0.0	0.0	0.0	0.0
ALK	96	6450.5	5984.1	-0.1	127.2	80.3
H	113	10.2	9.3	-0.1	1.1	3.2
TOT AL	59	129.2	120.4	-0.1	8.3	11.4

Variable	N	Corroboration Period				
		MSE	VAR	EFF	MEAN	RMSE
CA	66	2051.5	1492.2	-0.4	208.7	45.3
MG	66	88.6	63.7	-0.4	52.1	9.4
NA	66	142.3	79.2	-0.8	43.8	11.9
K	66	11.3	4.7	-1.4	12.8	3.4
NH4	66	2.2	1.3	-0.7	1.0	1.5
SO4	66	215.7	203.2	-0.1	118.4	14.7
CL	66	5.2	4.4	-0.2	12.4	2.3
NO3	66	671.7	638.1	-0.1	24.5	25.9
TOT F	5	3.0	1.9	-0.6	7.1	1.7
ALK	66	4667.0	2980.7	-0.6	150.90	68.3
H	71	2.4	2.4	0.0	0.4	1.6
TOT AL	82	27.5	22.2	-0.2	1.0	5.2

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Section 6: Predicted vs. Observed Plots

Plots of simulated and observed ANC, S04, Cl and discharge for the data intensive calibration of Woods, Panther, and Clear.

In comparing the simulated to observed for the intensively studied sites several main points need to be made.

- 1) TOPMODEL was applied using a daily time step, therefore, the hydrology simulations show rapid response and simulate the discharges faithfully (including snowmelt). The mean monthly flow routings from TOPMODEL were input to MAGIC.
- 2) MAGIC was applied using a monthly time step. MAGIC is formulated as a long-term model and thus has (at best) a monthly (i.e., seasonal) variability. The mean observed monthly depositions were used as inputs to MAGIC. MAGIC will not be able a priori to match episodic response. The model was calibrated to match the volume weighted annual average concentrations over the period. For conservative ions (i.e., chloride) which are not episodic, the match is very good. For ions which can be episodic (S04 and ANC) due to snowmelt, etc., the daily fit is not as good, but the average response is correct as expected.
- 3) MAGIC does not have a detailed lake mixing component. The lake thus acts as a stirred reactor which serves to further damp the short-term response of ionic concentrations. MAGIC is basically a soils model and the soils reactions have longer time constants than the lake reactions or mixing.
- 4) Although MAGIC damps the episodic response, the MSE's from MAGIC are comparable to the other models, suggesting that the best any of the models can do (in an MSE sense) is to faithfully model the mean chemistry. That is, the short term models show more high-frequency variation, but the fit of that variable output is equivalent to the damped output from MAGIC. The other models show episodic response, but that response is well constrained.
- 5) Note that the plotted output from MAGIC appears as a piecewise linear graph. MAGIC only gives one value for each month, so the model output is plotted as a series of flat (monthly) values.

Fixed Parameter Values for Magic (cont'd)

1. The average start depth of the "C" horizon for all available samples in the ILWAS file SMIGEOL on card 85 was used as the depth of the A+B horizons. The sample sizes and standard deviations were 12 and 0.14 m for Woods and 17 and 0.16 m for Panther. The Clear Pond catchment value was based on one sample in RILWAS file COLX. The C horizon thickness was the difference between the average depth to bedrock and the A+B depth. The average depths to bedrock were those cited by Peters and Murdoch (1985) for Woods and Panther and a value of 55m for Clear Pond was a preliminary value for the deep till region determined by Robert Newton (Ron Munson, personal communication).
2. Bulk density = $(1 - \text{porosity}) * 2.65 * 1000$, where 2.65 g/cc is an assumed specific gravity of the soil solids.
3. Porosity was assumed to be equal to the percent soil moisture by volume at saturation. The values used are the depth-weighted averages of one profile each from the Woods and Panther catchments found on card 93 of the SMIGEOL file. Since no data were available for the Clear Pond catchment, the averages of Woods and Panther were used.
4. CEC data for Woods and Panther were obtained from the ILWAS file UMACEC. Depth-weighted averages were used. For Woods, 7 profiles were averaged for the A+B value and 6 for the C. The Panther averages were based on 9 profiles of the A+B and 6 of the C. The values for Clear Pond were based on one profile from the COLX RILWAS file.
5. KALOH3 values were based on concentrations of total monomeric aluminum and hydrogen ion found in the ILWAS file CORAL and from the analysis by Schofield (1983).
6. S04 half-saturation constant. Assumed.
7. ILWAS values are from Peters and Murdoch (1985). Clear Pond lake and catchment areas supplied by EPA (M.R. Church, pers. com.).
8. Lake residence time was calculated as lake volume divided by mean annual discharge. Lake volumes for Woods and Panther are from Peters and Murdoch (1985). Mean annual discharges were calculated from the ILWAS file USGFLOW. Clear Pond volume was estimated from the hypsographic curve supplied by Tetra Tech and discharge from RILWAS file USGSTAGE and the observed yield.

APPENDIX A.2

WATERSHED SIMULATED BY ETD, ILWAS, AND MAGIC

Table A.2-1. Watersheds Simulated by MAGIC in the Northeast (Lakes) and Southern Blue Ridge Province (Streams)

Lake ID	State	Latitude	Longitude	ANC ($\mu\text{eq L}^{-1}$)
1A1-003 HAWK POND	NY	43.9569	74.9583	-21.7
1A1-012 WHITNEY LAKE	NY	43.5875	74.5625	11.4
1A1-014 WILMURT LAKE	NY	43.4292	74.7250	30.0
1A1-017 CONSTABLE POND	NY	43.8333	74.7958	-7.4
1A1-020 FOURTH LAKE (BISBY LAKES)	NY	43.5708	74.9708	6.0
1A1-028 DRY CHANNEL POND	NY	44.3528	74.4375	1.8
1A1-029 MIDDLE POND	NY	44.3389	74.3792	111.9
1A1-033 KIWASSA LAKE	NY	44.2958	74.1583	183.2
1A1-038 NICKS POND	NY	44.1431	74.9680	97.2
1A1-039 JOHN POND	NY	44.1125	74.7639	-1.7
1A1-046 PARTLOW LAKE	NY	44.0042	74.8333	56.3
1A1-049 MIDDLE SOUTH POND	NY	43.9894	75.0183	-30.3
1A1-057 HITCHCOCK LAKE	NY	43.8500	75.0417	-18.0
1A1-061 WOLF LAKE	NY	43.6292	74.6542	-53.0
1A1-064 MT ARAB LAKE	NY	44.1883	74.6008	82.9
1A1-066 WOODHULL LAKE	NY	43.5917	74.9869	1.8
1A1-073 GULL LAKES (SOUTH)	NY	43.8561	74.8208	-28.1
1A2-002 ST. JOHN LAKE	NY	43.4417	74.0611	1.8
1A2-006 LAKE FRANCES	NY	44.6958	74.3250	33.5
1A2-037 FISH PONDS (NORTHEAST)	NY	43.5472	74.0611	161.2
1A2-039 OXBOW LAKE	NY	43.4417	74.4833	140.9
1A2-041 MUD LAKE	NY	43.3405	74.4539	22.4
1A2-042 NORTH BRANCH LAKE	NY	43.3125	74.7944	6.2
1A2-045 WOODS LAKE	NY	43.2528	74.3167	7.8
1A2-046 NINE CORNER LAKE	NY	43.1958	74.5500	12.9
1A2-048 (NO NAME)	NY	43.1275	74.5889	-5.3
1A2-052 CHUB LAKE	NY	43.2583	74.5305	1.1
1A2-054 TROUT LAKE	NY	43.3467	74.7139	-14.7
1A3-001 NATE POND	NY	43.8583	74.0917	76.9
1A3-040 ZACK POND	NY	43.9333	74.1833	69.2
1A3-042 CHENEY POND	NY	43.8778	74.1625	30.0
1A3-043 UNKNOWN POND	NY	43.8194	74.2833	238.4
1A3-046 LONG POND	NY	43.6375	74.2889	18.2
1A3-048 GRASS POND	NY	43.6930	75.0611	7.3
1A3-065 SOUTH LAKE (EAST BRANCH)	NY	43.5105	74.8922	0.5
1B1-010 GANOGE LAKE	PA	41.3583	76.3208	-23.9
1B1-023 TWIN LAKES (BRINK P)	PA	41.3833	74.9042	33.3
1B1-029 NO NAME(WILSON CREEK DAM)	PA	41.2917	75.2389	166.0
1B1-055 ROCK HILL POND	PA	41.3136	75.0161	52.9
1B2-028 MILL CREEK RESERVOIR	PA	41.2625	75.7500	14.6
1B3-004 GUILFORD LAKE	NY	42.4125	75.5000	342.7
1B3-012 LITTLE BUTLER LAKE	PA	41.8625	75.6278	342.2
1B3-019 HARTLEY POND	PA	41.6583	75.7083	218.5
1B3-021 CORD POND	PA	41.6528	75.8500	380.8
1B3-025 TROUT LAKE	NY	41.5861	74.6805	30.4
1B3-032 WIXON POND	NY	41.3958	73.7347	332.5
1B3-041 EAST STROUDSBURG RESERV.	PA	41.0667	75.1667	89.7
1B3-043 TROUT LAKE	PA	41.0042	75.3417	143.0
1B3-051 BARRETT POND	NY	41.4344	73.7403	275.3
1B3-052 (NO NAME)	NY	41.4897	74.5389	16.4
1B3-053 NO NAME(SNOWFLAKE LAKE)	PA	41.9050	75.4103	245.8
1B3-059 ISLAND POND	NY	41.2572	74.1403	-4.4
1B3-060 SLY LAKE	PA	41.8236	75.3372	190.9
1B3-062 BASSETT POND	PA	41.5925	75.7111	376.4

Continued

Table A.2-1 (Continued)

Lake ID	State	Latitude	Longitude	ANC ($\mu\text{eq L}^{-1}$)
1C1-009 UPPER BAKER POND	NH	43.9083	71.9917	105.7
1C1-017 WELHERN POND	ME	45.2125	70.4944	325.9
1C1-018 DECKER PONDS (EASTERN)	ME	45.1958	69.9375	173.3
1C1-021 CLEAR POND	ME	45.1083	69.9875	122.5
1C1-031 HUNT POND	ME	44.0833	71.0000	62.9
1C1-050 BILLINGS POND	NH	43.2833	71.9417	63.6
1C1-084 UPPER BEECH POND	NH	43.6483	71.2042	41.7
1C1-086 STAR LAKE	NH	43.4619	72.0555	25.7
1C2-002 IRON POND	ME	45.4583	70.3750	69.2
1C2-012 BLACK POND	ME	44.1458	70.8000	71.5
1C2-016 TRAFTON POND	ME	43.8458	70.8917	128.8
1C2-028 SUNSET LAKE	NH	43.4708	71.3000	51.7
1C2-033 LONG POND	NH	43.2039	71.8119	97.3
1C2-035 SMITH POND	NH	43.1542	72.0292	64.7
1C2-037 MENDUMS POND	NH	43.1750	71.0667	5.5
1C2-041 JUGGERNAUT POND	NH	42.9597	72.0125	2.2
1C2-048 CRANBERRY POND	NY	42.7444	73.4333	11.5
1C2-050 MOORES POND	MA	42.6555	72.3472	45.0
1C2-056 DRURY POND	ME	44.7042	70.2417	213.0
1C2-057 BABBRIDGE RESERVOIR	NH	42.9347	72.2167	19.6
1C2-062 PEMIGEWASSET LAKE	NH	43.6153	71.5958	36.4
1C2-064 HANCOCK POND	ME	44.9556	69.9861	86.2
1C2-066 TURTLE POND	NH	43.2542	71.5167	67.7
1C2-068 QUIMBY POND	ME	44.9908	70.7419	285.5
1C3-030 PELHAM LAKE	MA	42.7000	72.8917	86.8
1C3-031 SADAUGA LAKE	VT	42.7833	72.8750	122.4
1C3-063 MARTIN MEADOW POND	NH	44.4417	71.6083	325.9
1D1-034 ROCKY POND	MA	41.8861	70.6958	9.8
1D1-037 EZEKIEL POND	MA	41.8042	70.6125	5.3
1D1-046 ROBBINS POND	MA	41.7056	70.1111	13.1
1D1-054 UPPER MILLPOND	MA	41.7308	70.1167	63.4
1D1-056 LITTLE WEST POND	MA	41.9214	70.7067	3.5
1D2-025 LITTLE QUITTACAS POND	MA	41.7917	70.9167	71.8
1D2-074 STETSON POND	MA	42.0278	70.8275	80.3
1D2-084 GOOSE POND	MA	41.6939	70.0078	142.5
1D3-020 LITTLE ALUM POND	MA	42.1292	72.1542	104.0
1D3-025 LONG POND	CT	42.0208	71.8167	162.1
1D3-033 (NO NAME)	CT	41.6583	73.1917	368.5
1D3-044 MIDDLE FARMS POND	NY	41.2750	71.9778	41.5
1E1-009 PEEP LAKE	ME	44.9083	67.8917	11.1
1E1-011 FOURTH DAVIS POND	ME	45.2583	69.3944	19.5
1E1-025 BEAN PONDS (MIDDLE)	ME	45.8125	69.1917	98.0
1E1-040 LT.GREENWOOD POND (WEST)	ME	45.3667	69.4083	36.8
1E1-050 LOWER OXBROOK LAKE	ME	45.2833	67.8417	43.8
1E1-054 DUCK LAKE	ME	45.1500	68.1000	33.4
1E1-061 LITTLE SEAVEY LAKE	ME	44.9375	67.6333	66.0
1E1-062 LONG POND	ME	44.9167	68.2697	86.2
1E1-073 GEORGES POND	ME	44.6167	68.2417	52.3
1E1-074 CRAIG POND	ME	44.5833	68.6667	70.2
1E1-077 PARKER POND	ME	44.3722	68.7083	81.0
1E1-082 STEVENS POND	ME	44.3667	69.3000	89.0
1E1-092 GREAT POND	ME	44.6008	68.2833	77.5
1E1-111 LONG POND	ME	44.5339	68.1703	6.3

Continued

Table A.2-1 (Continued)

Lake ID	State	Latitude	Longitude	ANC ($\mu\text{eq L}^{-1}$)
1E2-002 (NO NAME)	ME	45.9944	69.7833	256.7
1E2-007 FAIRBANKS POND	ME	44.3891	69.8311	75.4
1E2-030 ROUND LAKE	ME	45.0167	67.2667	174.3
1E2-038 NELSON POND	ME	44.4153	70.2625	9.4
1E2-049 GROSS POND	ME	44.0583	69.3931	-3.7
1E2-054 BRETTUNS POND	ME	44.3917	70.2500	228.9
1E2-056 PEABODY POND	ME	43.9422	70.6869	58.8
1E2-063 KALERS POND	ME	44.1080	69.4228	25.6
1E2-069 (NO NAME)	ME	46.1242	68.7792	238.1
1E3-022 NUMBER NINE LAKE	ME	46.4167	68.0500	222.1
1E3-040 NOKOMIS POND	ME	44.8708	69.3000	229.1
1E3-041 ROUND POND	ME	44.7389	69.2250	349.4
1E3-042 SAND POND	ME	44.5694	70.1194	162.5
1E3-045 MCCLURE POND	ME	44.4833	68.9639	141.7
1E3-055 TOGUE POND	ME	46.9339	68.8919	299.5
1E3-062 CAIN POND	ME	44.4922	68.9675	153.7
Stream ID	State	Latitude	Longitude	ANC ($\mu\text{eq L}^{-1}$)
2A07701 SUGAR COVE BRANCH OF N. RIVER	TN	35.3222	84.1003	89.3
2A07703 HALL CREEK	TN	35.0956	84.3256	145.2
2A07802 PUNCHEON FORK	NC	35.9100	82.5489	219.5
2A07805 COSBY CREEK	TN	35.7936	83.2394	98.8
2A07806 ROARING FORK	NC	35.8214	82.8925	104.4
2A07812 CORRELL BRANCH	NC	35.6758	83.0886	102.7
2A07813 LITTLE SANDYMUSH CREEK	NC	35.7033	82.7606	371.7
2A07817 FORNEY CREEK	NC	35.5133	83.5578	30.4
2A07821 GRASSY CREEK	NC	35.4642	82.2819	126.5
2A07823 BRUSH CREEK	NC	35.3189	83.5167	102.5
2A07826 HENDERSON CREEK	NC	35.3783	82.3847	347.7
2A07827 WELCH MILL CREEK	NC	35.1850	83.8939	234.7
2A07828 WHITEOAK CREEK	NC	35.2258	83.6186	48.2
2A07829 CATHEYS CREEK	NC	35.2133	82.7858	64.8
2A07830 MUD CREEK	NC	35.2547	82.5006	217.2
2A07833 ALLISON CREEK	NC	35.1214	83.4744	211.8
2A07834 BRUSH CREEK	NC	35.1139	83.2578	43.2
2A07835 MIDDLE SALUDA RIVER	SC	35.1206	82.5386	96.3
2A07882 LITTLE BRANCH CREEK	NC	35.4497	83.0639	106.5
2A08802 DUNN MILL CREEK	GA	34.9492	84.4383	87.8
2A08803 OWENBY CREEK	GA	34.9869	84.1464	171.1
2A08804 BEAR CREEK	GA	34.8244	84.5661	58.6
2A08805 WEAVER CREEK	GA	34.8711	84.3000	118.2
2A08806 UNNAMED TRIB. TO KIUTUESTIA CR.	GA	34.8589	84.0236	164.3
2A08808 WHITE PATH CREEK	GA	34.7375	84.4331	202.8
2A08810 BRYANT CREEK	GA	34.6097	83.9992	138.0
2A08811 HINTON CREEK	GA	34.4853	84.4214	121.3
2A08901 PERSIMMON CREEK	GA	34.9131	83.5019	120.5
2A08904 SHE CREEK	GA	34.8350	83.3450	186.5
2A08906 DEEP CREEK	GA	34.6769	83.4561	72.7

Table A.2-2. Watersheds Simulated by ETD in the Northeast (Lakes)

Lake ID	State	Latitude	Longitude	ANC ($\mu\text{eq L}^{-1}$)
1A1-003 HAWK POND	NY	43.9569	74.9583	-21.7
1A1-012 WHITNEY LAKE	NY	43.5875	74.5625	11.4
1A1-014 WILMURT LAKE	NY	43.4292	74.7250	30.0
1A1-017 CONSTABLE POND	NY	43.8333	74.7958	-7.4
1A1-020 FOURTH LAKE (BISBY LAKES)	NY	43.5708	74.9708	6.0
1A1-028 DRY CHANNEL POND	NY	44.3528	74.4375	1.8
1A1-029 MIDDLE POND	NY	44.3389	74.3792	111.9
1A1-038 NICKS POND	NY	44.1431	74.9680	97.2
1A1-039 JOHN POND	NY	44.1125	74.7639	-1.7
1A1-046 PARTLOW LAKE	NY	44.0042	74.8333	56.3
1A1-049 MIDDLE SOUTH POND	NY	43.9894	75.0183	-30.3
1A1-057 HITCHCOCK LAKE	NY	43.8500	75.0417	-18.0
1A1-061 WOLF LAKE	NY	43.6292	74.6542	-53.0
1A1-064 MT ARAB LAKE	NY	44.1883	74.6008	82.9
1A1-066 WOODHULL LAKE	NY	43.5917	74.9869	1.8
1A1-073 GULL LAKES (SOUTH)	NY	43.8561	74.8208	-28.1
1A2-002 ST. JOHN LAKE	NY	43.4417	74.0611	1.8
1A2-004 DUCK LAKE	NY	43.2355	74.4525	-32.0
1A2-037 FISH PONDS (NORTHEAST)	NY	43.5472	74.0611	161.2
1A2-041 MUD LAKE	NY	43.3405	74.4539	22.4
1A2-042 NORTH BRANCH LAKE	NY	43.3125	74.7944	6.2
1A2-045 WOODS LAKE	NY	43.2528	74.3167	7.8
1A2-046 NINE CORNER LAKE	NY	43.1958	74.5500	12.9
1A2-048 (NO NAME)	NY	43.1275	74.5889	-5.3
1A2-052 CHUB LAKE	NY	43.2583	74.5305	1.1
1A2-054 TROUT LAKE	NY	43.3467	74.7139	-14.7
1A2-058 TROUT LAKE	NY	44.3631	75.2689	391.6
1A3-001 NATE POND	NY	43.8583	74.0917	76.9
1A3-040 ZACK POND	NY	43.9333	74.1833	69.2
1A3-042 CHENEY POND	NY	43.8778	74.1625	30.0
1A3-046 LONG POND	NY	43.6375	74.2889	18.2
1A3-048 GRASS POND	NY	43.6930	75.0611	7.3
1A3-065 SOUTH LAKE (EAST BRANCH)	NY	43.5105	74.8922	0.5
1B1-010 GANOGA LAKE	PA	41.3583	76.3208	-23.9
1B1-055 ROCK HILL POND	PA	41.3136	75.0161	52.9
1B2-028 MILL CREEK RESERVOIR	PA	41.2625	75.7500	14.6
1B3-019 HARTLEY POND	PA	41.6583	75.7083	218.5
1B3-025 TROUT LAKE	NY	41.5861	74.6805	30.4
1B3-041 EAST STROUDSBURG RESERV.	PA	41.0667	75.1667	89.7
1B3-053 NO NAME(SNOWFLAKE LAKE)	PA	41.9050	75.4103	245.8
1B3-056 RIGA LAKE	CT	42.0217	73.4833	-6.0
1B3-059 ISLAND POND	NY	41.2572	74.1403	-4.4
1B3-060 SLY LAKE	PA	41.8236	75.3372	190.9
1C1-009 UPPER BAKER POND	NH	43.9083	71.9917	105.7
1C1-017 WELHERN POND	ME	45.2125	70.4944	325.9
1C1-018 DECKER PONDS (EASTERN)	ME	45.1958	69.9375	173.3
1C1-021 CLEAR POND	ME	45.1083	69.9875	122.5
1C1-031 HUNT POND	ME	44.0833	71.0000	62.9
1C1-068 LINCOLN POND	MA	42.6694	71.9125	-43.1
1C1-084 UPPER BEECH POND	NH	43.6483	71.2042	41.7

Continued

Table A.2-2. (Continued)

Lake ID	State	Latitude	Longitude	ANC ($\mu\text{eq L}^{-1}$)
1C2-002 IRON POND	ME	45.4583	70.3750	69.2
1C2-012 BLACK POND	ME	44.1458	70.8000	71.5
1C2-028 SUNSET LAKE	NH	43.4708	71.3000	51.7
1C2-033 LONG POND	NH	43.2039	71.8119	97.3
1C2-035 SMITH POND	NH	43.1542	72.0292	64.7
1C2-041 JUGGERNAUT POND	NH	42.9597	72.0125	2.2
1C2-048 CRANBERRY POND	NY	42.7444	73.4333	11.5
1C2-056 DRURY POND	ME	44.7042	70.2417	213.0
1C2-057 BABBIDGE RESERVOIR	NH	42.9347	72.2167	19.6
1C2-064 HANCOCK POND	ME	44.9556	69.9861	86.2
1C2-068 QUIMBY POND	ME	44.9908	70.7419	285.5
1D2-027 SANDY POND	MA	41.7722	70.6542	-6.0
1D3-002 DYKES POND	MA	42.6042	70.7294	1.6
1D3-025 LONG POND	CT	42.0208	71.8167	162.1
1E1-011 FOURTH DAVIS POND	ME	45.2583	69.3944	19.5
1E1-025 BEAN PONDS (MIDDLE)	ME	45.8125	69.1917	98.0
1E1-040 LT.GREENWOOD POND (WEST)	ME	45.3667	69.4083	36.8
1E1-050 LOWER OXBROOK LAKE	ME	45.2833	67.8417	43.8
1E1-054 DUCK LAKE	ME	45.1500	68.1000	33.4
1E1-062 LONG POND	ME	44.9167	68.2697	86.2
1E1-106 GREENWOOD POND	ME	45.5353	69.2328	22.7
1E1-111 LONG POND	ME	44.5339	68.1703	6.3
1E2-002 (NO NAME)	ME	45.9944	69.7833	256.7
1E2-038 NELSON POND	ME	44.4153	70.2625	9.4
1E2-049 GROSS POND	ME	44.0583	69.3931	-3.7
1E2-056 PEABODY POND	ME	43.9422	70.6869	58.8
1E2-063 KALERS POND	ME	44.1080	69.4228	25.6
1E3-022 NUMBER NINE LAKE	ME	46.4167	68.0500	222.1
1E3-040 NOKOMIS POND	ME	44.8708	69.3000	229.1
1E3-041 ROUND POND	ME	44.7389	69.2250	349.4
1E3-055 TOGUE POND	ME	46.9339	68.8919	299.5

Table A.2-3. Watersheds Simulated by ILWAS in the Northeast (Lakes) and Southern Blue Ridge Province (Streams)

Lake ID	State	Latitude	Longitude	ANC ($\mu\text{eq L}^{-1}$)
1A1-003 HAWK POND	NY	43.9569	74.9583	-21.7
1A1-064 MT ARAB LAKE	NY	44.1883	74.6008	82.9
1A2-002 ST. JOHN LAKE	NY	43.4417	74.0611	1.8
1A2-042 NORTH BRANCH LAKE	NY	43.3125	74.7944	6.2
1A2-045 WOODS LAKE	NY	43.2528	74.3167	7.8
1A2-048 (NO NAME)	NY	43.1275	74.5889	-5.3
1A2-052 CHUB LAKE	NY	43.2583	74.5305	1.1
1A3-048 GRASS POND	NY	43.6930	75.0611	7.3
1B1-010 GANOGA LAKE	PA	41.3583	76.3208	-23.9
1B1-055 ROCK HILL POND	PA	41.3136	75.0161	52.9
1B2-028 MILL CREEK RESERVOIR	PA	41.2625	75.7500	14.6
1B3-025 TROUT LAKE	NY	41.5861	74.6805	30.4
1B3-056 RIGA LAKE	CT	42.0217	73.4833	-6.0
1C1-031 HUNT POND	ME	44.0833	71.0000	62.9
1C1-068 LINCOLN POND	MA	42.6694	71.9125	-43.1
1C1-084 UPPER BEECH POND	NH	43.6483	71.2042	41.7
1C2-012 BLACK POND	ME	44.1458	70.8000	71.5
1C2-028 SUNSET LAKE	NH	43.4708	71.3000	51.7
1C2-035 SMITH POND	NH	43.1542	72.0292	64.7
1C2-048 CRANBERRY POND	NY	42.7444	73.4333	11.5
1C2-057 BABBBIDGE RESERVOIR	NH	42.9347	72.2167	19.6
1D2-027 SANDY POND	MA	41.7722	70.6542	-6.0
1E1-011 FOURTH DAVIS POND	ME	45.2583	69.3944	19.5
1E1-050 LOWER OXBROOK LAKE	ME	45.2833	67.8417	43.8
1E1-062 LONG POND	ME	44.9167	68.2697	86.2
1E1-106 GREENWOOD POND	ME	45.5353	69.2328	22.7
1E1-111 LONG POND	ME	44.5339	68.1703	6.3
1E2-056 PEABODY POND	ME	43.9422	70.6869	58.8
1E2-063 KALERS POND	ME	44.1080	69.4228	25.6

Stream ID	State	Latitude	Longitude	ANC ($\mu\text{eq L}^{-1}$)
2A07701 SUGAR COVE BRANCH OF N. RIVER	TN	35.3222	84.1003	89.3
2A07703 HALL CREEK	TN	35.0956	84.3256	145.2
2A07805 COSBY CREEK	TN	35.7936	83.2394	98.8
2A07806 ROARING FORK	NC	35.8214	82.8925	104.4
2A07811 FALSE GAP	NC	35.6997	83.3839	16.2
2A07812 CORRELL BRANCH	NC	35.6758	83.0886	102.7
2A07823 BRUSH CREEK	NC	35.3189	83.5167	102.5
2A07828 WHITEOAK CREEK	NC	35.2258	83.6186	48.2
2A07829 CATHEYS CREEK	NC	35.2133	82.7858	64.8
2A07834 BRUSH CREEK	NC	35.1139	83.2578	43.2
2A07835 MIDDLE SALUDA RIVER	SC	35.1206	82.5386	96.3
2A08802 DUNN MILL CREEK	GA	34.9492	84.4383	87.8
2A08805 WEAVER CREEK	GA	34.8711	84.3000	118.2
2A08806 KIUTUESTIA CREEK	GA	34.8589	84.0236	164.2
2A08810 BRYANT CREEK	GA	34.6097	83.9992	138.0
2A08811 HINTON CREEK	GA	34.4853	84.4214	121.3
2A08901 PERSIMMON CREEK	GA	34.9131	83.5019	120.5
2A08904 SHE CREEK	GA	34.8350	83.3450	186.5

APPENDIX A.3

UNCERTAINTY ESTIMATES AND CONFIDENCE BOUNDS FOR MODEL PROJECTIONS

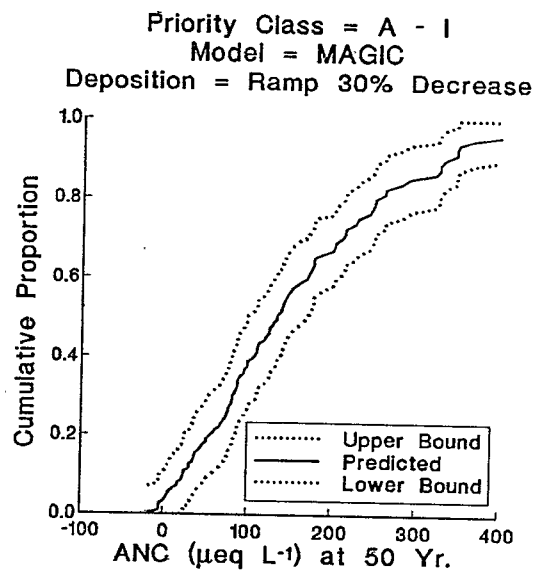
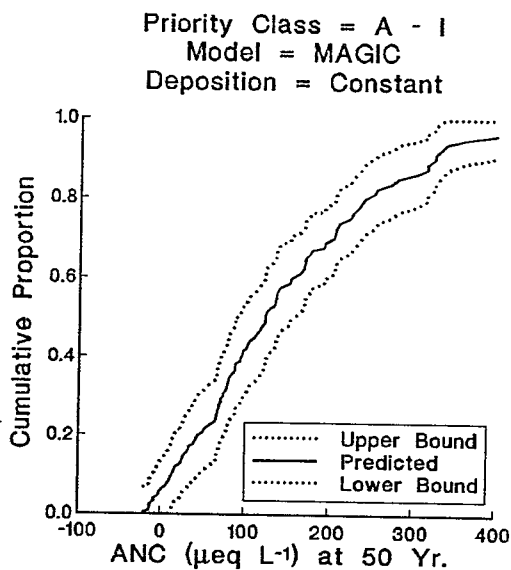
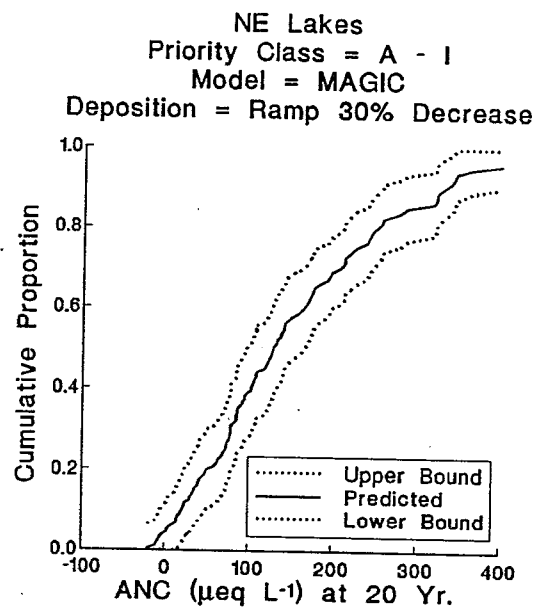
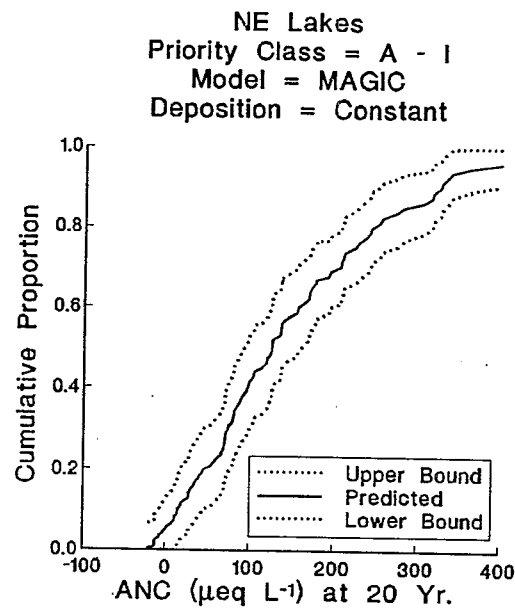


Figure A.3-1. ANC projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - I lakes using MAGIC.

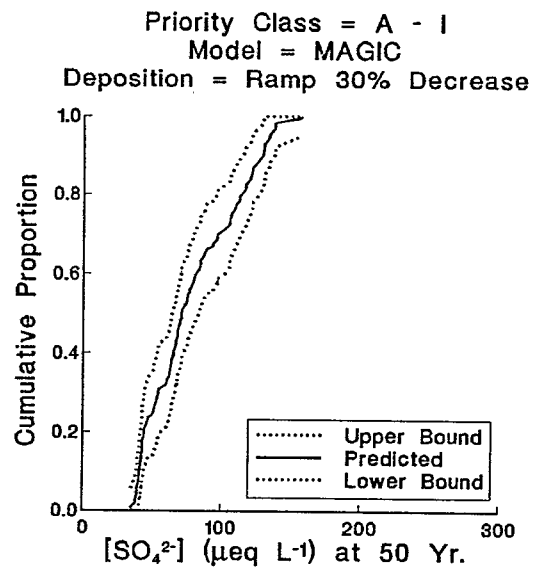
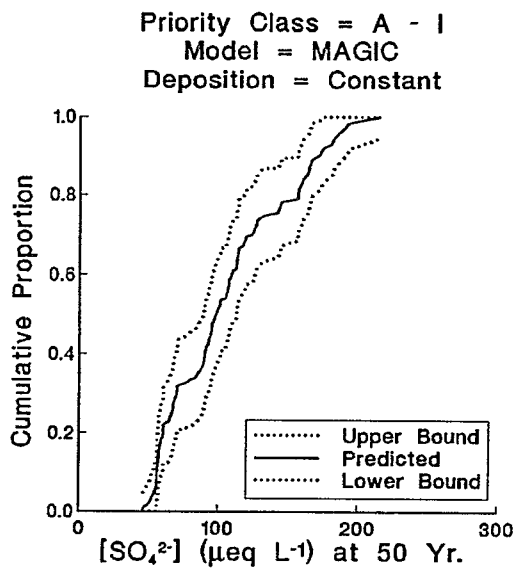
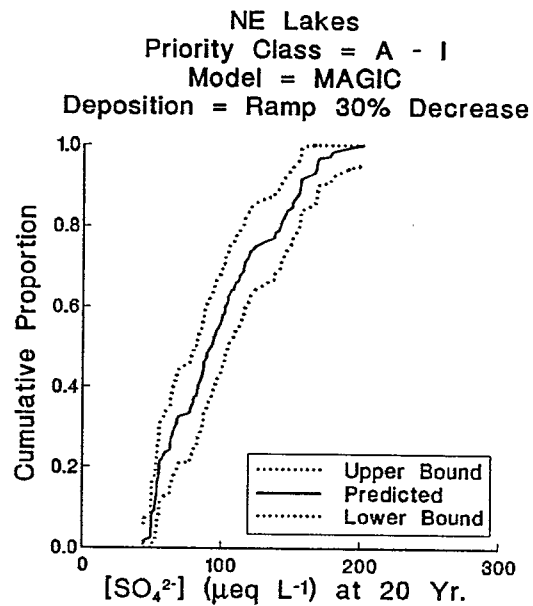
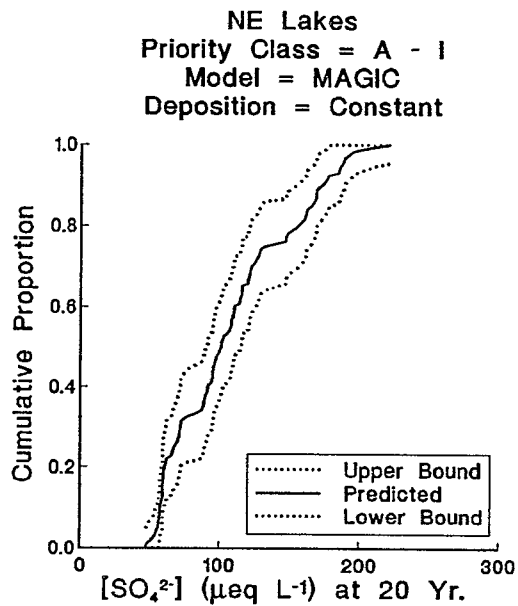


Figure A.3-2. Sulfate projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - I lakes using MAGIC.

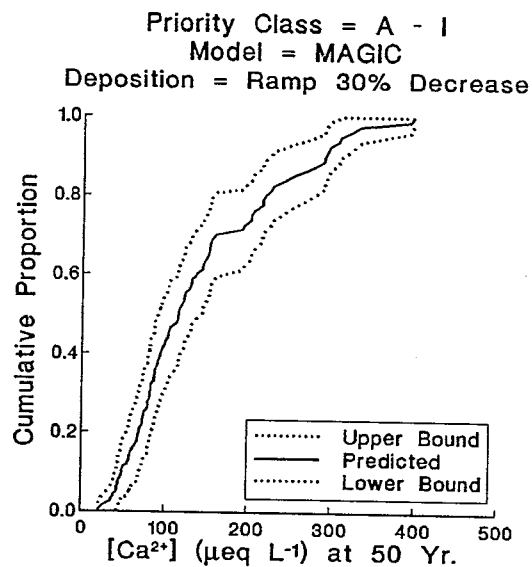
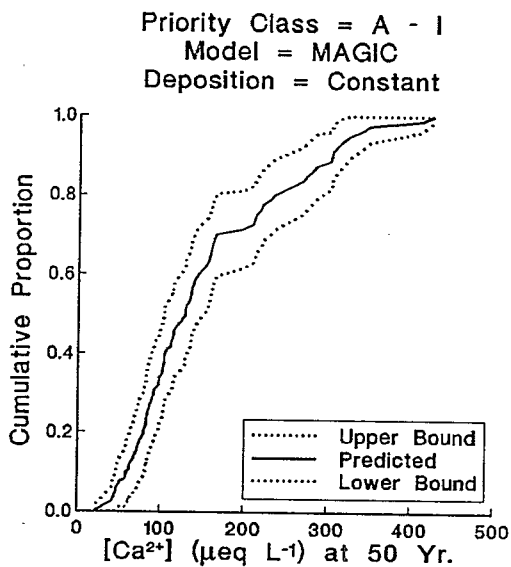
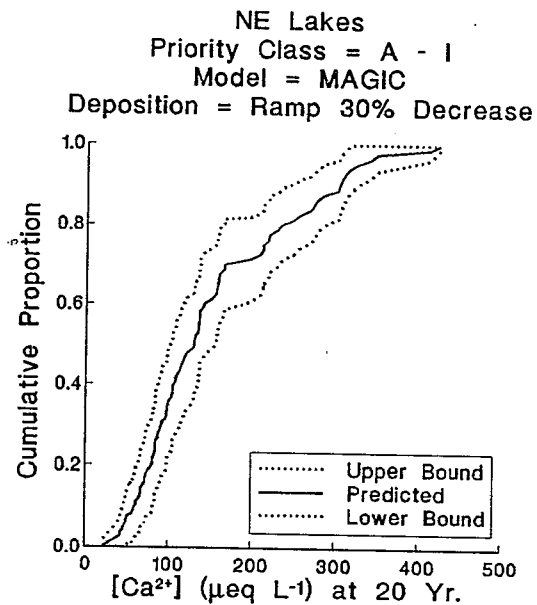
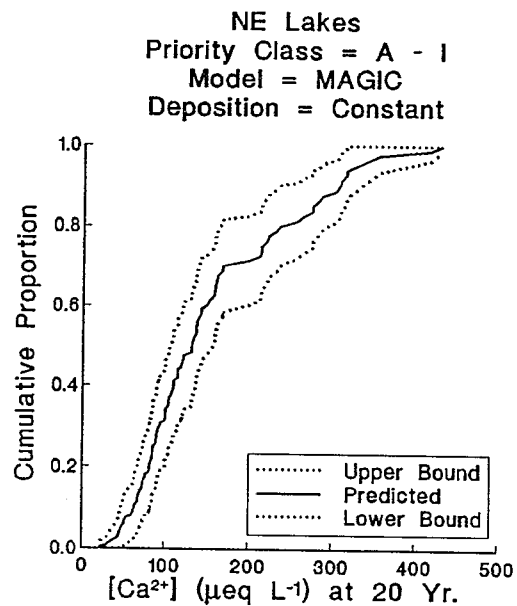


Figure A.3-3. Calcium projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - I lakes using MAGIC.

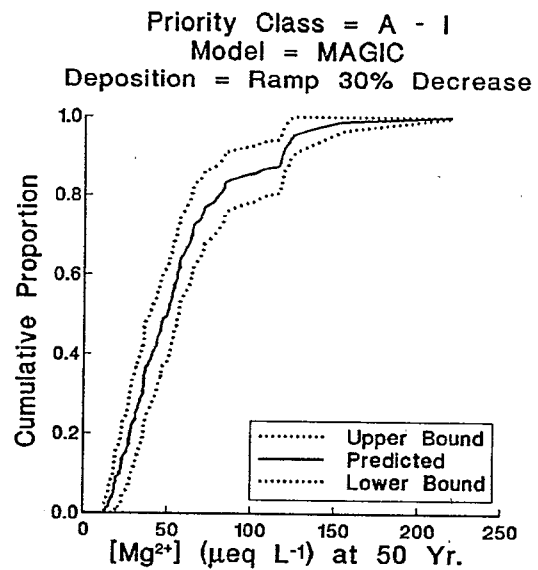
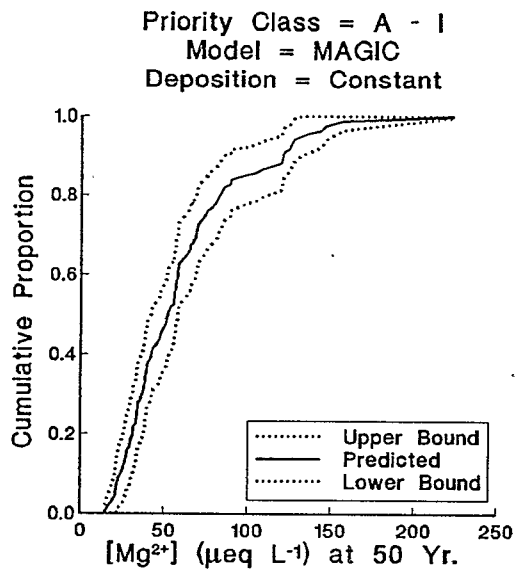
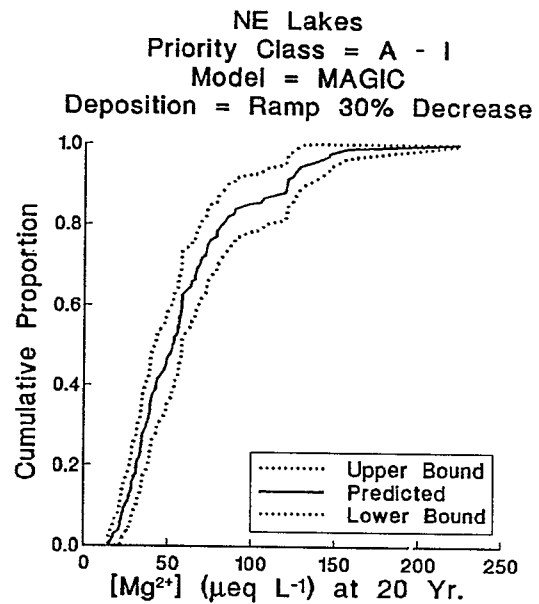
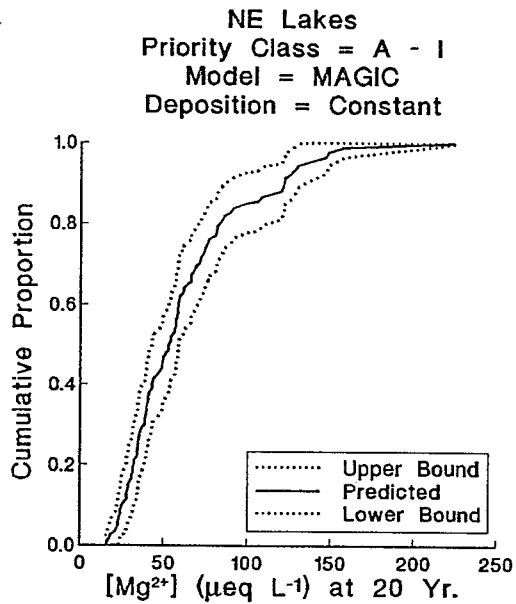


Figure A.3-4. Magnesium projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - I lakes using MAGIC.

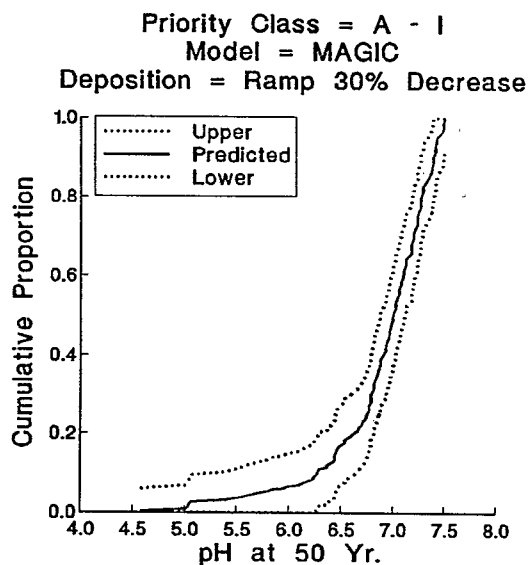
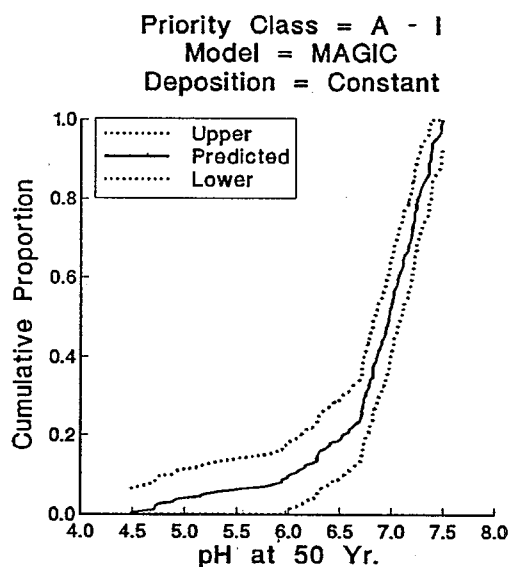
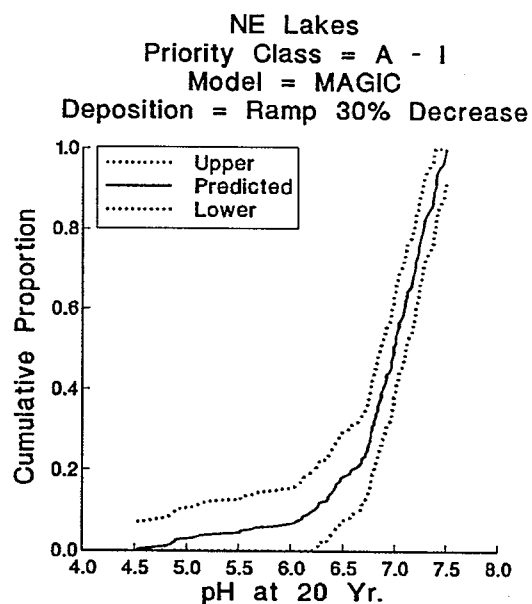
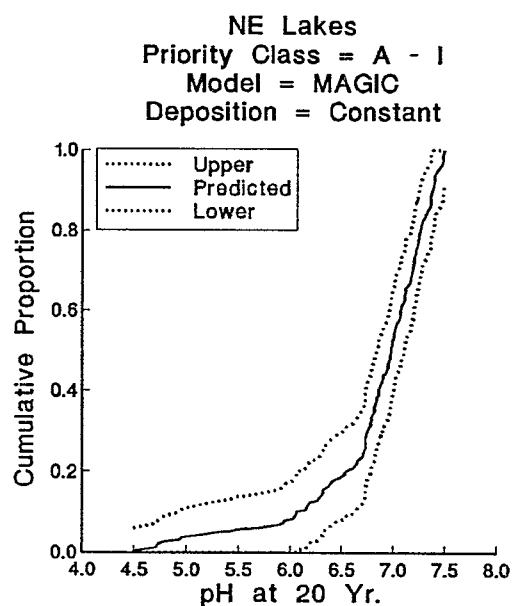


Figure A.3-5. pH projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - I lakes using MAGIC.

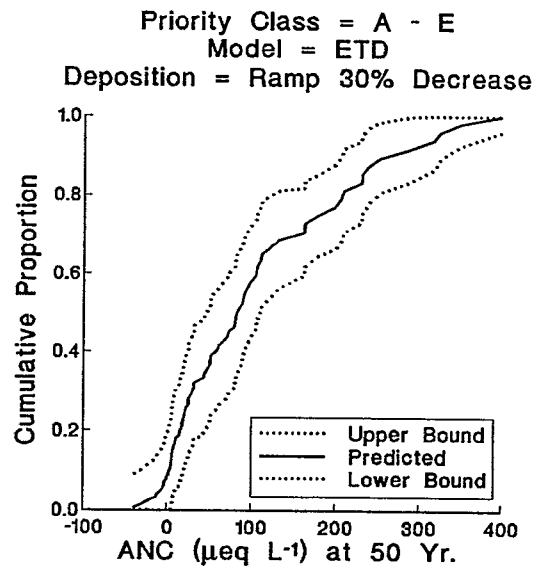
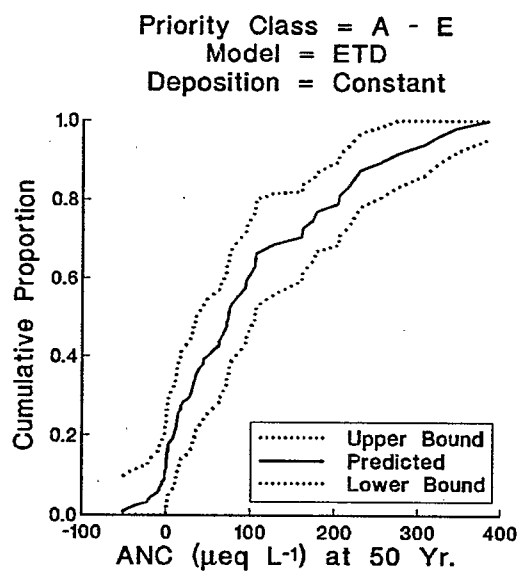
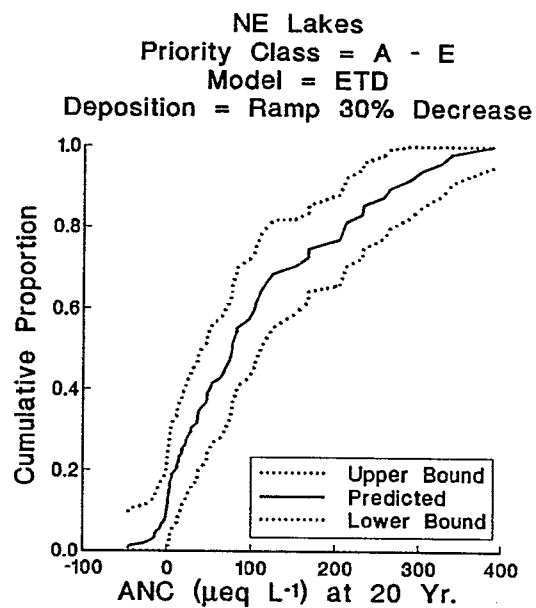
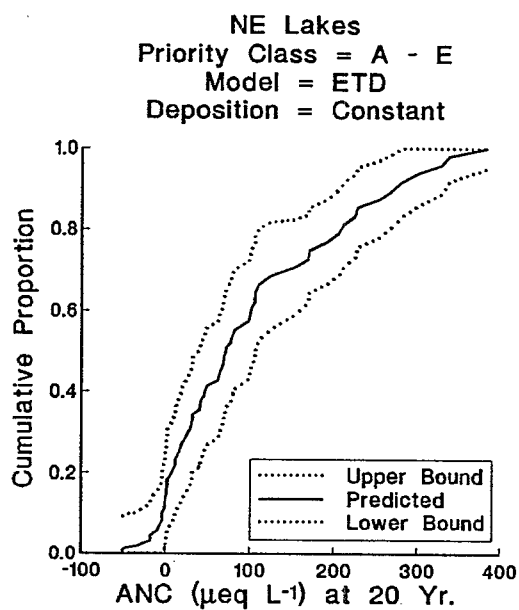


Figure A.3-6. ANC projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using ETD.

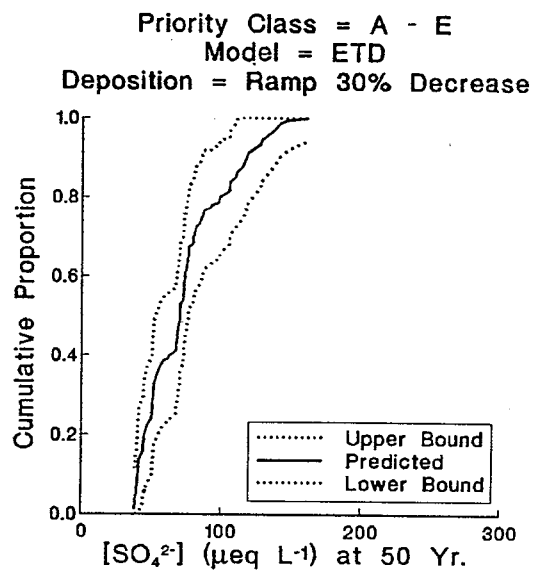
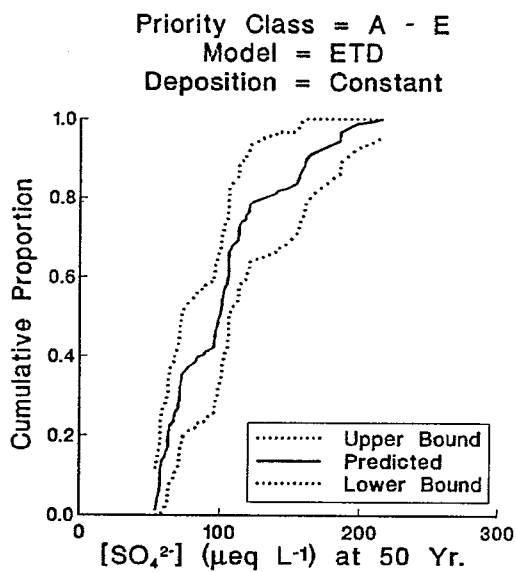
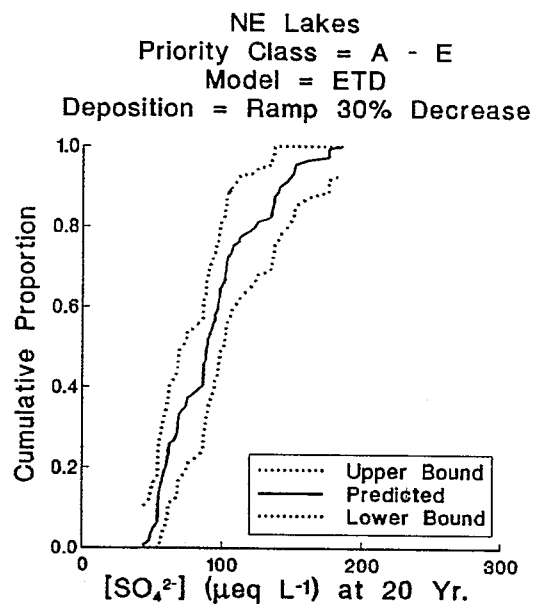
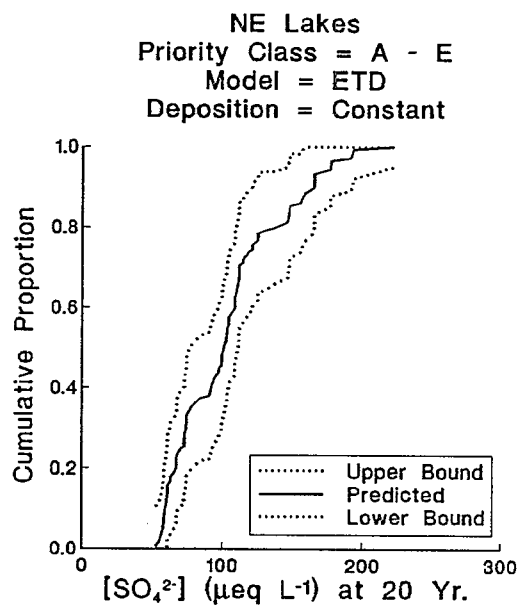


Figure A.3-7. Sulfate projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using MAGIC.

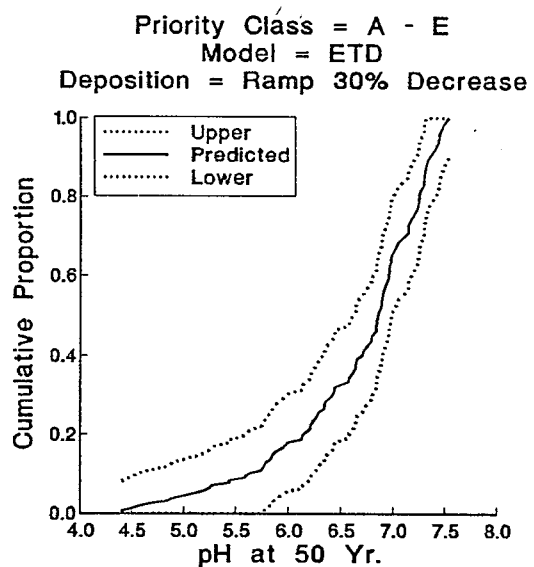
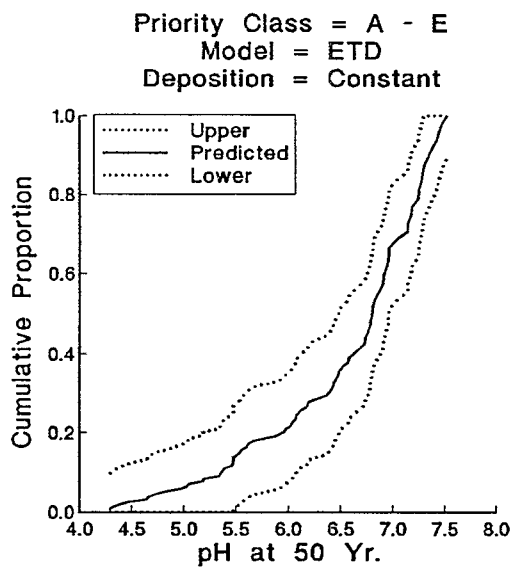
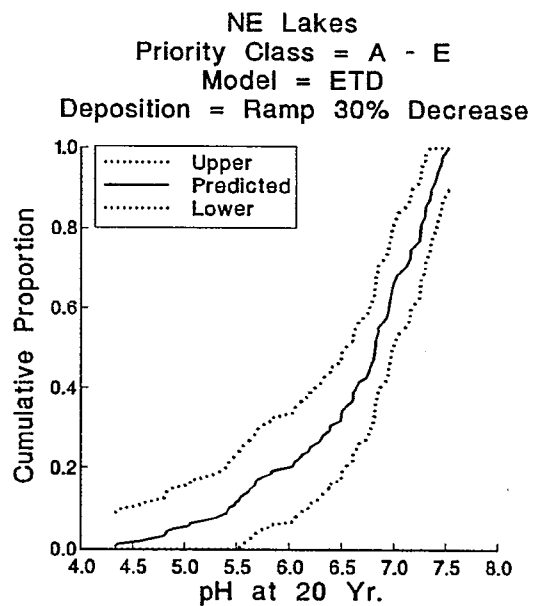
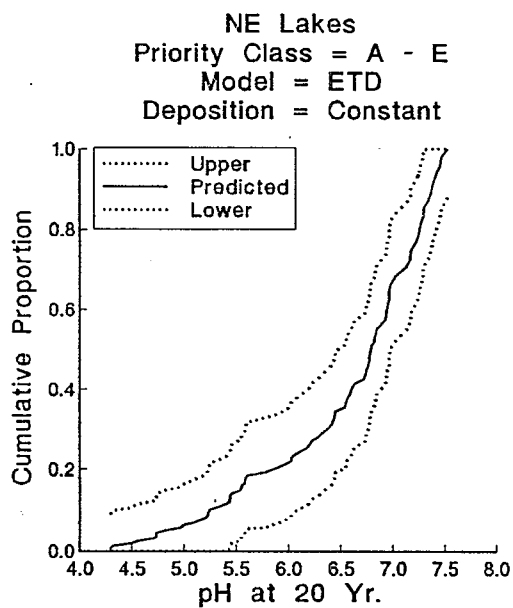


Figure A.3-8. pH projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using ETD.

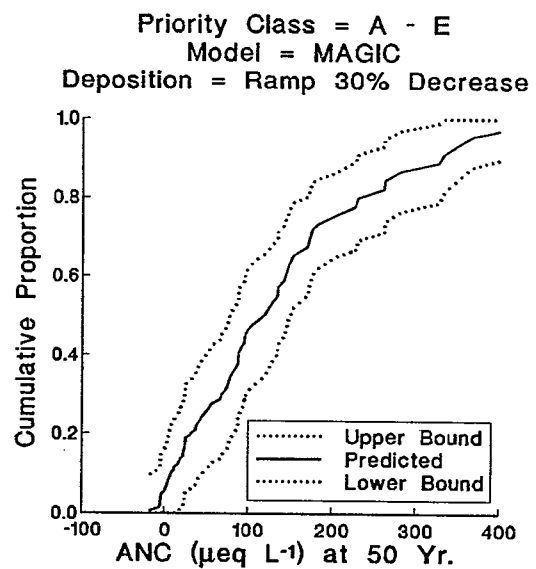
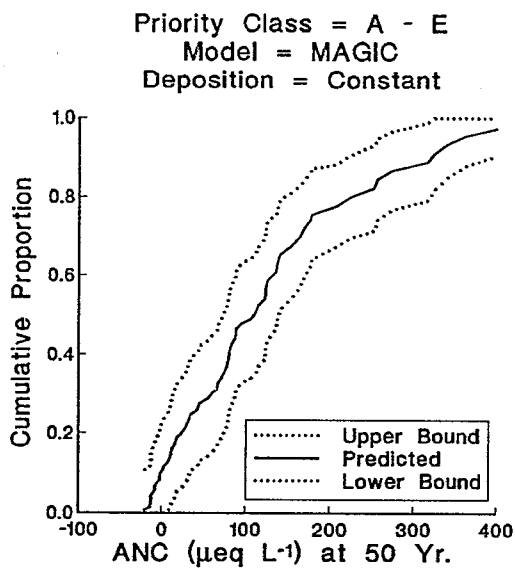
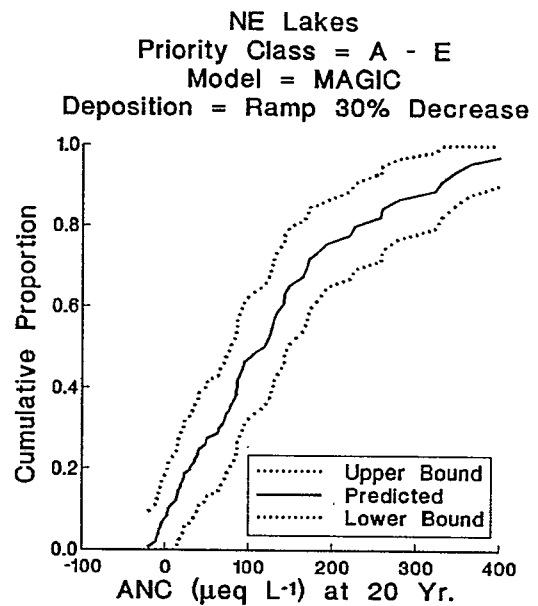
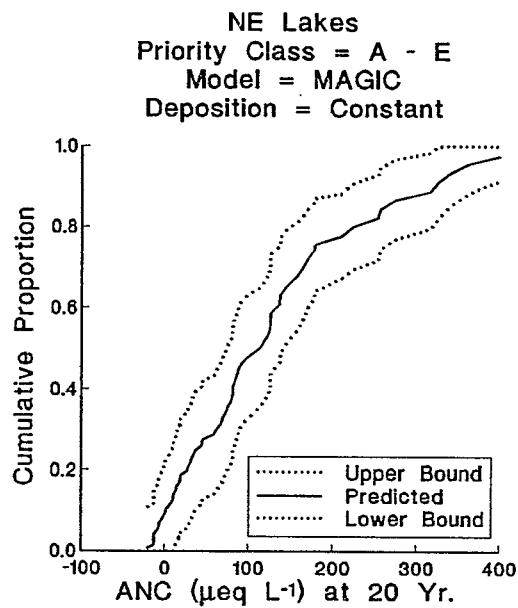


Figure A.3-9. ANC projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using MAGIC.

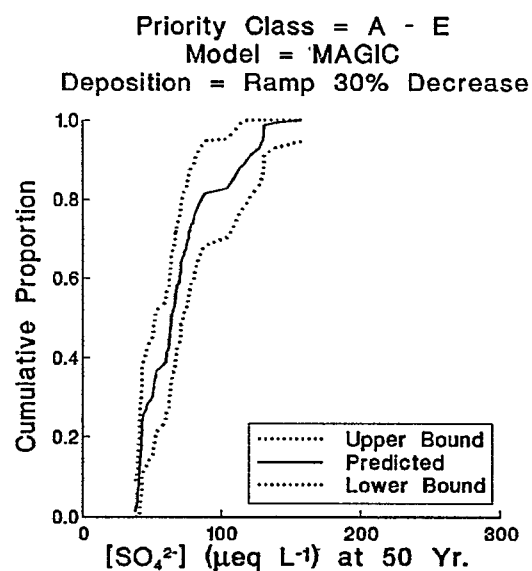
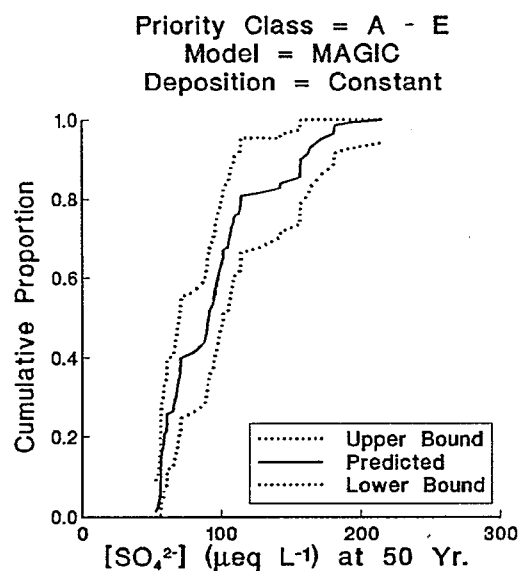
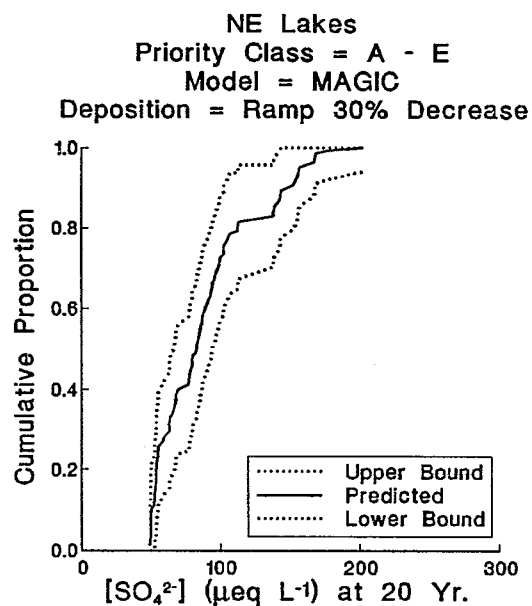
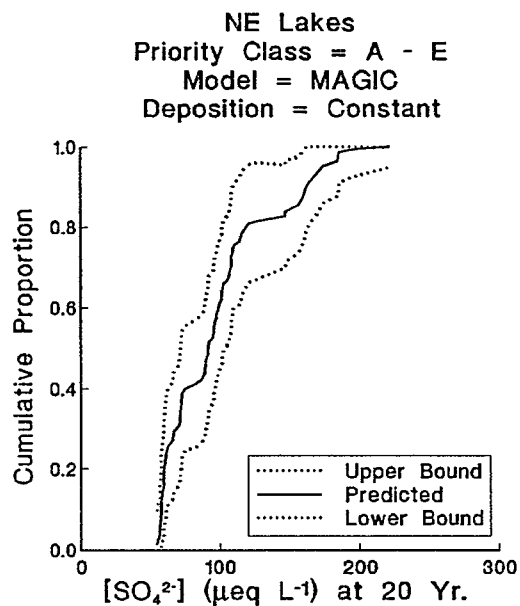


Figure A.3-10. Sulfate projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using MAGIC.

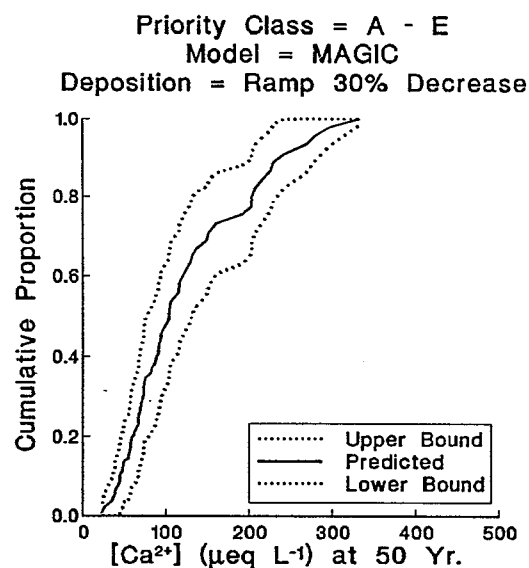
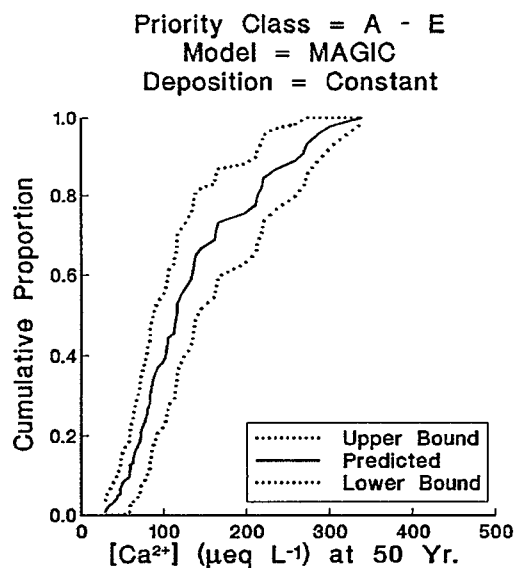
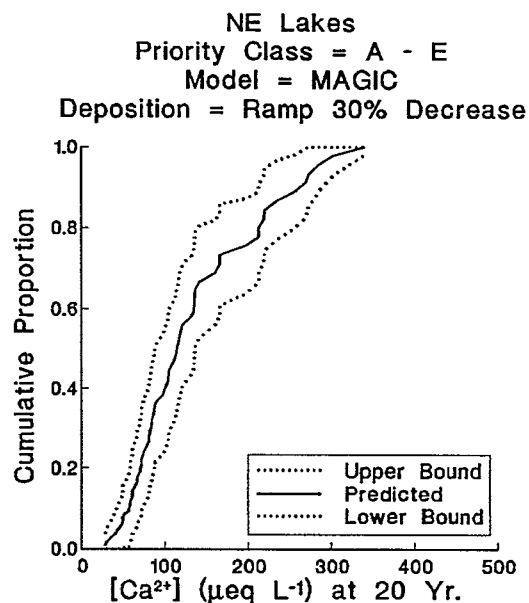
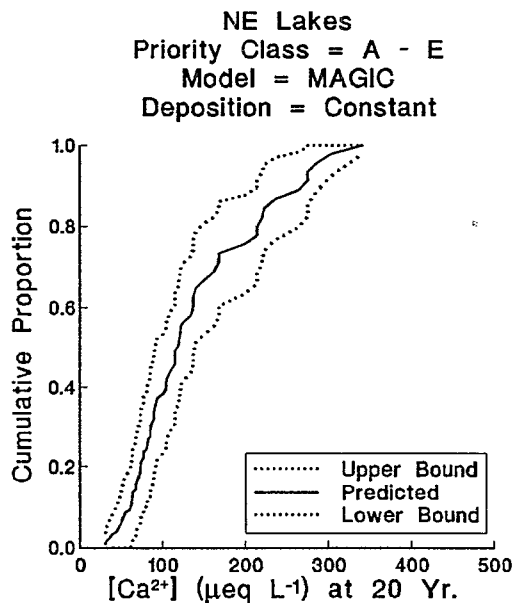


Figure A.3-11. Calcium projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using MAGIC.

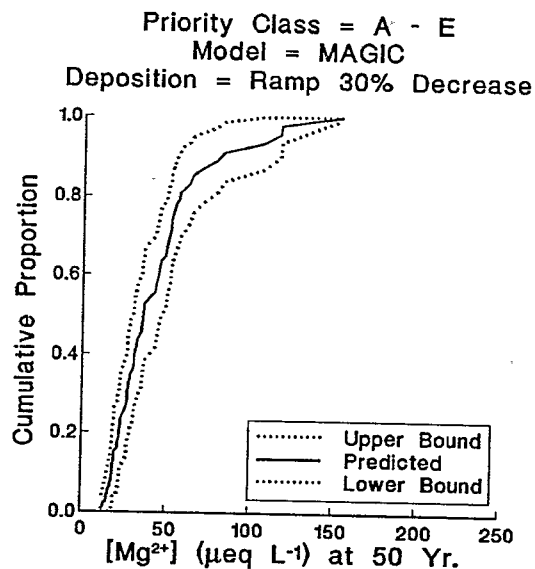
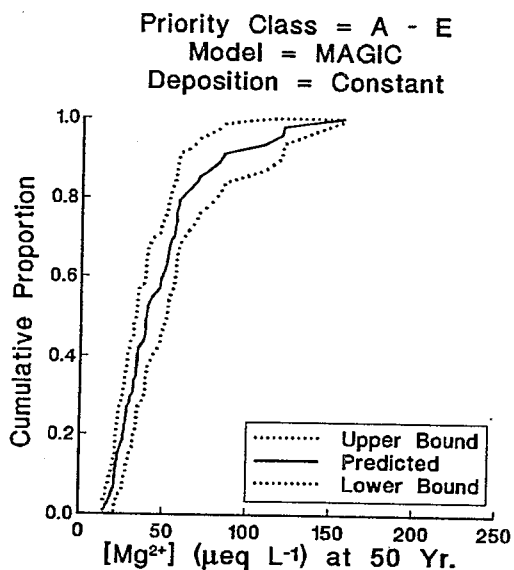
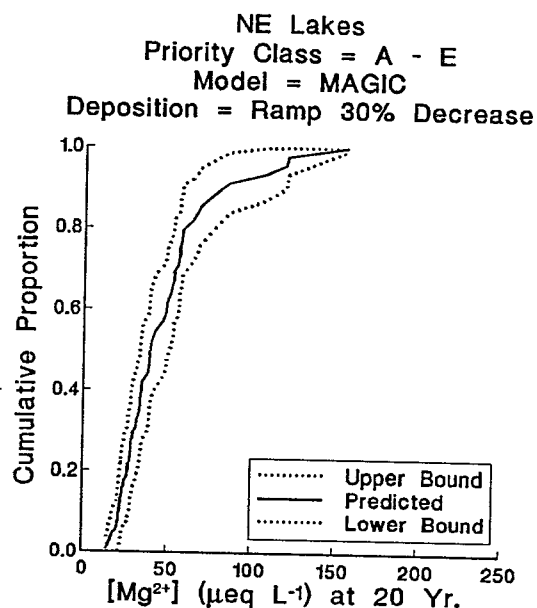
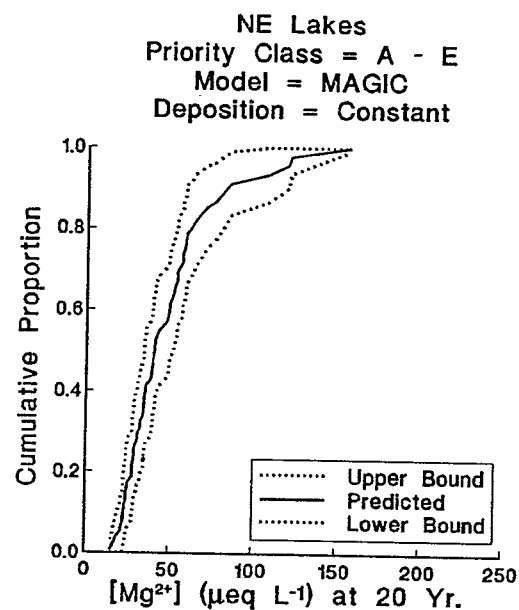


Figure A.3-12. Magnesium projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using MAGIC.

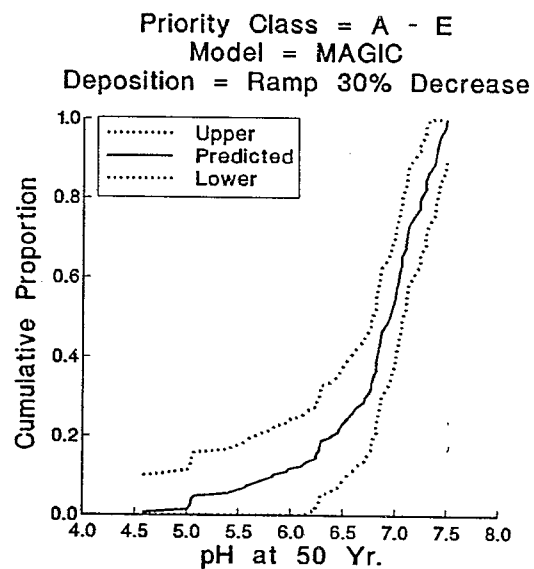
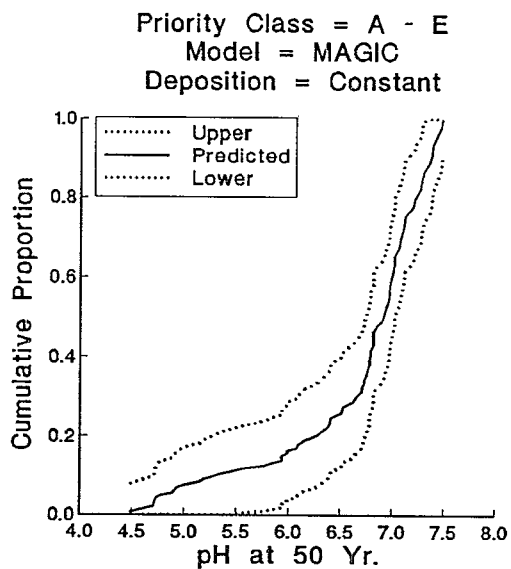
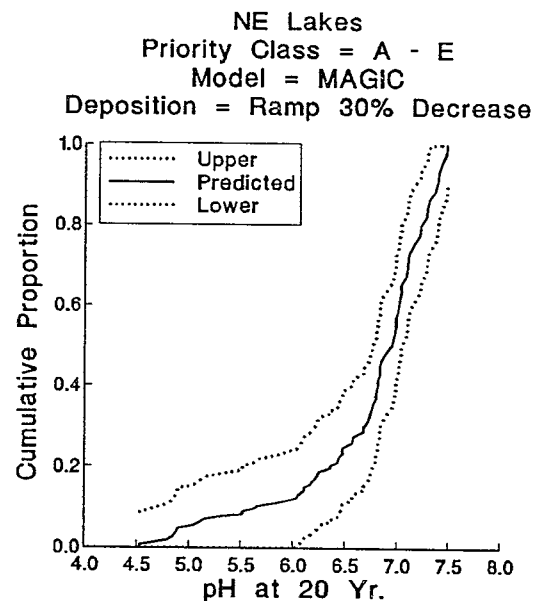
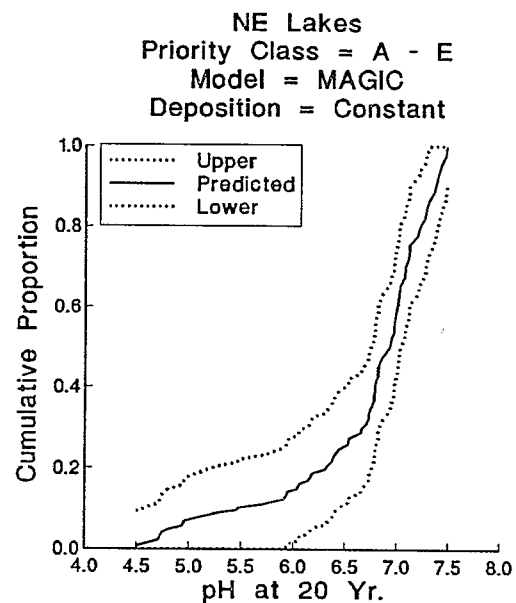


Figure A.3-13. pH projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using MAGIC.

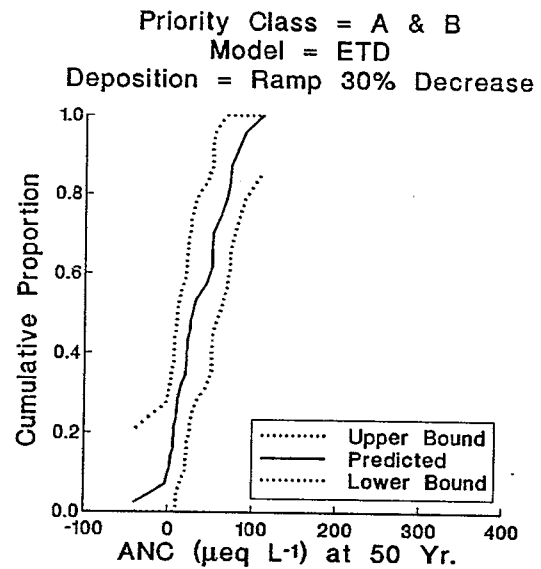
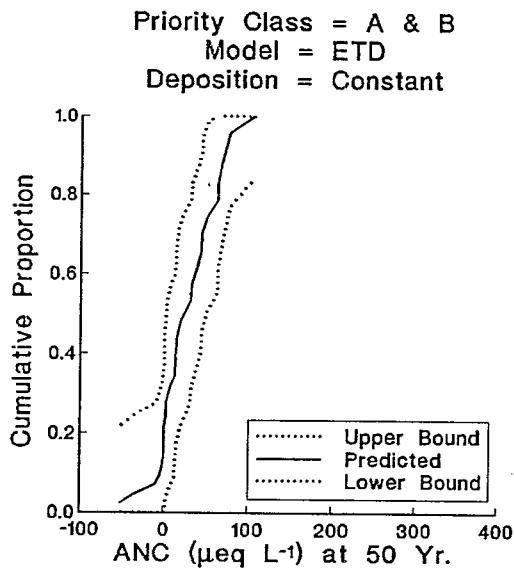
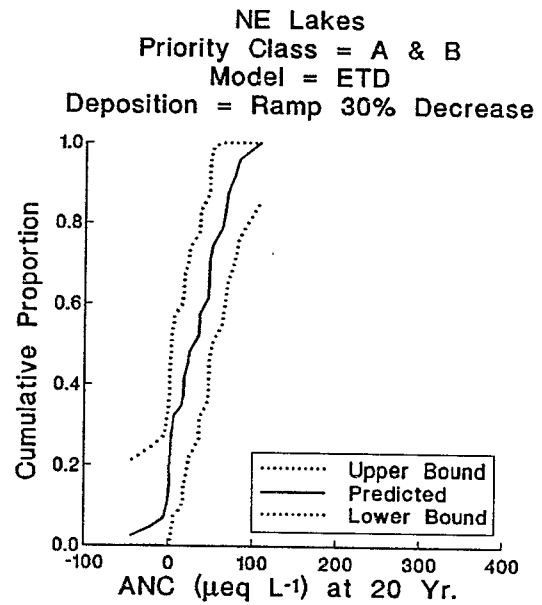
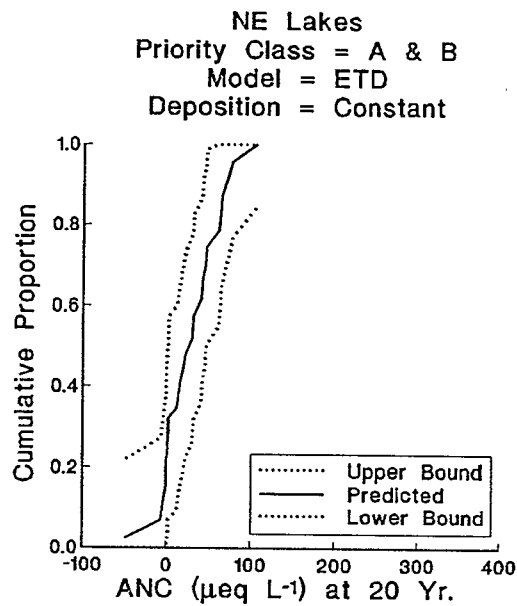


Figure A.3-14. ANC projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - B lakes using ETD.

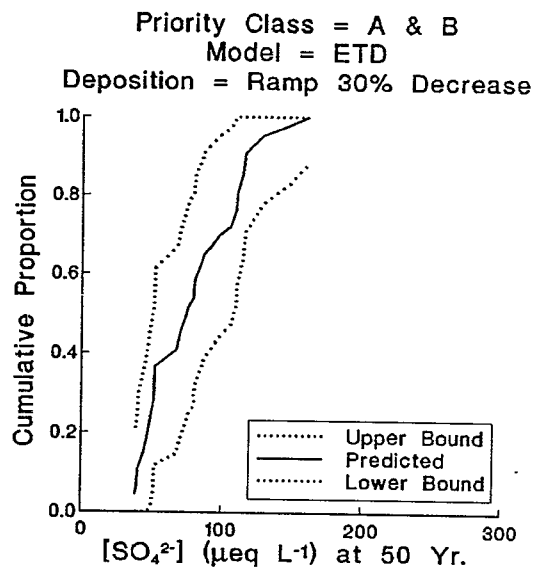
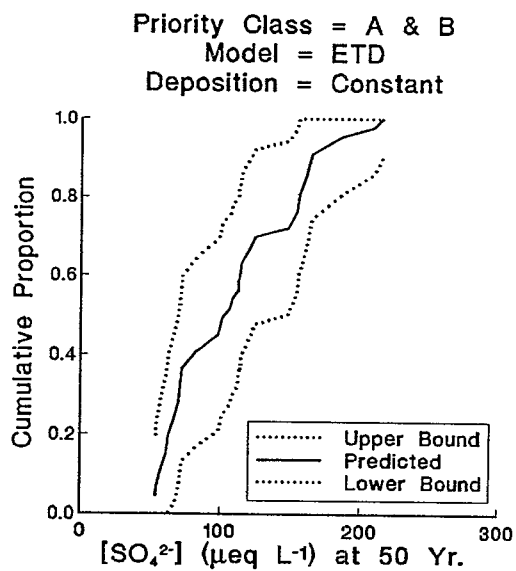
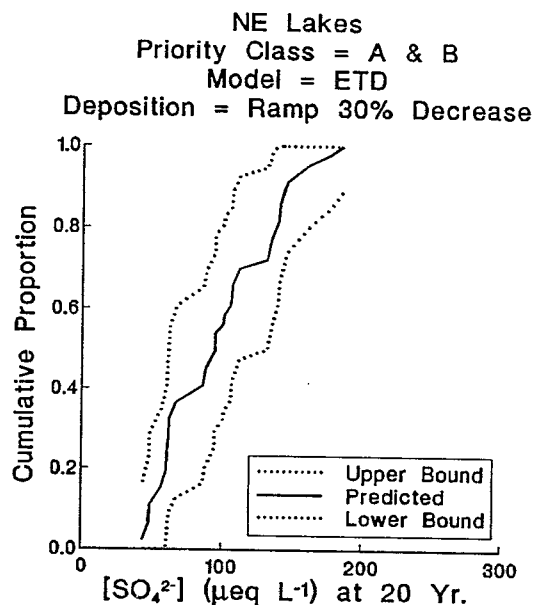
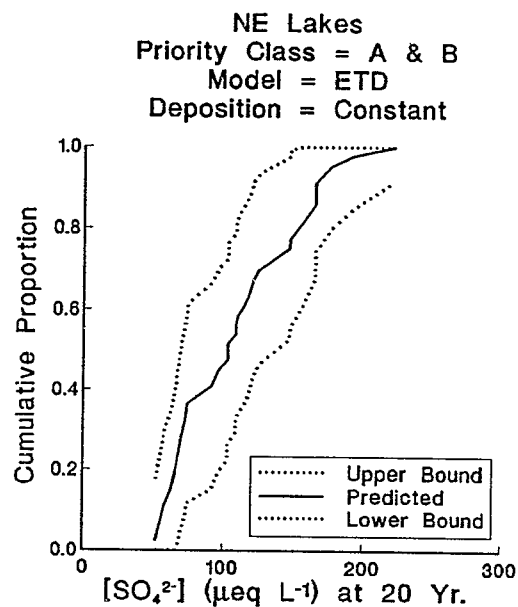


Figure A.3-15. Sulfate projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - B lakes using ETD.

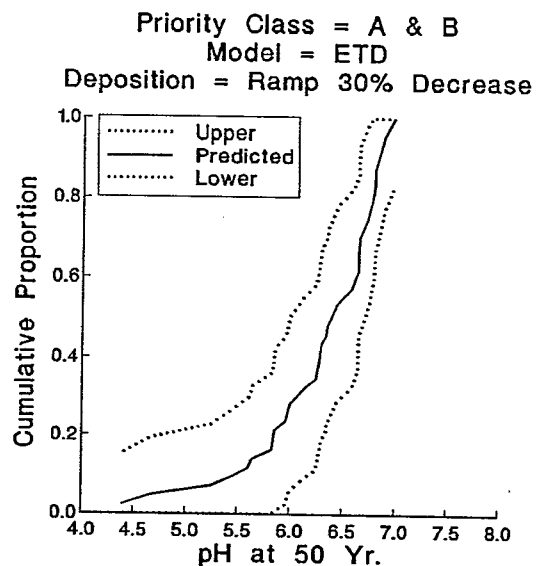
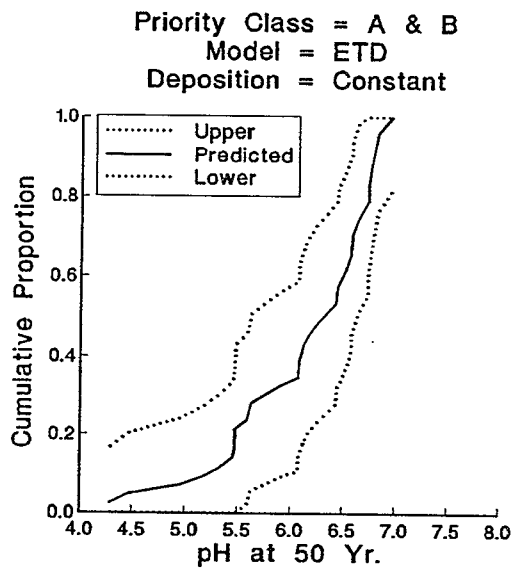
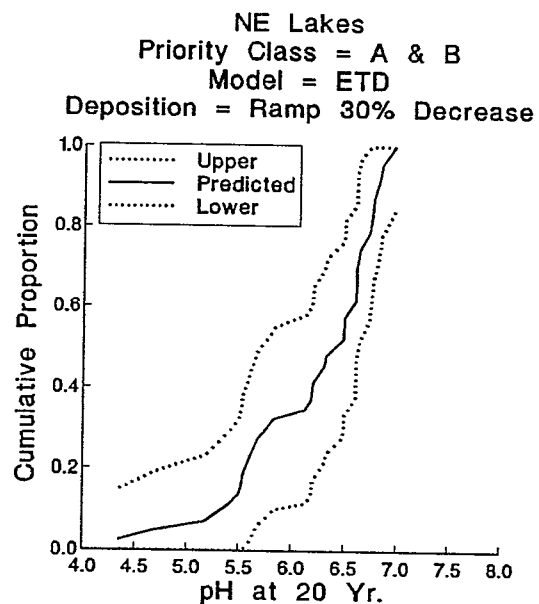
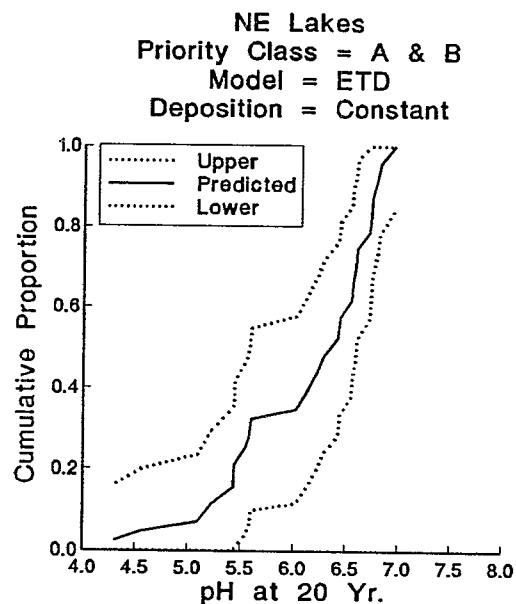


Figure A.3-16. pH projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - B lakes using ETD.

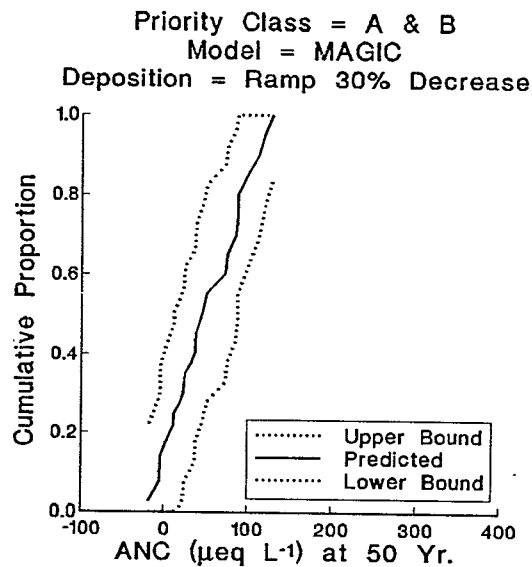
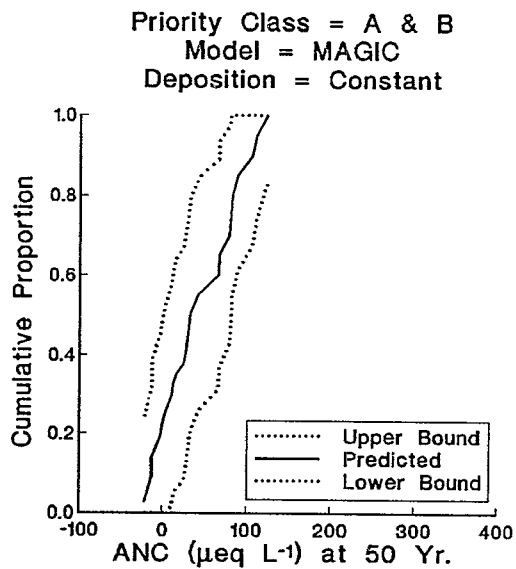
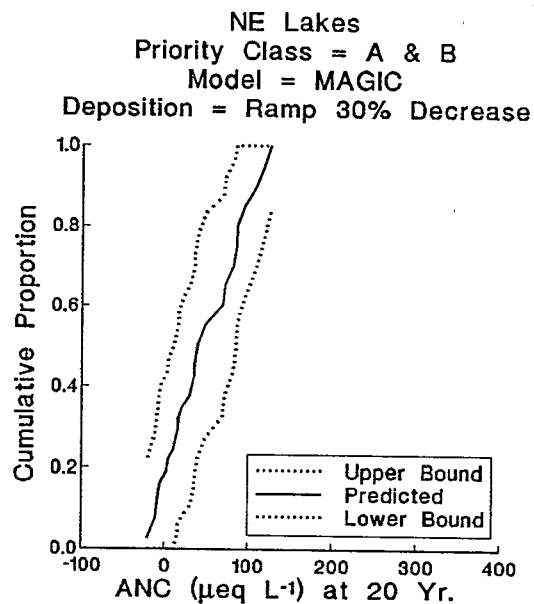
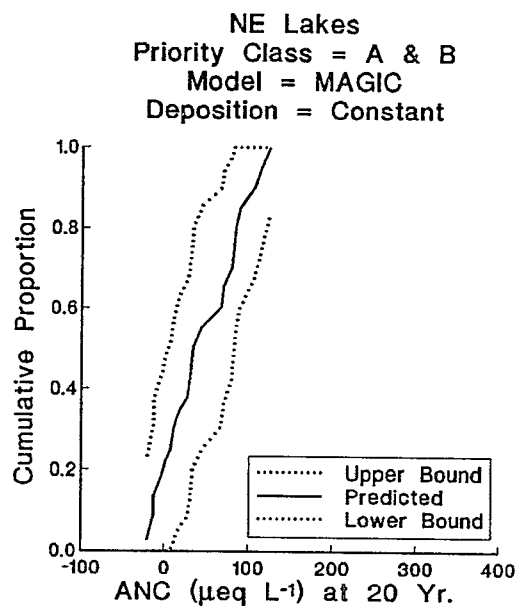


Figure A.3-17. ANC projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - B lakes using MAGIC.

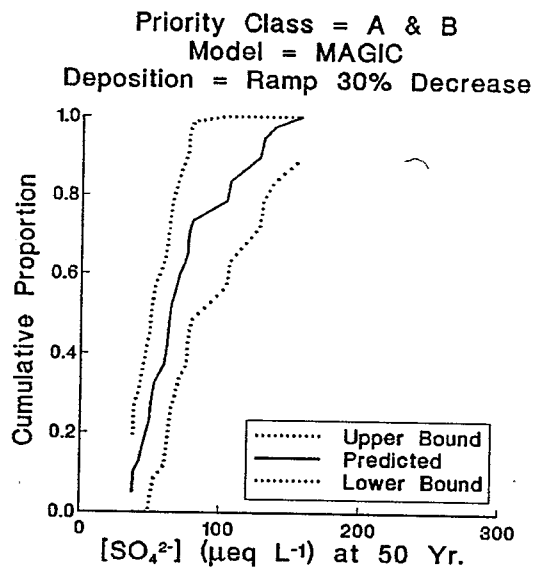
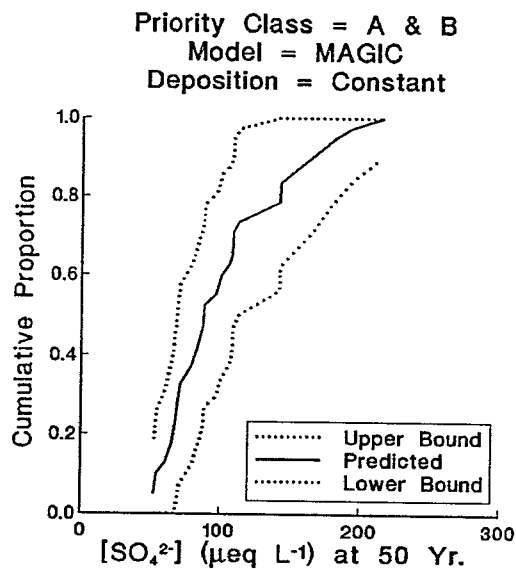
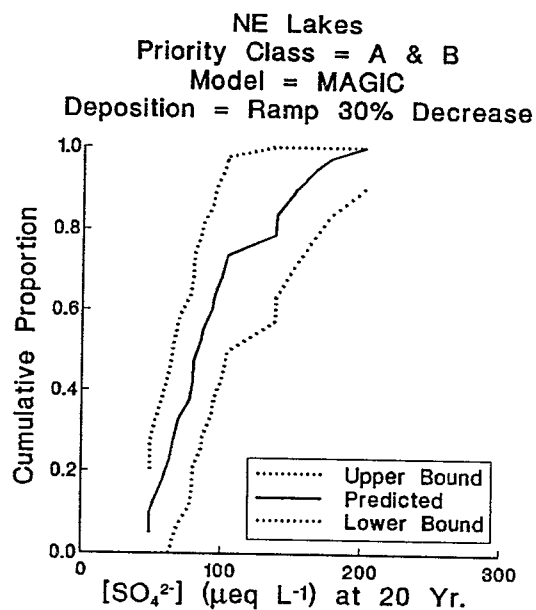
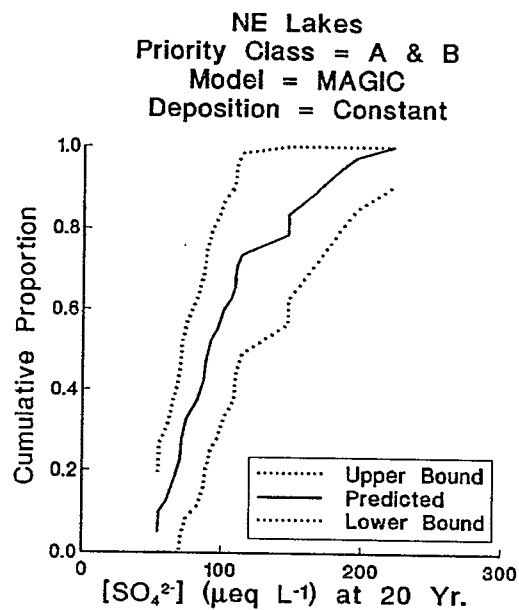


Figure A.3-18. Sulfate projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - B lakes using MAGIC.

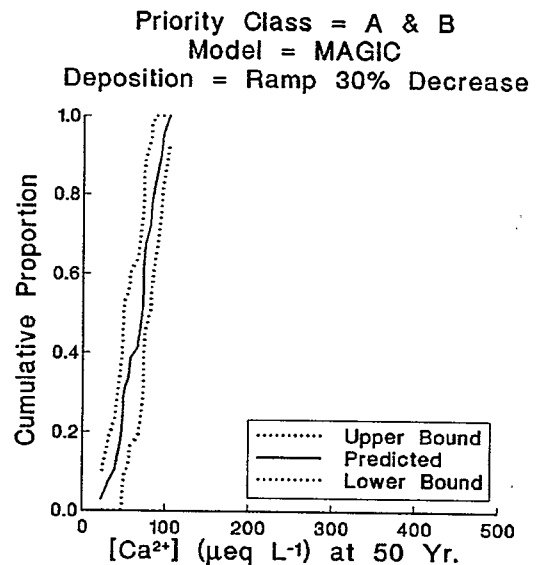
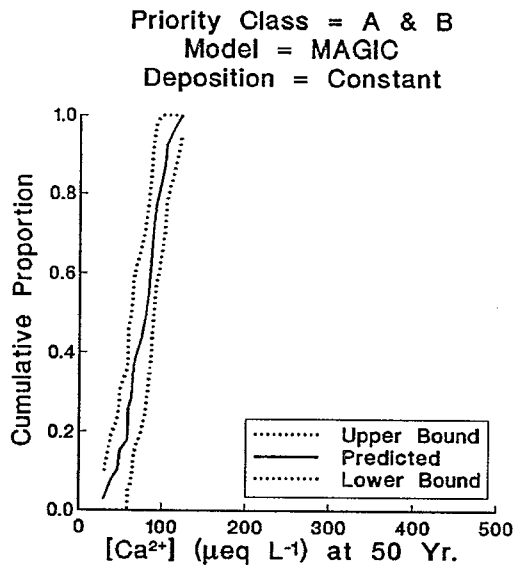
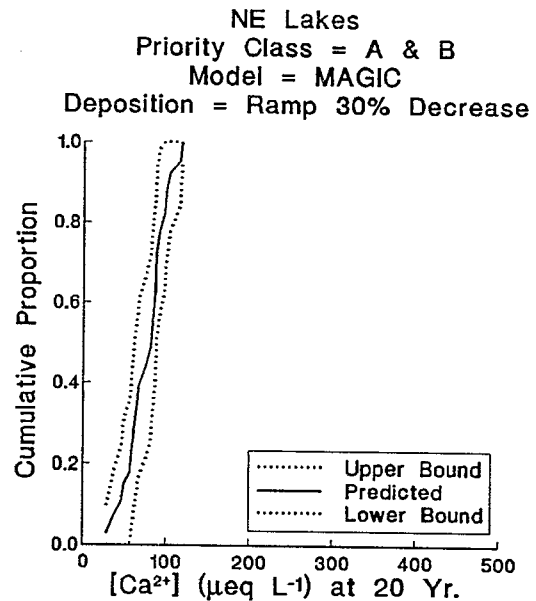
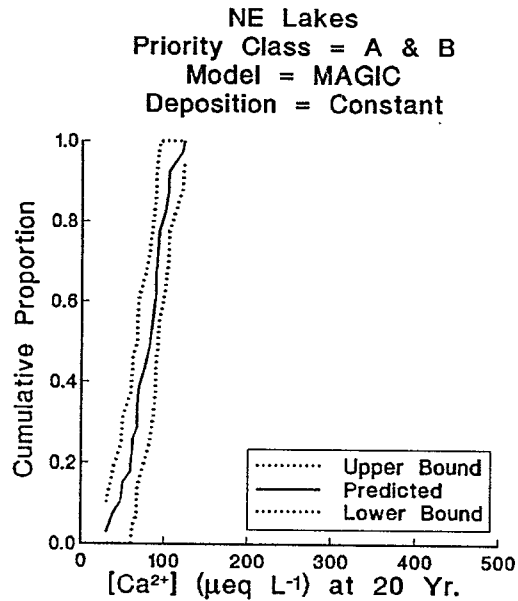


Figure A.3-19. Calcium projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - B lakes using MAGIC.

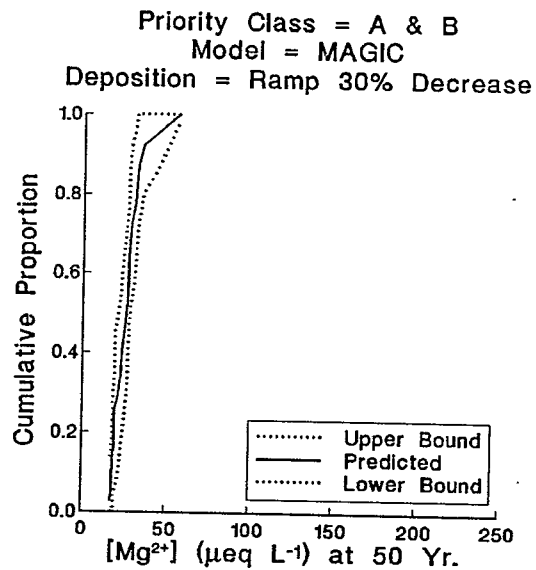
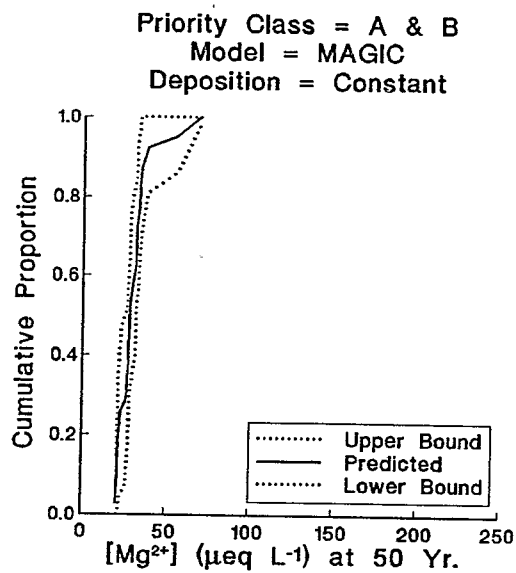
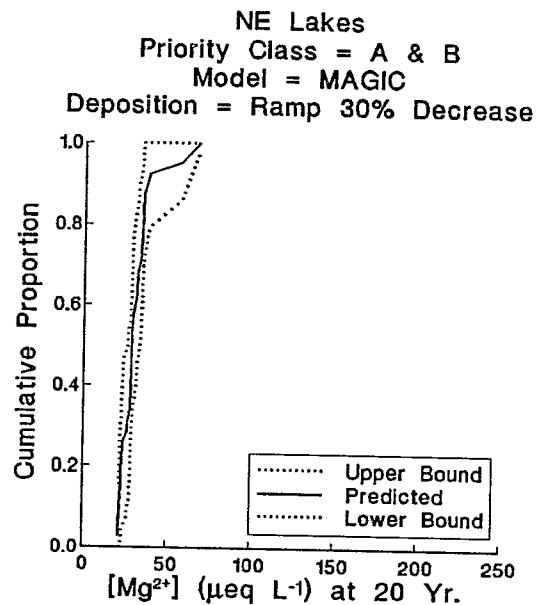
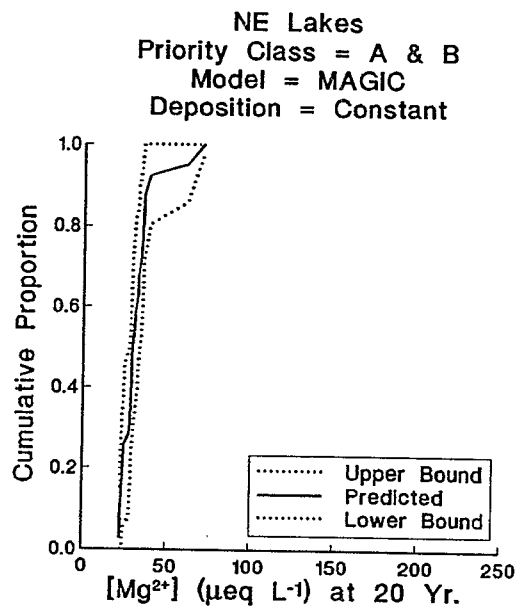


Figure A.3-20. Magnesium projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - B lakes using MAGIC.

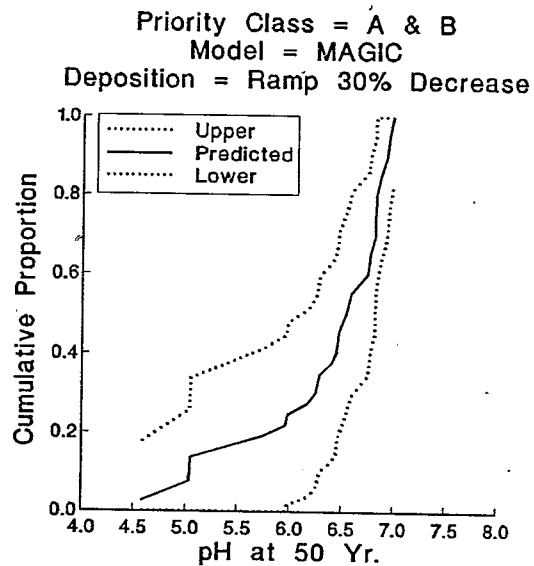
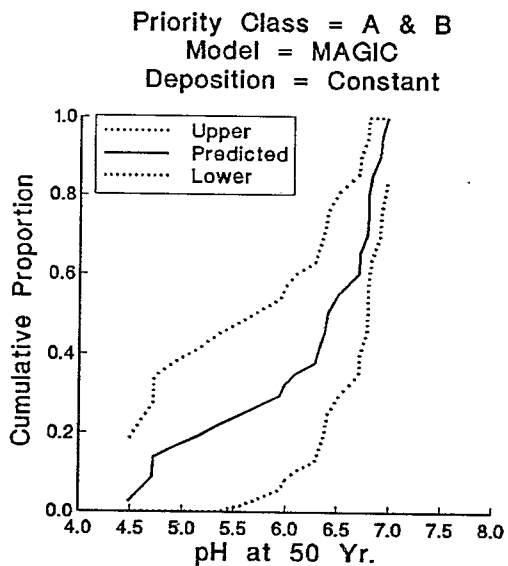
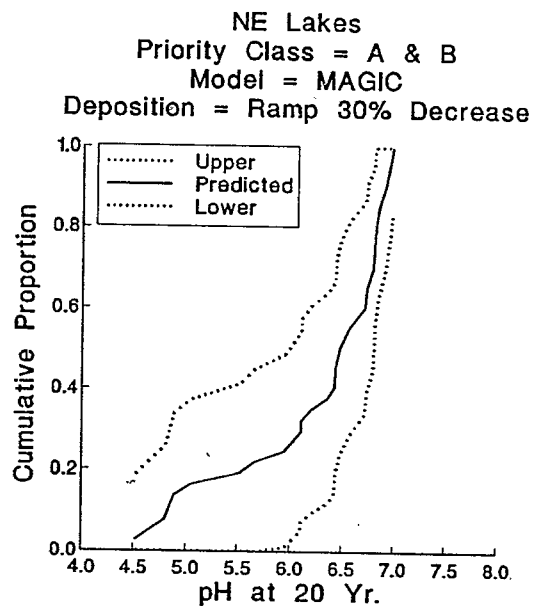
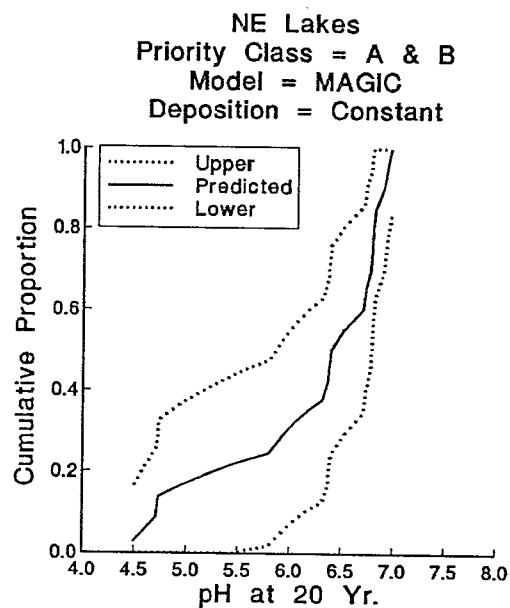


Figure A.3-21. pH projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - B lakes using MAGIC.

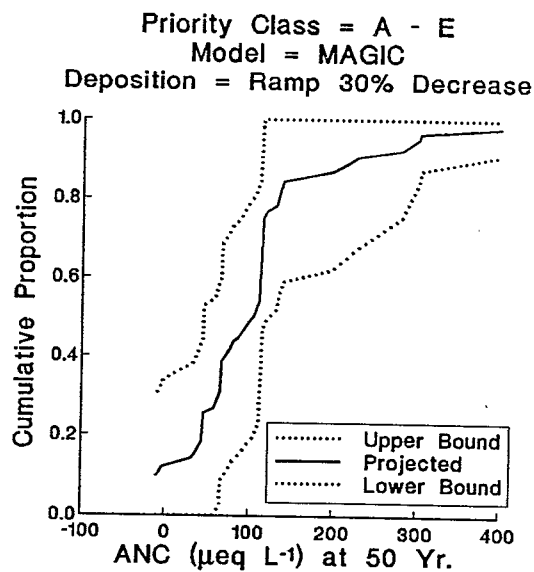
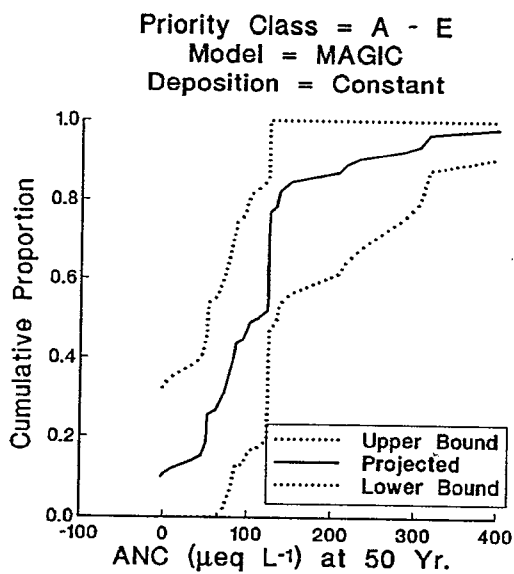
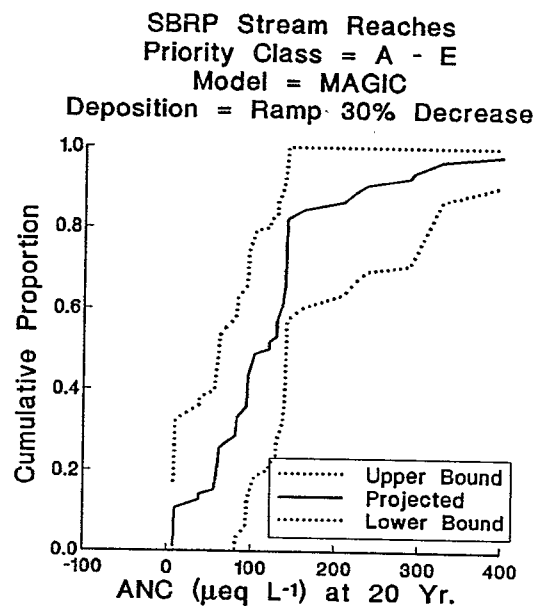
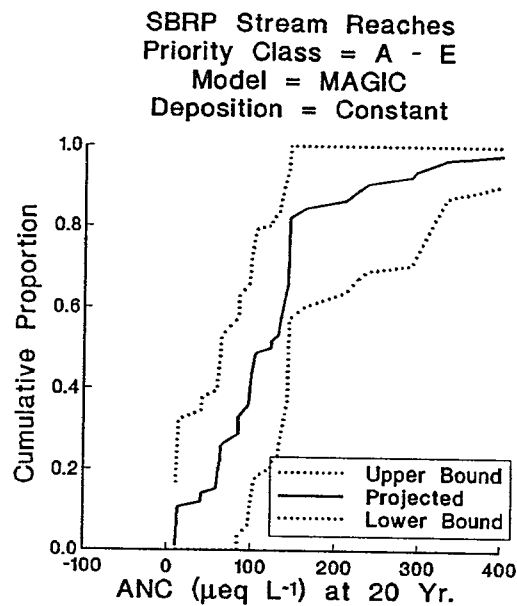


Figure A.3-22. ANC projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - E streams using MAGIC.

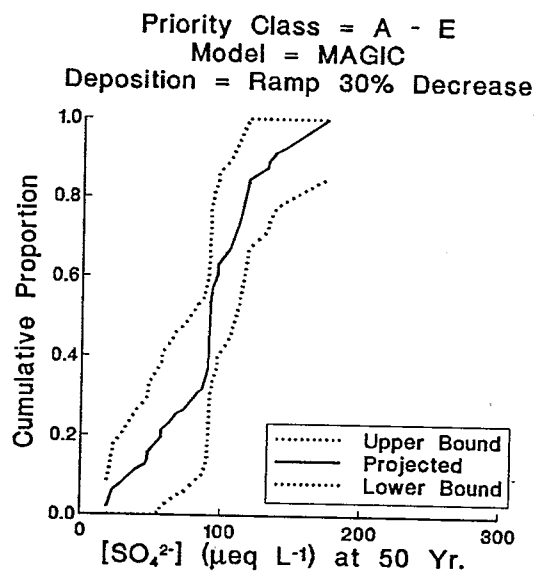
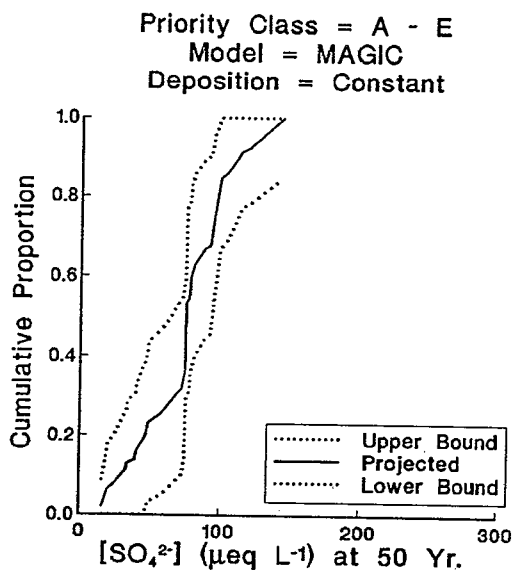
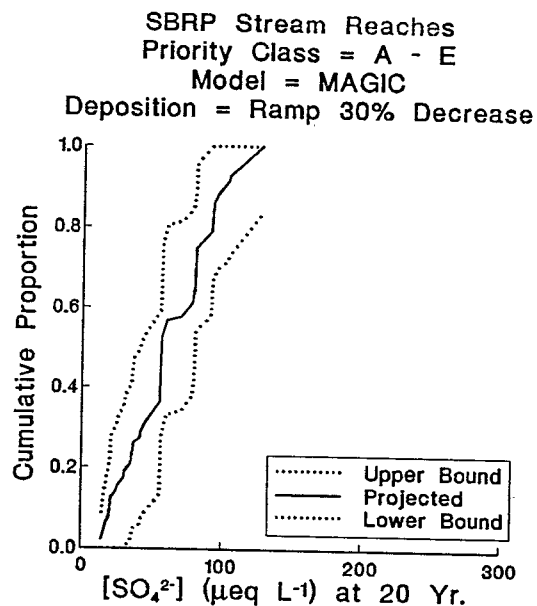
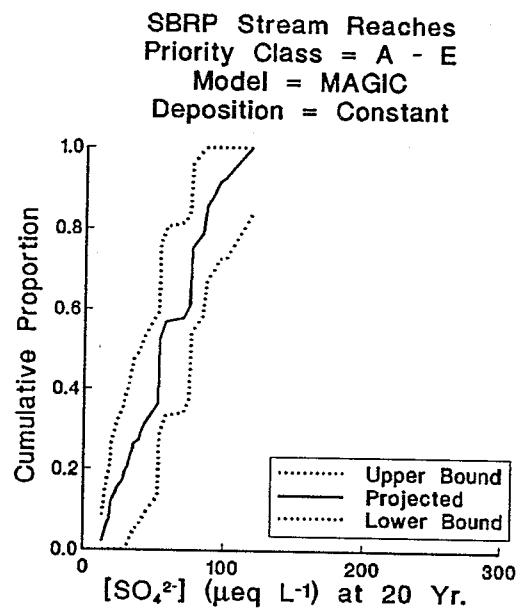


Figure A.3-23. Sulfate projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - E streams using MAGIC.

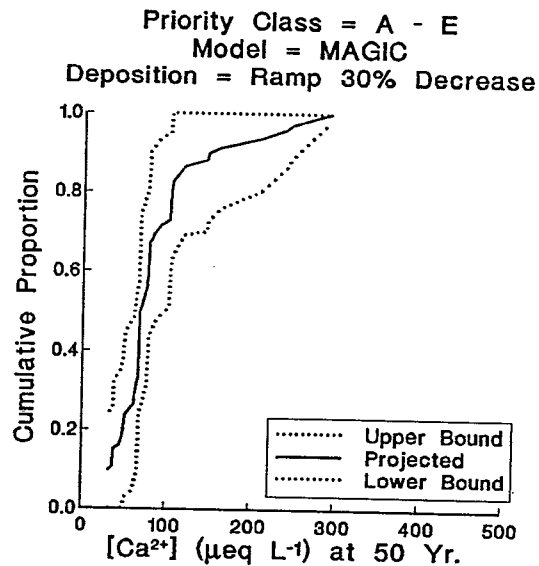
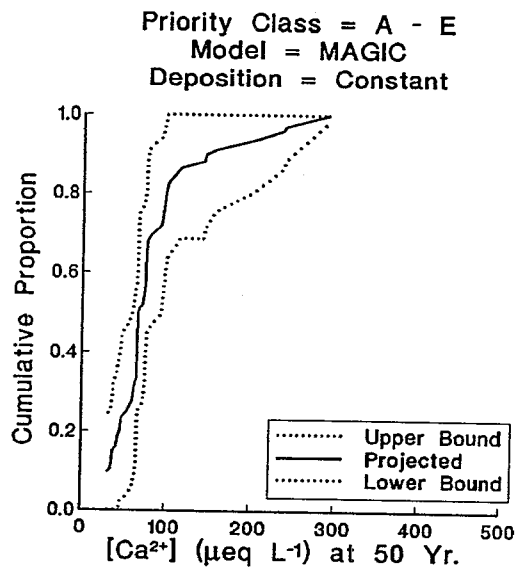
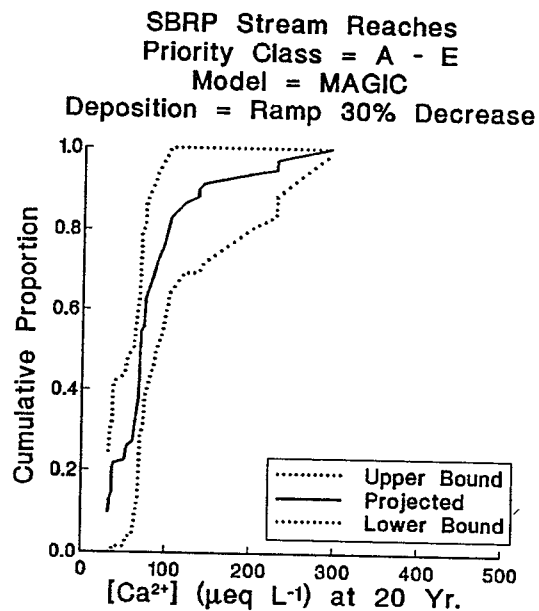
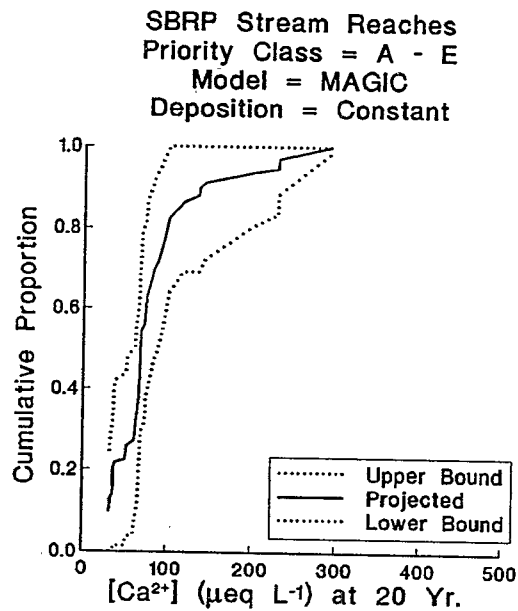


Figure A.3-24. Calcium projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - E streams using MAGIC.

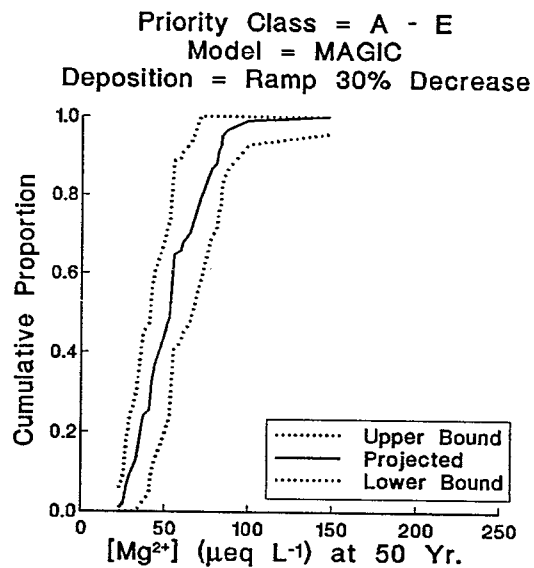
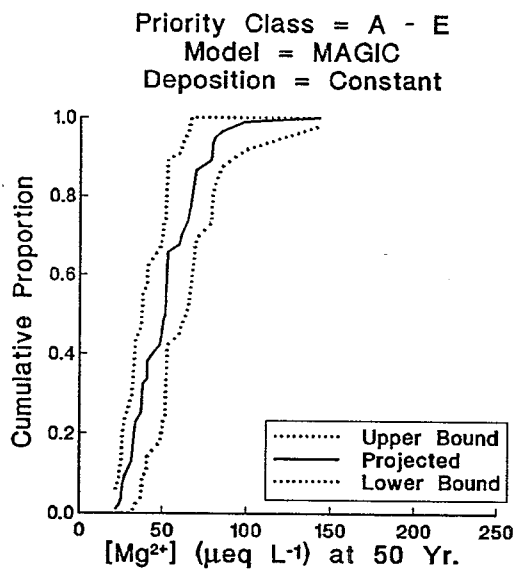
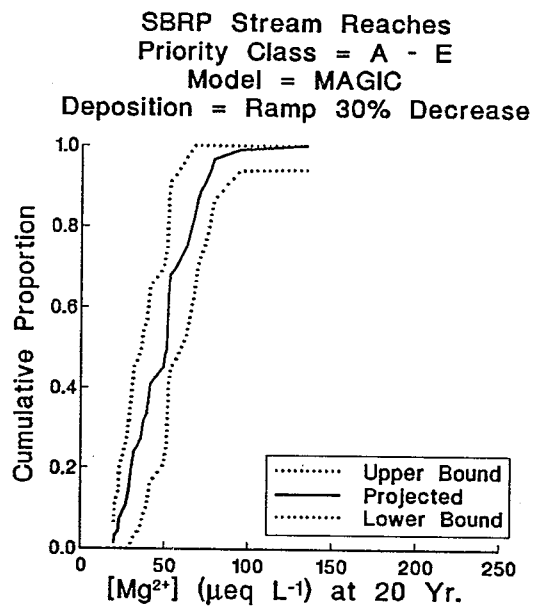
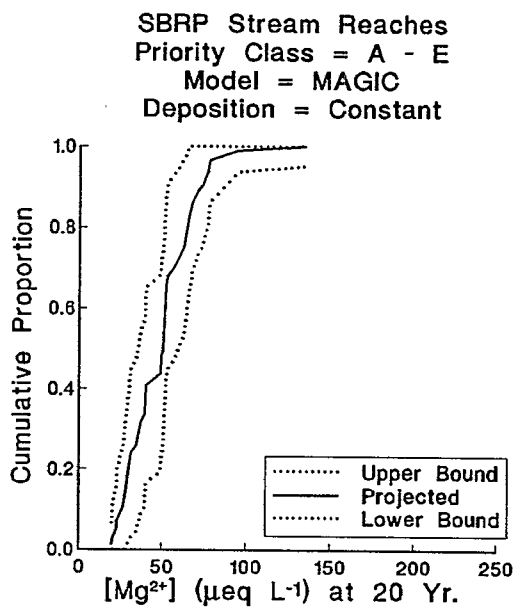


Figure A.3-25. Magnesium projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - E streams using MAGIC.

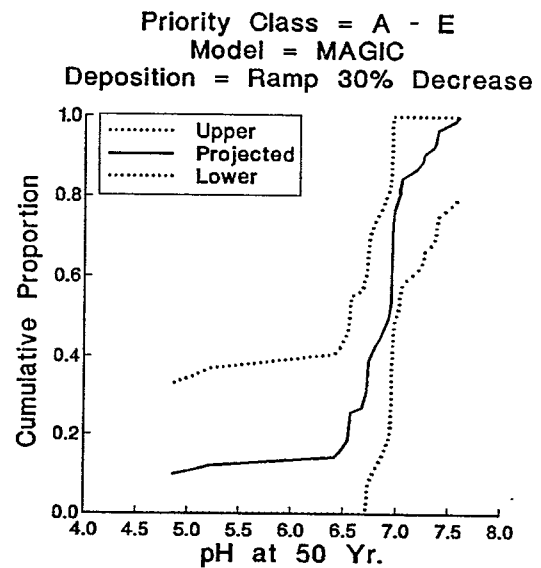
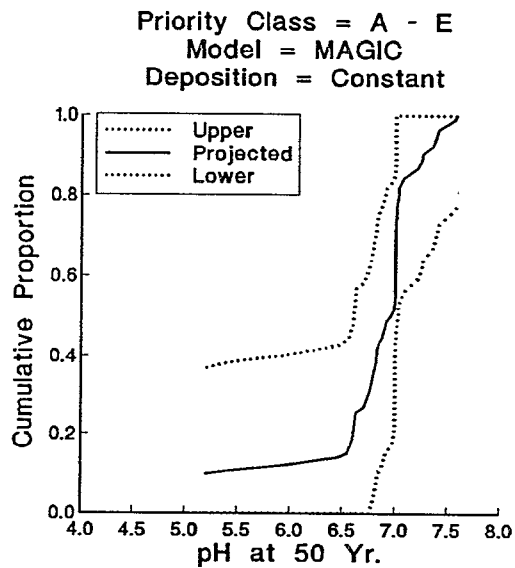
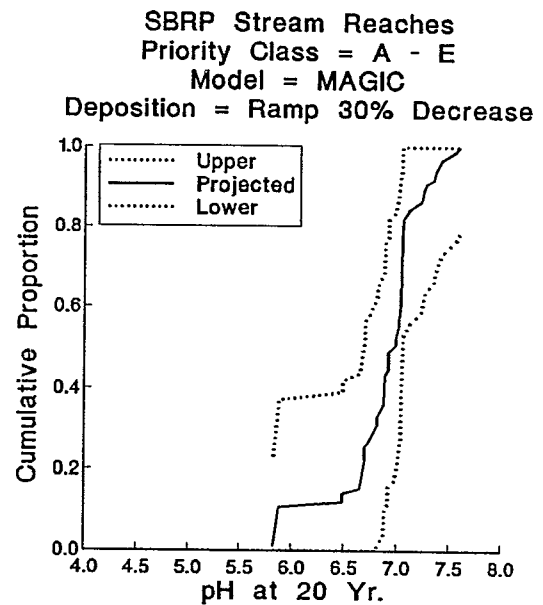
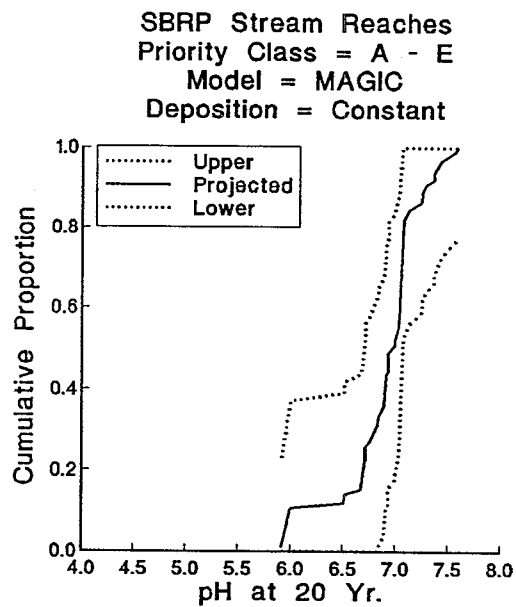


Figure A.3-26. pH projections with upper and lower bounds for a 90 percent confidence interval for NE Priority Class A - E lakes using MAGIC.

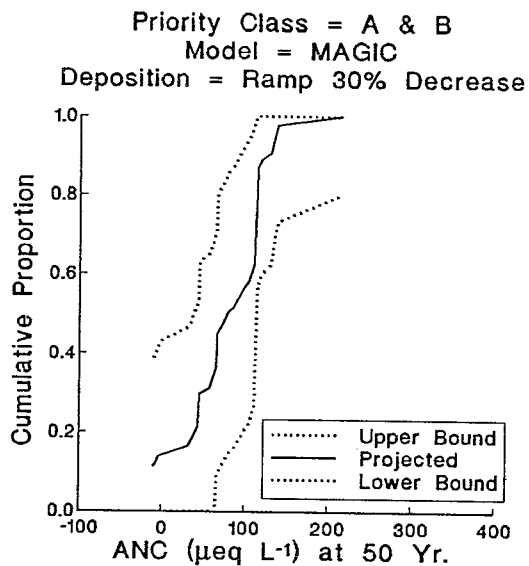
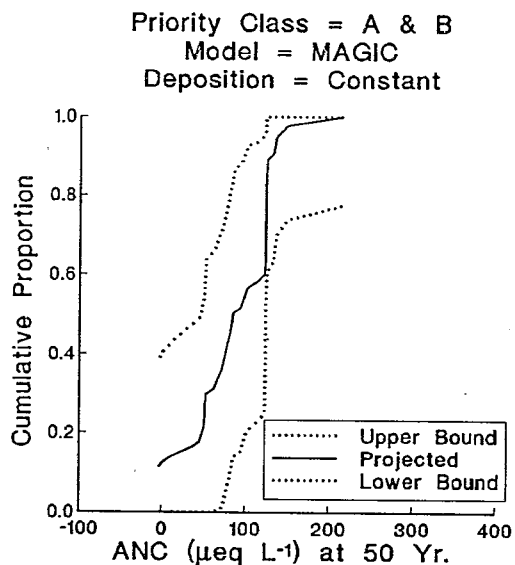
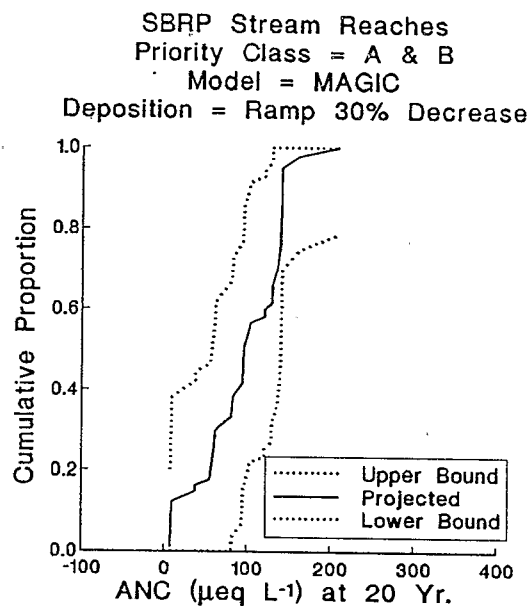
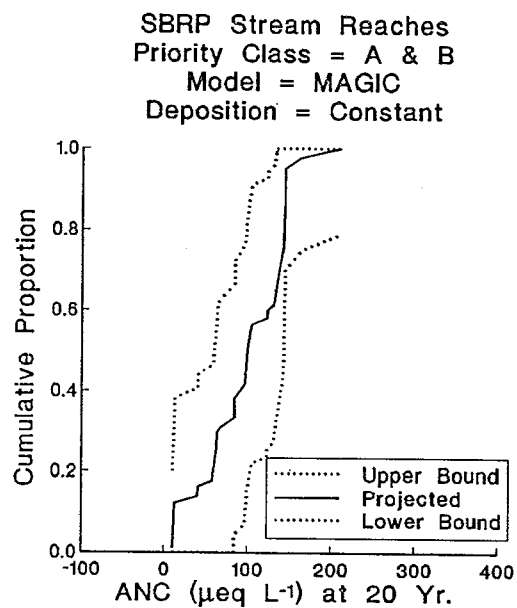


Figure A.3-27. ANC projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - B streams using MAGIC.

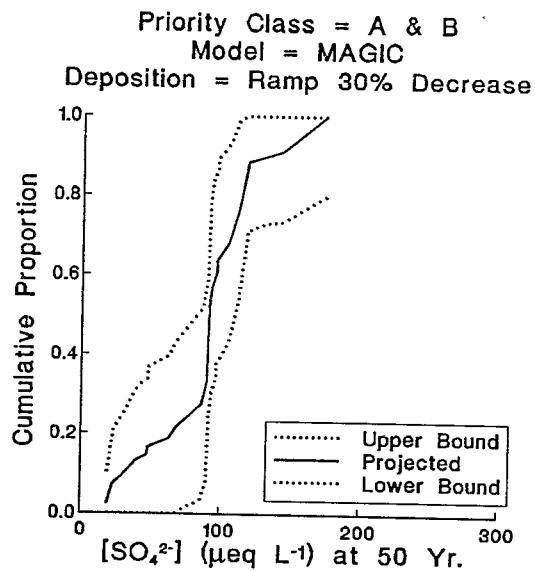
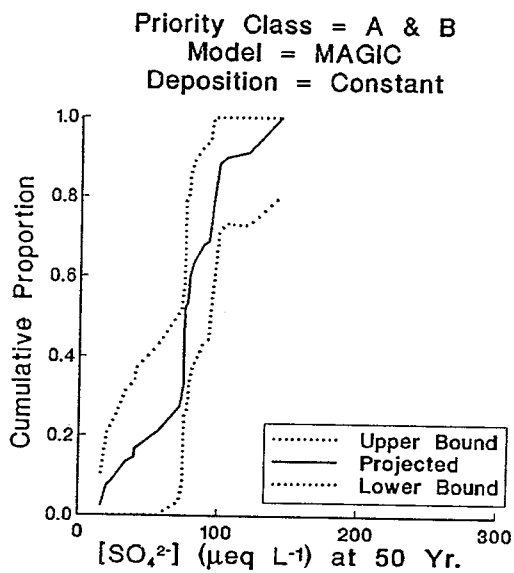
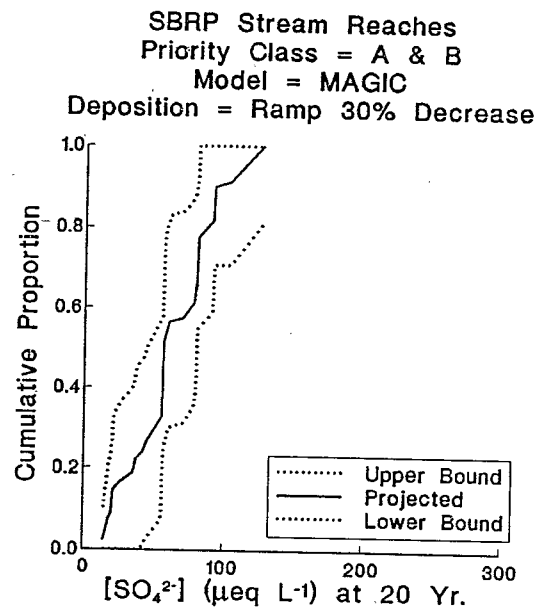
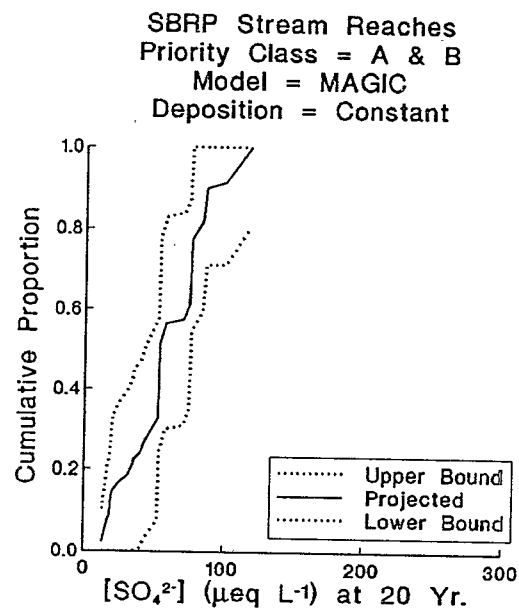


Figure A.3-28. Sulfate projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - B streams using MAGIC.

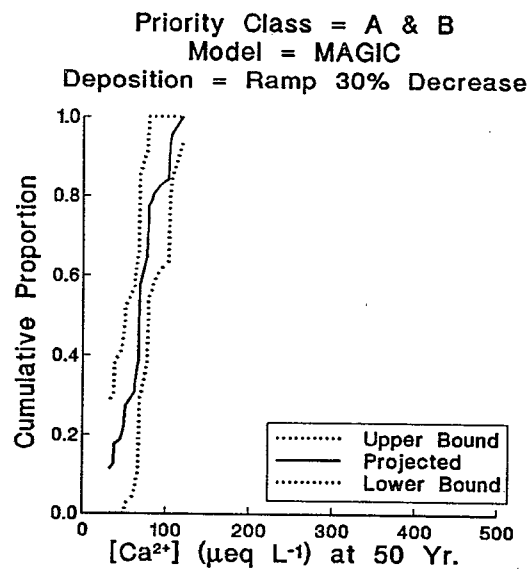
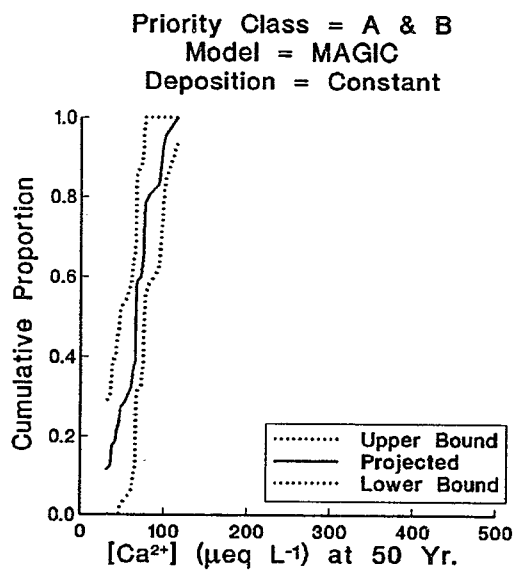
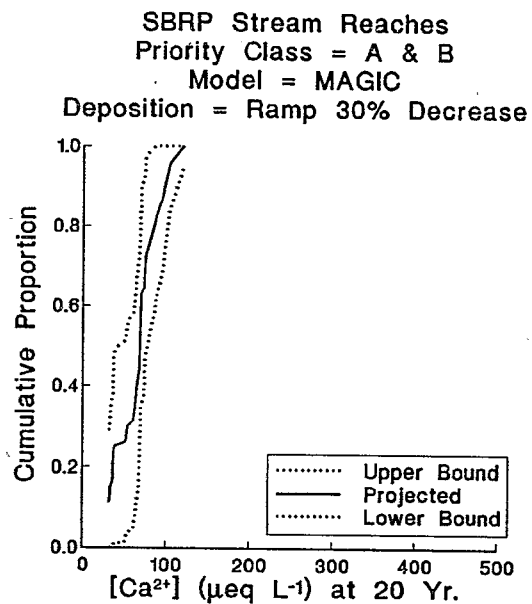
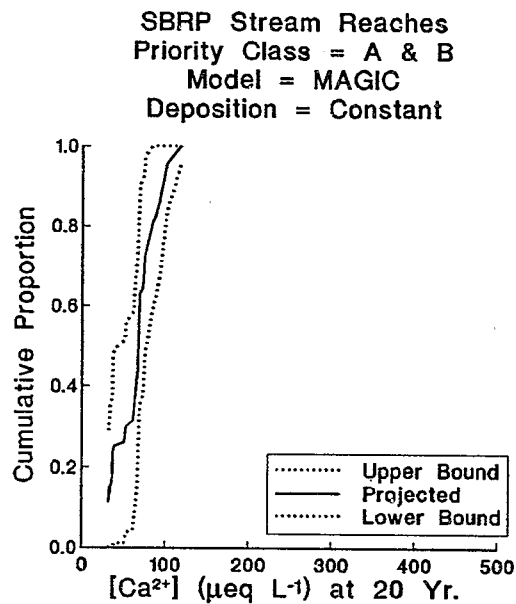


Figure A.3-29. Calcium projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - B streams using MAGIC.

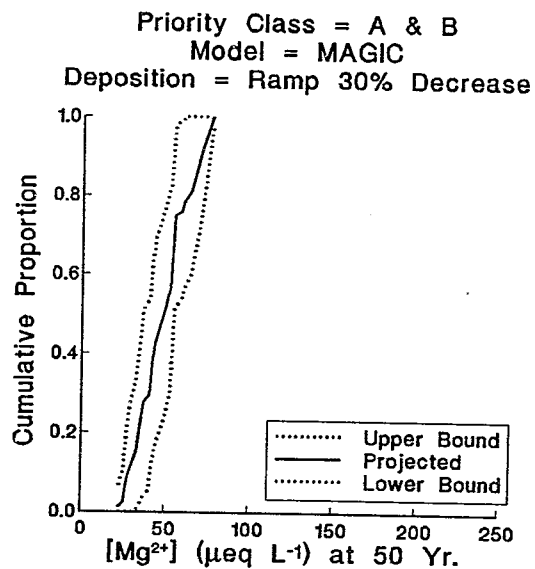
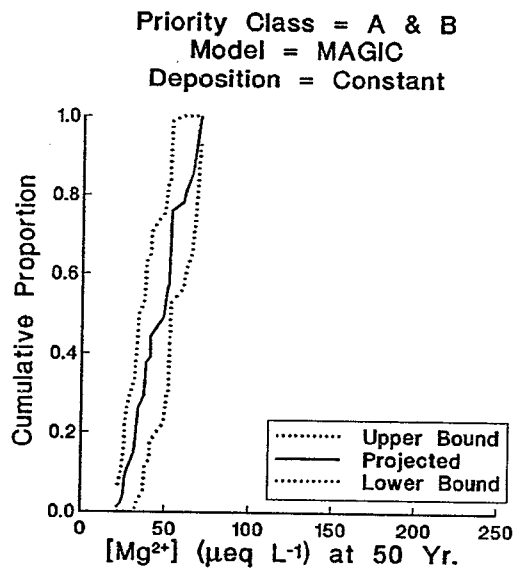
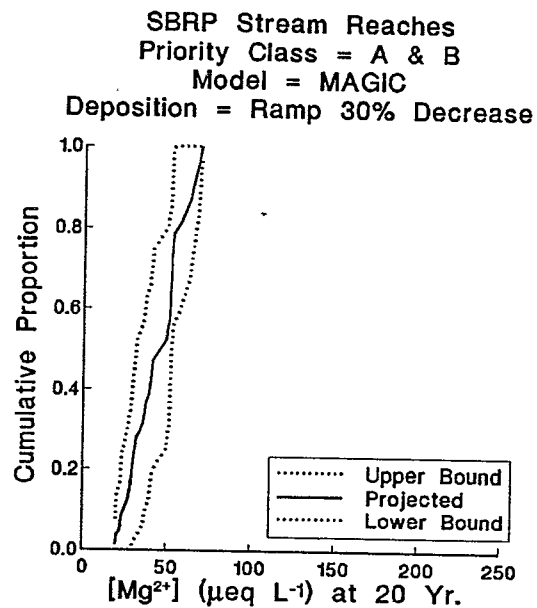
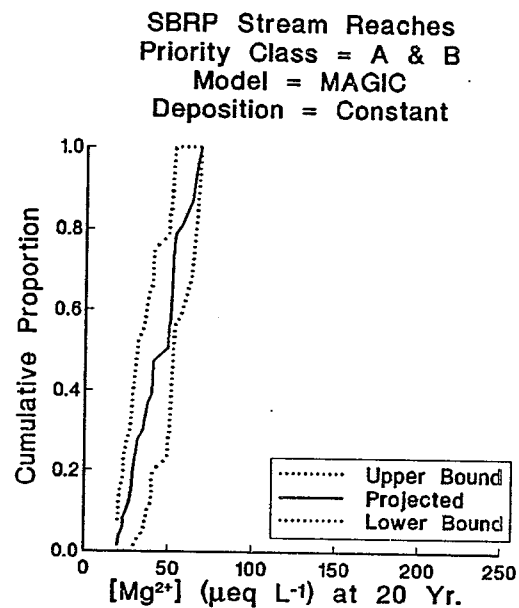


Figure A.3-30. Magnesium projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - B streams using MAGIC.

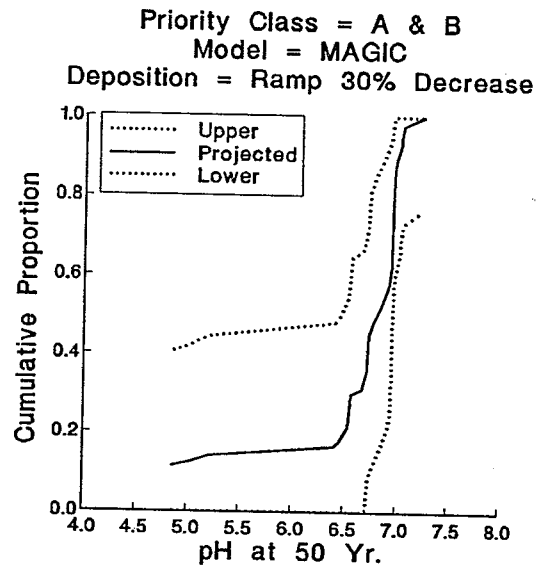
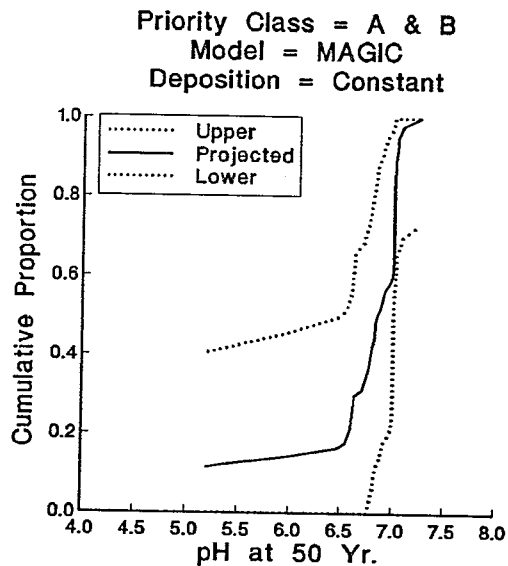
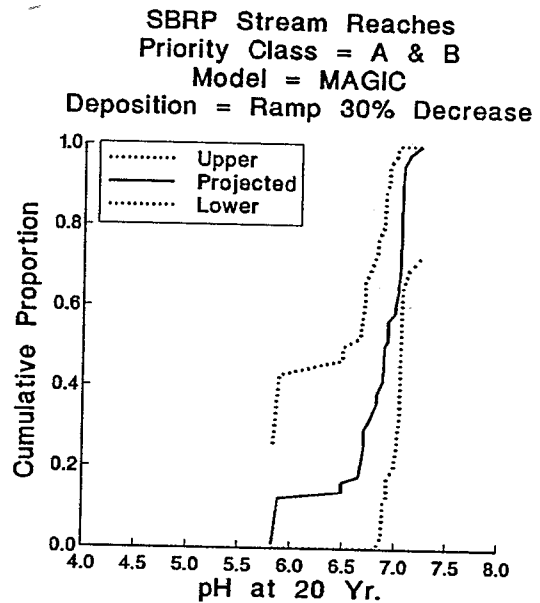
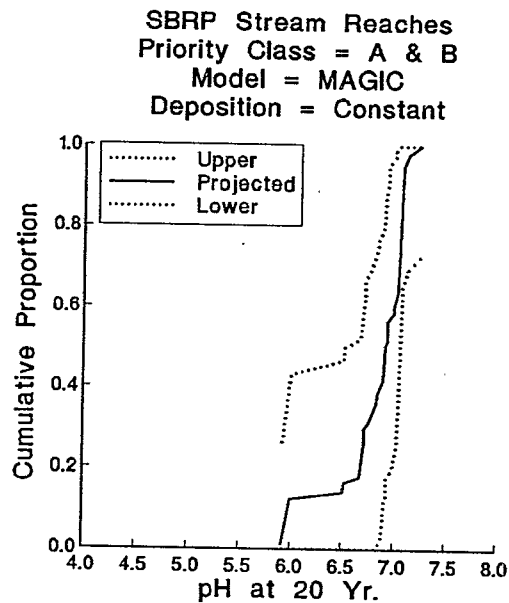


Figure A.3-31. pH projections with upper and lower bounds for a 90 percent confidence interval for SBRP Priority Class A - B streams using MAGIC.