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# Susceptibility of Northern Minnesota Lakes to Acid Deposition Impacts

CLIFFORD J. TWAROSKI, J. DAVID THORNTON, RICK L. STRASSMAN and PATRICK L. BREZONIK

**ABSTRACT**—Lake chemistry surveys indicate a large number of lakes with acid neutralizing capability (ANC) below 200  $\mu\text{eq/L}$  occur in northeast Minnesota where shallow soils over bedrock and exposed rock outcrops predominate, and in moraine areas having rolling to steep topography in north-central and east-central Minnesota. In the Boundary Waters area, lake chemistry is strongly associated with bedrock geology. Lakes with ANC <100  $\mu\text{eq/L}$  are associated with granite, basalt, and gabbro formations, while lakes with ANC of 100-200  $\mu\text{eq/L}$  are associated with slate and greenstone formations. In the rest of the state where soils are deep, landform, soil type, and lake hydrology determine lake chemistry. Most low ANC lakes are found in terminal moraine areas. These lakes are generally small (<40 ha in area), have limited groundwater inflow, and typically classed as precipitation-dominated seepage lakes. Higher ANC lakes (>400  $\mu\text{eq/L}$ ) are often associated with agricultural and residential land uses. Relationships found between ANC and bedrock geology, and between ANC and landform and soils, provided the basis for mapping the distribution of low ANC surface waters in Minnesota.

Empirical and process models used to evaluate the actual susceptibility of low ANC lakes in the Upper Midwest to acid deposition impacts and indicated precipitation pH 4.6-4.7 is a threshold level for lake acidification. Modeling also indicated lakes with ANC <50  $\mu\text{eq/L}$  are very susceptible to acidic inputs and are considered critically sensitive.

At present, no culturally acidified lakes have been found in northeast Minnesota, although acid lakes have been found in north-central Wisconsin (3% of the lake population) and the Upper Peninsula of Michigan (9.8% of the lake population). The Hovland-Grand Marais-Isabella area of northeast Minnesota currently receives precipitation with an annual average pH of 4.7. This area is considered to be on the edge of the "effects area" and is a major focus of the Minnesota Pollution Control Agency's long-term research and monitoring program on lake and stream response to annual and episodic inputs of acids.

## Introduction

Since the late 1970s, acid rain has been recognized as a potential threat to aquatic and terrestrial ecosystems in northeast Minnesota. In 1980 the Minnesota Legislature passed the Acid Precipitation Act, initiating a one-year program coordinated by the Minnesota Pollution Control Agency (MPCA) to research and investigate the phenomenon of acid precipitation as it related to Minnesota. Findings from this study (1) indicated the potential for impacts to occur, and resulted in the passage of the 1982 Acid Deposition Control Act (Minnesota Statutes 116.42-116.45). This Act was the first of its kind in the nation and required the MPCA to broaden its research program to:

- a) identify areas in the state containing resources sensitive to acid deposition (maps published in 1983 and 1985);
- b) adopt an acid deposition standard for the sensitive areas (standard of 11 kg/ha/yr was adopted by the State of Minnesota in August 1986, and is associated with an annual average precipitation pH of 4.7);

- c) establish a control plan, addressing both in-state and out-of-state emission sources, to attain and maintain the standard (the Control Plan was also adopted in August 1986 and contains provisions for reducing sulfur dioxide ( $\text{SO}_2$ ) emissions from in-state sources:
  - 60,000 ton/yr reduction in  $\text{SO}_2$  emissions statewide by 1994
  - reductions in  $\text{SO}_2$  emissions from two power plants by 1990
  - caps utility emissions of  $\text{SO}_2$  at 130 percent of 1984 emissions as of 1990);
- d) ensure that all Minnesota sources subject to the control plan are in compliance by January 1, 1990 (as of this writing, all 1990 deadlines will be met, and it is anticipated statewide  $\text{SO}_2$  emissions will be reduced by more than 60,000 tons/yr by 1994).

This paper summarizes the activities undertaken by the MPCA to accomplish tasks a) and b) listed above. The results of this work provide estimates of the susceptibility of Minnesota's lakes to acid deposition impacts and threshold levels for acidity in precipitation.

## Identification of Areas Containing Sensitive Resources

The sensitivity of aquatic resources has been extensively researched since the mid-1970s. A lake's ability to neutralize strong acid inputs is dependent upon the buffering capabilities of vegetation (2), soils and bedrock in the terrestrial

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watershed (3), the import of alkalinity from upstream sources (4), groundwater inflow (5), and in-lake alkalinity generating processes (6, 7). The relative routing of water through a watershed and the residence time water spends in contact with soils on its way to the lake are major determinants of lakewater chemistry and the sensitivity to acidification by atmospheric deposition (8).

#### *Measure of Sensitivity*

Alkalinity is a common measure of a lake's acid neutralizing capacity (ANC) and the relative sensitivity of lakes to acid deposition (9). Agency staff evaluated the data available to map sensitive areas and selected ANC as measured by alkalinity as the best single indicator of a lake's sensitivity to acid deposition. Based on previous research (10, 11), an index of sensitivity was developed by the MPCA (1, 12) for an assessment of sensitive resources in 1983.

These lake sensitivity criteria were subsequently modified in 1985 to reflect research findings (8) that lakes with ANC  $>200 \mu\text{eq/L}$  would be sufficiently buffered against strong acid inputs (13). The modified sensitivity index was utilized in mapping updates in 1985 and 1987 and reflects the current knowledge of acid deposition impacts on lake systems: 0-100  $\mu\text{eq/L}$  - sensitive; 100-200  $\mu\text{eq/L}$  - potentially sensitive;  $>200 \mu\text{eq/L}$  - nonsensitive.

#### *Review of Sensitive Areas Mapping*

Maps depicting sensitive lake systems have been prepared for various regions of North America, including Minnesota. An established relationship between water chemistry and some watershed descriptor was used to delineate areas containing sensitive lake systems. Bedrock geology has been used to map the occurrence of sensitive lake systems on national, regional, and state scales (9, 10). A more refined approach (3) used surficial soil information in conjunction with bedrock geology to provide a better estimate of sensitive surface waters in the northeast U.S. Others (14) produced a set of criteria for sensitivity mapping that included important contributing factors such as soil chemistry, soil depth and drainage, landform and relief, bedrock geology, and vegetation cover. Utilizing as many parameters as possible (based on the availability and quality of data) would improve the accuracy of sensitivity maps, as would mapping on a local scale. The MPCA's work incorporated a number of watershed factors into the sensitive areas mapping, following closely the recommendation of Cowell *et al.* (14).

#### *Study Areas - Sensitive Areas Mapping*

To determine if a relationship between water chemistry and some watershed descriptor could be established to map the occurrence of low ANC lake systems, four study areas were designated in northeast Minnesota (12): Boundary Waters Canoe Area (BWCA) and adjacent areas in the Superior National Forest; Carlton County; Itasca County; and Crow Wing County. These study areas were considered to be representative of lake chemistry and bedrock and geomorphic settings (landform types) in northern and central Minnesota. The BWCA area is noted for its shallow soils over bedrock, and exposed rock outcrops. The other three study areas contain a variety of glaciated features such as terminal and ground moraines, outwash and lacustrine plains, and drumlin fields. Relationships established between water chemistry and watershed descriptors in the study areas would be easily extrapolated to other parts of northern and central Minnesota.

Regional surveys of lake chemistry data were conducted by the MPCA in 1980 and 1981 (1, 15). Lake data for Carlton, Crow Wing, and Itasca Counties were collected in 1982 (12). Supplemental lake data for the BWCA were obtained from Glass and Loucks (16), while additional lake data for Itasca County was obtained from the Environmental Protection Agency's STORET database.

#### *Water Chemistry - Watershed Parameter Relationships*

Lake data were combined with data resources from the State Planning Agency's Land Management Information Center (LMIC) to provide the best available data for mapping sensitive areas (12). Lake data from the four study areas were associated with soil, bedrock, and watershed information. Maps of each study area were generated by LMIC showing the distribution of sampled lakes. Patterns of lake ANC concentrations were readily apparent.

For the BWCA, potentially sensitive lakes (ANC 100-200  $\mu\text{eq/L}$ ) are associated with slate and greenstone bedrock formations. Sensitive lakes (ANC 0-100  $\mu\text{eq/L}$ ) are associated with gabbro, granite, and basalt bedrock formations. These patterns in lake ANC concentrations are in general agreement with previous predictions for the BWCA area (10). Rapp *et al.* (17) and Brousseau *et al.* (18) also found a strong relationship between lake ANC (sensitivity) and bedrock type in recent quantitative assessments of lakes in northeast Minnesota and the Thunder Bay District of Ontario, respectively.

In mapping sensitive lakes in areas characterized by shallow soils ( $<1 \text{ m}$ ) over bedrock, bedrock type was found to be the integrating watershed factor. As deeper soil areas were encountered in the western and southern edges of the BWCA study area, surficial geology information was needed to predict the presence of low ANC lakes (3, 18).

Maps for Carlton, Crow Wing, and Itasca Counties showed 96 percent of the sampled lakes with ANC  $<200 \mu\text{eq/L}$  were in terminal moraine areas and clustered in specific Minnesota Soil Atlas mapping units (12). Topography in these mapping units is rolling to steep. Soil textures range from loamy sands to loams, with small inclusions of clay soils (12). Examination of additional lake physical and chemical parameters indicated these low ANC lakes are small ( $<40 \text{ ha}$  in area), at relatively high elevations (19), have low conductivity (indicating limited contact with alkaline groundwater) (20), and typically classed as precipitation-dominated seepage systems (5). High ANC lakes ( $>200 \mu\text{eq/L}$ ) are often associated with agricultural and residential land use (8), and outwash and lacustrine plains. These lakes tend to be large ( $>100 \text{ ha}$  in area), have high conductivities (indicating extensive contact with alkaline groundwater) (20), and typically are flow-through systems with large streams entering and leaving them (5).

Similar to other findings (5), precipitation-dominated seepage systems tended to exhibit the lowest ANC of any lake type in the state. For deep soil areas, landform and soil type were the integrating watershed factors. The relationship between low ANC lakes and specific soil types in moraine areas was sufficiently strong to provide the basis for the mapping of areas outside the BWCA. Likewise, the relationship between high ANC lakes and land use was used to classify a large part of the state as containing nonsensitive lakes (12).

#### *Extrapolation and Mapping of Sensitive Areas*

The relationships established between ANC and terrain factors for the study areas were used to map additional areas

of the state. These relationships were incorporated into a sensitivity model (12), along with additional data in the LMIC database (Figure 1). This model was used to select areas of the state geomorphically similar to the study areas. The actual decision to label these areas as containing sensitive, nonsensitive, or potentially sensitive lakes was made by assessing the lake data available for those particular areas and using the sensitivity criteria previously described (Figure 2). The final product is a map of the areas known to contain, and likely to contain, sensitive aquatic resources (Figure 3).

This 1987 map is an update of previous mapping efforts and represents the current state of knowledge on the distribution and extent of poorly buffered waters in Minnesota.

### Lake Susceptibility to Acid Deposition

As a regulatory agency, the MPCA deals with ambient concentration standards for a variety of pollutants set to protect the most sensitive humans from adverse health impacts. An acid deposition standard for lakes was developed in a manner similar to the ambient concentration standards. A deposition standard would limit the amount of acid, in the form of wet sulfate, falling on sensitive lakes and would

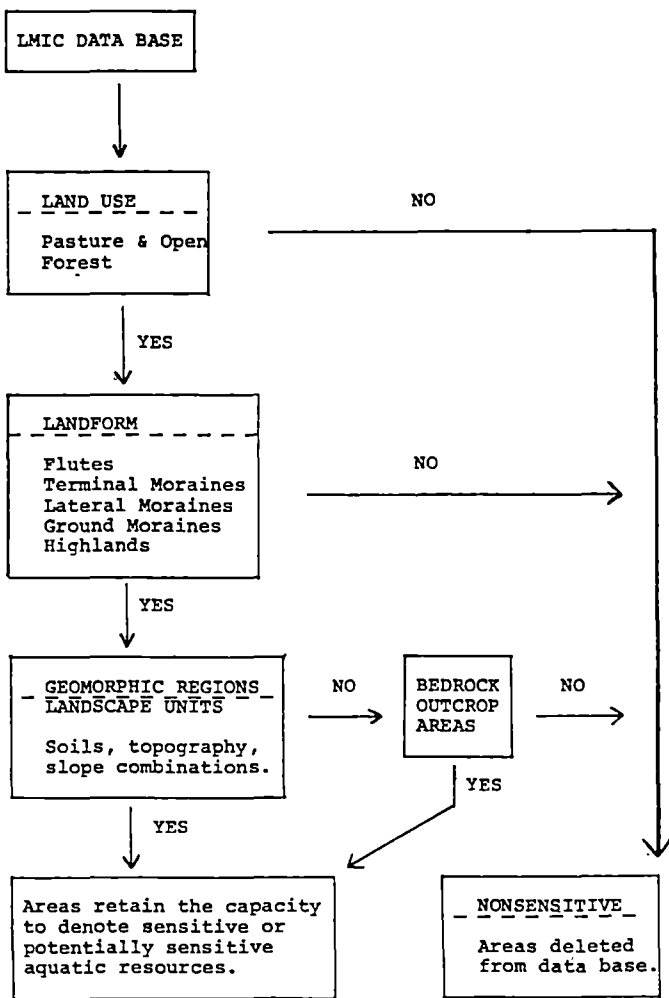


Figure 1. Flow diagram of the model used to select areas in Minnesota containing or likely to contain poorly buffered lakes (alkalinities  $\leq 400$   $\mu\text{eq/L}$ ), utilizing data from the Land Management Information Center (LMIC) at the Minnesota State Planning Agency. [adapted from Twaroski *et al.* (12)]

protect the most sensitive lakes. By protecting these lakes from acid deposition impacts, the MPCA was fairly confident other lakes, and other resources, would also be protected. This approach to developing the standard would also mean a degree of overprotection for some of Minnesota's lakes, at some economic cost. However, due to the nondegradation emphasis of the Acid Precipitation Program, the Agency felt this was an acceptable cost for maintaining the most sensitive lakes in their current chemical and biological condition.

The primary objective in setting an acid deposition standard was to assess the amount of acidification that could occur in Minnesota's lakes at current or increased levels of atmospheric deposition. This was accomplished by using an empirical dose/response model developed for the Upper Midwest (21, 22) and a mechanistic model of lake-watershed acidification (23, 24). In both cases, the most sensitive lake systems were to be assessed: a) flashy hydrographs where water runs quickly through shallow soils down steep slopes to the lake and b) precipitation-dominated seepage lakes (8).

### Empirical Modeling

A large database containing lake and precipitation chemistry data, watershed factors, and lake hydrologic classifications (Figure 4) for the Upper Great Lakes Region was used by Rogalla and Brezonik (22) to develop an empirical model similar to Henriksen (25) and Wright (26). All these models describe the acidification process as a large-scale titration of a bicarbonate lake solution by strong acid from precipitation.

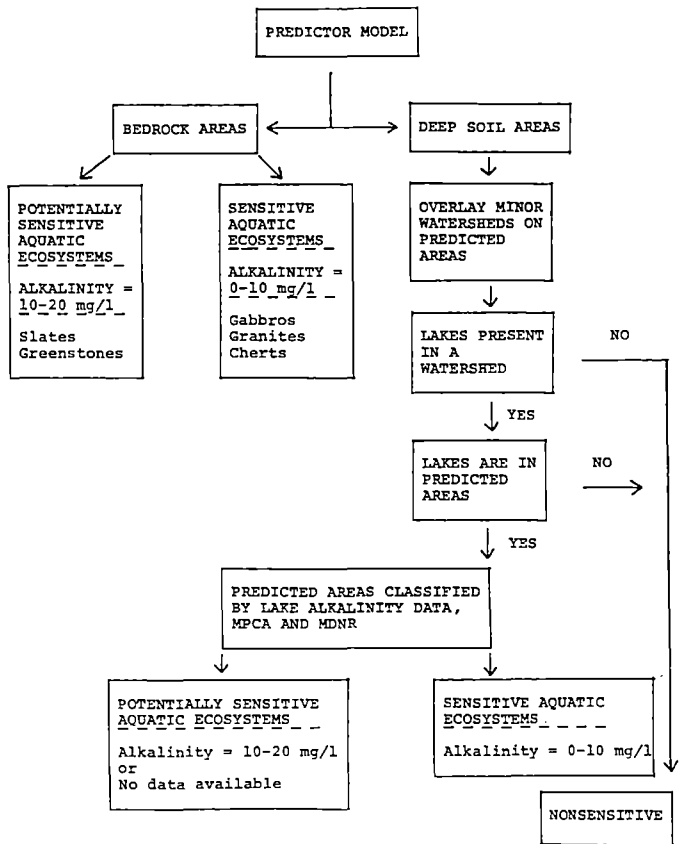
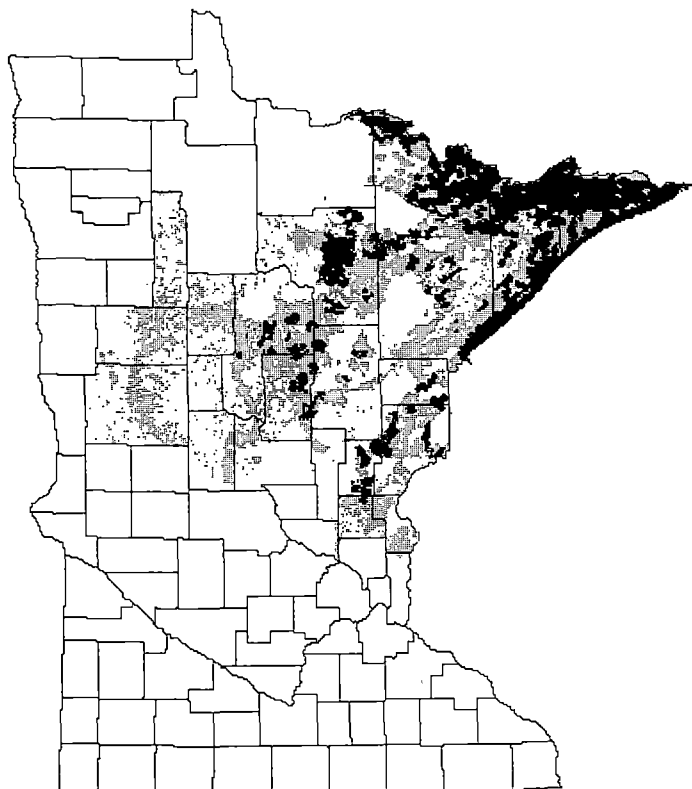


Figure 2. Flow diagram for sensitivity classifications of bedrock and moraine areas (selected by the model described in Figure 1) in Minnesota based on lake alkalinity data. [adapted from Twaroski *et al.* (12)]



Map produced by the Planning Information Center, State Planning Agency. Funding provided by the Minnesota Future Resources Commission.

	AREAS WITH NONSENSITIVE LAKES	19,320,194 ha (87.74%)
	AREAS WITH SENSITIVE LAKES	1,048,518 ha (4.76%)
	AREAS WITH POTENTIALLY SENSITIVE LAKES	1,652,162 ha (7.50%)

Figure 3. Areas in Minnesota estimated to contain lake systems considered sensitive or potentially sensitive to acid deposition (June 1987 update).

Two indicators of lake chemical change were used: loss of alkalinity (ANC) and net increase in sulfate. These indicators were estimated from current lake and precipitation chemistry and used to formulate an empirical model relating them to precipitation acidity.

Another component of the model is the F-factor (weathering factor), the ratio of the change in the sum of base cations to the change in sulfate in lakewater ( $LSO_4$ ). Enhanced mineral weathering in the lake's watershed can increase base cation availability. Increases in  $LSO_4$  would then be compensated with additional base cations, rather than a loss of ANC. F has been estimated to range from 0.2-0.4 for drainage lakes (25, 26) although Henriksen (25) found that most of the  $SO_4$  increase in some lakes resulted in a loss of ANC corresponding to F near 0. This situation would be typical of precipitation-dominated seepage lakes. For Minnesota lakes, a range of F values were used (0, 0.2, 0.4) in the predictive equations to obtain a better estimate of potential acidification impacts.

The predictive model used regression equations that relate a decrease in lake ANC or an increase in sulfate to precipitation acidity (21, Figure 5) and statistically significant

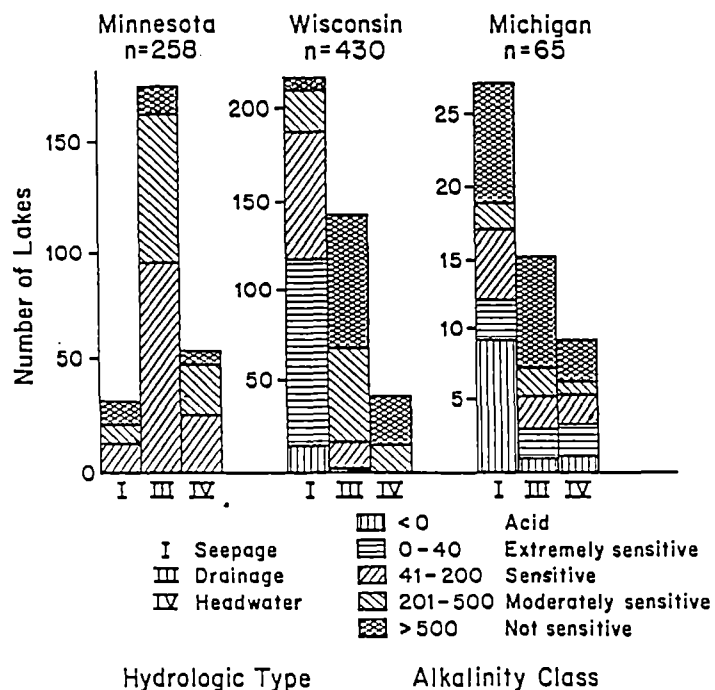


Figure 4. Classification of lakes in Minnesota, Wisconsin and Michigan according to three hydrologic types and distribution of lakes among five ranges of alkalinity. [adapted from Rogalla and Brezonik (22)]

relationships were obtained for seepage lakes. Major findings from this research indicated:

- the acidification threshold for precipitation pH (the pH below which acidified lakes would be expected to occur) is 4.6-4.8;
- lakes with  $ANC < 45 \mu eq/L$  were most susceptible;
- precipitation-dominated seepage lakes ( $F=0$ ) were most sensitive to acid deposition; drainage lakes ( $F=0.2, 0.4$ ) were less sensitive;
- conservative estimates indicated lakes with  $ANC < 60 \mu eq/L$  will become acidified ( $ANC < 0 \mu eq/L$ ) at current levels of precipitation acidity (about 1.5 percent of the lakes sampled in Minnesota). If atmospheric loadings are increased by 50 percent, lakes with  $ANC < 100 \mu eq/L$  would become acidified (about 7 percent of the sampled lakes in Minnesota).

#### Mechanistic Modelling

Schnoor's compartmentalized, time variable "Trickle-down" model (23, 24) was used by the MPCA to assess the sensitivity of individual lakes to acid deposition. The model is based on a mass balance for alkalinity (ANC) in the watershed and lake. A time series of precipitation data, including acidity and dry deposition estimates, is used as input to the model. The hydrologic submodel simulates the rainfall events on the watershed and lake surface and tracks the movement of water from one compartment to the next. Each compartment is modeled as a completely mixed flow-through reactor. At the end of each timestep, the compartment water volumes are updated and used in the mass balance equations of the alkalinity submodel.

Five lakes in northeast Minnesota were selected for study as part of the Agency's Soil and Watershed Acidification Study funded by the Legislative Commission on Minnesota Resources. Moon and Crum lakes are Type I seepage systems with no inlets or outlets (5). Both lakes are situated near major watershed divides and are considered precipitation-dominated (20). Dunnigan lake has an intermittent outlet and is classed as a Type II seepage lake. Meander and Chester lakes are typical of low ANC lakes in the bedrock region of northeast Minnesota. Both have an intermittent inlet and permanent outlet and are classed as Type III (headwater) lakes (5, 27).

A variety of input data for the dynamic model were collected from the study lakes and their watersheds (13). Samples were collected monthly for lake and stream chemistry. Lake stage fluctuations were continuously recorded. Stream flow was measured on a monthly basis with a current meter and correlated with lake stage data to estimate outflow volume for Dunnigan, Chester, and Meander lakes. Recording rain gauges were placed as close as possible to each lake during the open water season. Soil and vegetation surveys were conducted in the watershed of each lake and additional information was obtained from topographic maps, hydrologic atlases, aerial photos, and Forest Service and Soil Conservation Service soil surveys.

A major goal of this work was to simulate long-term acidification of lakes by increasing acid loadings from present-day levels to levels that could occur in the future. Precipitation acidity was increased in successive model runs for each lake to determine the acidification threshold for precipitation pH (pH below which lakes acidify) (Figures 6, 7). Major findings from the predictive modeling studies were:

- Crum lake (ANC of approximately 44  $\mu\text{eq/L}$ ) was much more sensitive than the other four study lakes.
- Based on the Crum lake modeling, the acidification threshold for precipitation pH is 4.6-4.7. Currently, precipitation pH in the Crum lake area is 4.97.

## Modeling Discussion

Both modeling approaches indicate the acidification threshold for precipitation pH is approximately 4.7 for

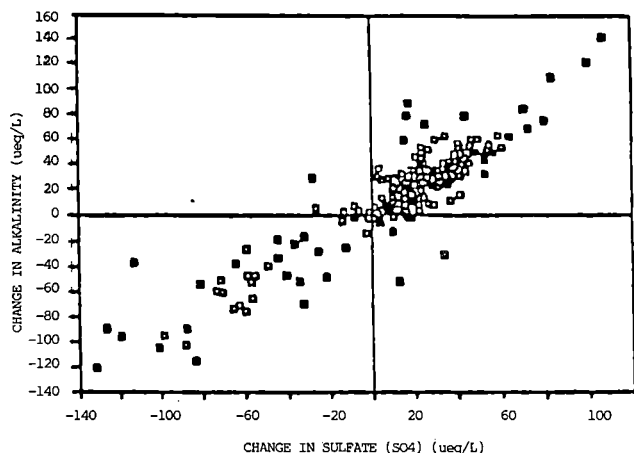


Figure 5. Change in alkalinity versus change in sulfate for seepage lakes contained in the lake database for the Upper Great Lakes Region. Background  $\text{SO}_4$  in precipitation = 20  $\mu\text{eq/L}$ . [adapted from Brezonik *et al.* (21)]

Minnesota lakes. Where precipitation pH is less than 4.6-4.7 on an average annual basis, one can expect to find acidic lakes. This finding is consistent with results obtained from other modeling work for the Upper Midwest (8, 26, 28, 29) and generally agrees with observations of precipitation pH and current numbers of acidified lakes across the northern Lake States, although research in the western portion (30) of the Upper Great Lakes Region indicates acidic inputs from individual storm events may have more influence on lake ANC than annual average precipitation acidity. The modeling work also indicated lakes with ANC < 50  $\mu\text{eq/L}$  (typically precipitation-dominated seepage lakes in the Upper Great Lakes States) are very sensitive to strong acid inputs. These lakes have been classified as critically sensitive (8, 13, 31).

Steady-state model estimates for lake acidification are conservative in that worst case results were used ( $F=0$ , no additional buffering supplied from the watershed to the lake) and internal alkalinity generation was not included in the model (22). Mechanistic modeling results are also conservative for Crum Lake because internal alkalinity generation was held constant rather than being modeled as a first order reaction. As acidity (sulfate) increases in the water column, internal alkalinity generation by sulfate reduction also increases. Because internal alkalinity generation was held constant, the model overestimated acid deposition impacts. In addition, groundwater-lakewater interactions were assumed to be negligible in Crum Lake. Recent studies (32, 33) indicate that even small amounts of groundwater inflow can have a significant influence on a lake's buffering capacity.

## Resources at Risk

Surveys conducted from 1980-1985 (16, 19, 15, 29, 34, 35), have found no culturally acidified lakes in the state. However, a large number of low ANC lakes have been found and the empirical and mechanistic modeling studies indicate they are susceptible to acid deposition impacts.

Acknowledging that the acidification modeling estimates are conservative, the Agency estimated resources at risk in Minnesota (13). As many as 200 lakes were considered critically sensitive to acidic deposition (ANC < 50  $\mu\text{eq/L}$ ), and an additional 1,982 lakes were estimated to be sensitive or potentially sensitive (ANC 50-200  $\mu\text{eq/L}$ ). These sensitive lakes are usually small, less than 40 ha in area, and often classified as precipitation-dominated seepage or headwater lakes. Cook, Lake, St. Louis, and Itasca Counties contain 82 percent of the lakes in the state with ANC < 200  $\mu\text{eq/L}$ ; Aitkin, Carlton, Pine, and Kanabec Counties, 8 percent of these lakes; and Cass, Crow Wing, Clearwater, and Hubbard Counties, 10 percent of these lakes. Although the number of sensitive lakes is considered an overestimate by the Agency, it compares well with statistically derived estimates for Cook, Lake, and St. Louis Counties from the U.S. EPA's Eastern Lake Survey (35) which estimated that 4.7 percent (143 lakes) of the lakes in northeast Minnesota (Voyageurs National Park, Boundary Waters Canoe Area, Superior National Forest) have ANC < 50  $\mu\text{eq/L}$  and 1,124 lakes have ANC < 200  $\mu\text{eq/L}$ . For this same area, the Agency estimates 138 lakes have ANC < 50  $\mu\text{eq/L}$ , and 1,247 lakes have ANC < 200  $\mu\text{eq/L}$ .

## Summary

While no culturally acidified lakes have been found in Minnesota, approximately 2,200 lakes are estimated to be sensitive to acid deposition, with 200 of these lakes consi-

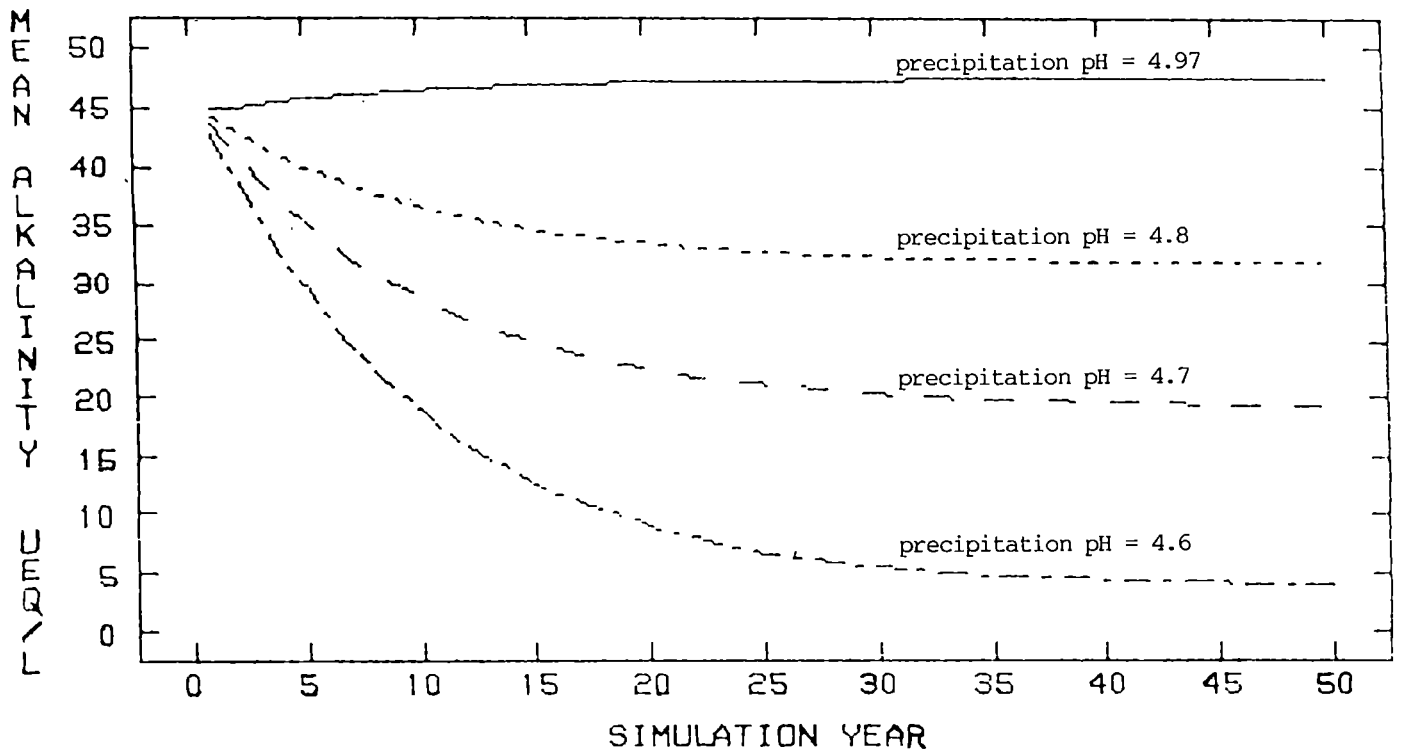


Figure 6. Projected alkalinity values for Crum Lake in response to lowering annual average precipitation pH during 50 year model simulations [adapted from (13)]

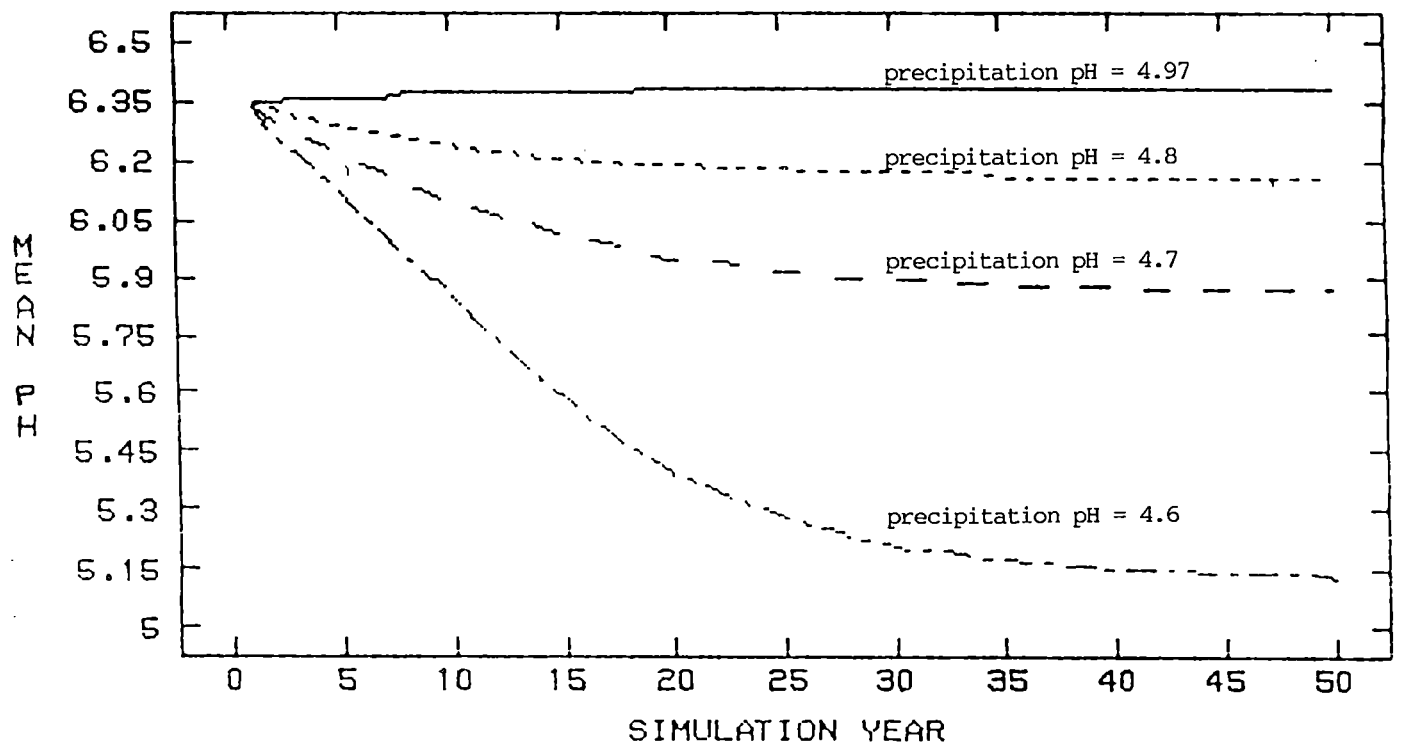


Figure 7. Projected pH values for Crum Lake in response to lowering annual average precipitation pH during 50 year model simulations [adapted from (13)]

dered critically sensitive (ANC <50 µeq/L). The majority of these lakes (82 percent) are found in Itasca, St. Louis, Lake, and Cook Counties.

Modeling results indicate that where precipitation pH is less than 4.6-4.7 on an average annual basis, acidic lakes are found. Lake survey data for the Upper Midwest also provide support for these results as culturally acidified lakes have been found in Michigan (9.8% of the lake population) and north-central Wisconsin (3% of the lake population), but not in Minnesota (35). Annual average precipitation pH ranges from approximately 4.4 in the Upper Peninsula of Michigan to 4.9 in northeast Minnesota.

The Hovland-Grand Marais-Isabella area of northeast Minnesota currently receives annual precipitation with a pH of 4.7 and is considered on the edge of the "effects area." There is concern that lakes, and possibly streams, in this area of the state may be experiencing subtle impacts from acid deposition. To address these concerns, the Agency continues to assess atmospheric inputs to sensitive lakes and their watersheds in the northeast part of the state and has initiated an episodic response project to investigate the impact of acidic snowmelt on trout streams along the North Shore of Lake Superior.

### Acknowledgements

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