

# UNDERSTANDING SIMPLIFIED LAKE ACIDIFICATION MODELS

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## INTRODUCTION AND PURPOSE

During the past 5 to 10 yr, significant interest and concern has centered around lake and impoundment acidification due to acid deposition. A number of analytical models have been developed to examine the degree of acidification in lakes and impoundments. Most of these analytical models are relatively simple, empirical models constructed from historical data of lakes and impoundments.

The purpose of this technical note is to review these models by evaluating their underlying assumptions, demonstrating their merits and pointing out their limitations. It is hoped that this review would assist analysts who would select and use a proper model.

## SIMPLIFIED LAKE ACIDIFICATION MODELS

**Excess Sulfate Method.**—This is called a method instead of a model because it is more a methodology than a modeling framework (2). In lakes experiencing acidification, sulfate replaces bicarbonate as the major anion as the alkalinity level is reduced. The concentration of excess sulfate serves as an indication of the degree of acidification that has occurred (5). The excess sulfate would be the sulfate in excess of that of marine and natural geological origins. The sulfate of marine origin can be estimated from the chloride concentration and the  $\text{SO}_4:\text{Cl}^-$  ratio in seawater. The sulfate of natural origin is more difficult to estimate, especially where there are no historical data. Therefore, this method is more suitable to areas where very little sulfur is supplied by weathering (2). The loss of alkalinity is defined as the difference between pre-acidification alkalinity and present-day alkalinity. In analyzing the chemistry data from 46 acidified lakes in South Norway, Henriksen (5) obtained a good correlation between the loss of alkalinity (in  $\mu\text{eq/L}$ ) and excess sulfate concentrations (in  $\mu\text{eq/L}$ ) (Fig. 1(a)). The least squares regression line in Fig. 1(a) is only slightly below the theoretical line. The theoretical line has a slope of 1 and intercept of 0. A slope lower than unity is interpreted as evidence of acid input. Thus, acidification of freshwater lakes (loss of alkalinity) can be estimated from present-day excess sulfate concentration.

**Pre-acidification Alkalinity Method.**—A direct means to estimate the loss of alkalinity is to determine pre-acidification alkalinity and compare it with present-day alkalinity. Henriksen (6) indicated that a consistent characteristic of acidified water is the replacement of bicarbonate by sul-

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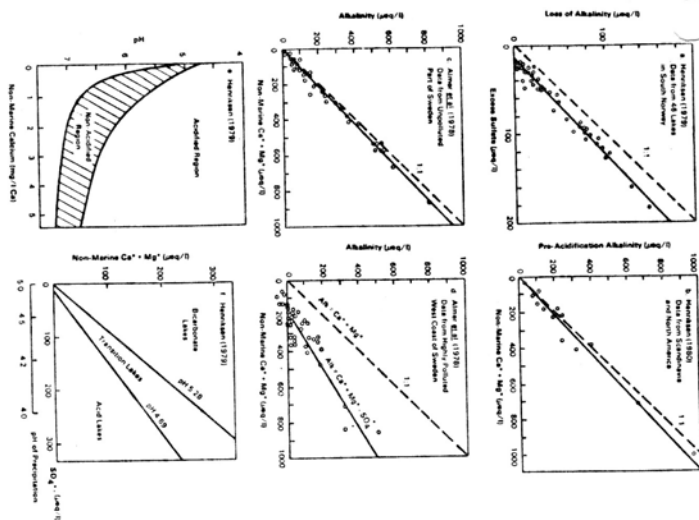


FIG. 1.—Schematic Representations of Empirical Models

late accompanied by little, if any, change in the relative concentrations of cations (e.g., calcium and magnesium). He derived empirical relationships between alkalinity and the sum of non-marine calcium and magnesium using 13 sets of data from Scandinavia and North America involving areas relatively unaffected by acid precipitation at the time of sampling:

$$\text{Pre-acidification Alkalinity} = 0.93(\text{Ca}^* + \text{Mg}^*) - 14 \quad (1)$$

$$\text{Pre-acidification Alkalinity} = 1.23 \text{Ca}^* - 10 \quad (2)$$

where  $\text{Ca}^*$  and  $\text{Mg}^*$  are in  $\mu\text{eq/L}$ . Thus, pre-acidification alkalinity can be estimated from the present-day sum of non-marine calcium and magnesium (Eq. 1), or alternatively, non-marine calcium (Eq. 2). Eqs. 1 and 2 are very easy to use as long as reliable data on calcium and magnesium are available. A graphical representation of Eq. 1 is shown in Fig. 1(b) along with the data that Henriksen used.

While using data from unpolluted Swedish lakes, Almer et al. (1) developed the same correlation between alkalinity (in this case, pre-acidification alkalinity due to its relatively unpolluted status) and the sum

of non-marine calcium and magnesium (Fig. 1(c)).

**Alkalinity versus Calcium and Magnesium Plot.**—Kramer and Tessier (7) derived the analytical basis for the empirical plots of Henriksen (Fig. 1(b)) and Almer, et al. (Fig. 1(c)) as follows:

$$\text{Alkalinity} = 2b[(\text{Ca}^{2+}) + (\text{Mg}^{2+}) - 2(\text{SO}_4^{2-})] \quad (3)$$

$$\text{Alkalinity} = 2b[(\text{Ca}^{2+}) - 2(\text{SO}_4^{2-})] \quad (4)$$

where [ ] indicates the molar concentrations (in  $\mu\text{mole/L}$ ) and  $b$  and  $b'$  are coefficients which characterize the calcium plus magnesium fraction of total cations and the calcium fraction, respectively. The implicit assumptions used by Kramer and Tessier are: (1) There is no input of  $\text{Cl}^-$  from the lake watershed; (2) nitrate and ammonium levels are negligible; and (3) calcium and magnesium are the major cations.

Further simplification of Eq. 3 can be achieved by assuming that sodium and potassium are negligible; therefore,  $b = 1$  and Eq. 3 becomes:

$$\text{Alkalinity} = \text{Ca}^* + \text{Mg}^* - \text{SO}_4^* \quad (5)$$

in which  $\text{Ca}^*$ ,  $\text{Mg}^*$ , and  $\text{SO}_4^*$  are in  $\mu\text{eq/L}$ . Fig. 1(d) shows a plot of Eq. 5 in terms of alkalinity (in  $\mu\text{eq/L}$ ) versus  $\text{Ca}^* + \text{Mg}^*$  (in  $\mu\text{eq/L}$ ) with  $\text{SO}_4^* = 0$  (i.e., pre-acidification or unpolluted condition). Thus, Eq. 5 provides a theoretical basis for the empirical plots in Figs. 1(b) and 1(c).

Almer, et al. (1) also studied a number of lakes in the highly polluted west coast of Sweden. The values of alkalinity and non-marine calcium and magnesium are also plotted in Fig. 1(d). The significant variation from the equivalence line (slope,  $b = 1$  and intercept  $= 0$ ) is an indication of acid input for these polluted lakes. Further, the negative intercept is interpreted as the sulfate content of the lakes.

**pH versus Calcium Model.**—Henriksen (5) suggested that drawing an empirical curve of pH versus calcium could distinguish between acidified and unacidified waters. Henriksen developed such an empirical plot using the data from northern Norwegian lakes that are experiencing acidification (Fig. 1(e)). The surface waters that fall above the empirical curve are generally considered acidified. Since pH is closely related to alkalinity and is easier to measure, the empirical curve represents a logical simplification. This plot can be used to detect the first sign of acidification. A shortcoming of this model is that there may be significant diurnal and seasonal fluctuations in carbon dioxide levels caused by many biological processes such as photosynthesis and respiration and these  $\text{CO}_2$  variations can significantly affect pH measurements. Nevertheless, this model has been widely used by many researchers to assess acidification impacts (7).

**Calcium and Magnesium versus Sulfate Model.**—Working with the hypothesis that acidification of freshwaters can be described as a large-scale titration, Henriksen (6) developed another empirical plot of calcium and magnesium versus sulfate (Fig. 1(f)) using data from small lakes in south Norway whose surface waters have been receiving significant acid inputs. Two lines, with pH 5.3 and 4.7, are shown in Fig. 1(f). Lakes falling above the pH 5.3 line are bicarbonate lakes while those falling below the pH 4.7 line are acid lakes. Lakes lying between these two lines are transition lakes. This empirical plot was verified using a second in-

depend ) set of data. Subsequently, Henriksen added another scale, pH of precipitation (see Fig. 1(f)), obtained from a linear regression between pH of precipitation and sulfate in water. Thus, based on the calcium and magnesium concentrations in the lake and the average pH levels of precipitation, one may use Fig. 1(f) to determine whether a lake is acidified or not. Further, this empirical plot may be used to predict changes in lake pH in response to changes in precipitation pH.

#### SUMMARY

All these models are no more than statements of ionic balance in which many ions are negligible, cancel one another out, or do not contribute to acid-base reactions. First the electroneutrality condition in a lake can be written:

$$[H^+] + [Al^{3+}] + [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+] = [Cl^-] + [SO_4^{2-}] + [NO_3^-] + [HCO_3^-] + \text{organic anions} \quad (6)$$

Assuming there is no input of  $Cl^-$  from the watershed (i.e., subtracting seawater salts and sewage) and neglecting the minor ions 20  $\mu\text{eq/L}$  or less for  $NO_3^-$  and  $NH_4^+$ , one can rewrite Eq. 6 as

$$[H^+] + [Al^{3+}] + [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] = [SO_4^{2-}] + [HCO_3^-] + \text{organic anions} \quad (7)$$

Further,  $Na^+$  and  $K^+$  are usually in small amount and not related to ionic strength and can be neglected. In waters where organic anions are insignificant, Eq. 7 now becomes

$$[H^+] + [Al^{3+}] + [Ca^{2+}] + [Mg^{2+}] = [SO_4^{2-}] + [HCO_3^-] \quad (8)$$

One can rewrite Eq. 8, by introducing alkalinity =  $[HCO_3^-] + [H^+] - [Al^{3+}]$ , in the following form:

$$[Ca^{2+}] + [Mg^{2+}] = [SO_4^{2-}] + \text{alkalinity} \quad (9)$$

Under pre-acidification conditions,  $[SO_4^{2-}] = 0$  and Eq. 9 becomes

$$[Ca^{2+}] + [Mg^{2+}] = \text{alkalinity} \quad (10)$$

Thus, the models described in this paper are basically plots of the parameters in Eqs. 9 and 10.

An application of these graphs to three well studied lakes further confirms the aforementioned observation. Fig. 2 shows these three lakes on Henriksen's calcium plus magnesium versus sulfate plot. Panther Lake (3) is located in the bicarbonate lakes region of Fig. 2 while Woods Lake (3), an acidified lake, is classified as an acid lake. The Bickford Reservoir (4), a moderately acidified lake in central Massachusetts, is classified as a transition lake. These classifications seem to be consistent with field observations for these three lakes.

A few assumptions inherent in the simplified models need to be pointed out. First, all these empirical plots are based on chemical equilibrium assuming steady-state conditions. In reality, a lake rarely reaches a steady-state, but has seasonal cycles for various phenomena. Therefore, these simplified models cannot be used to examine the seasonal variation of

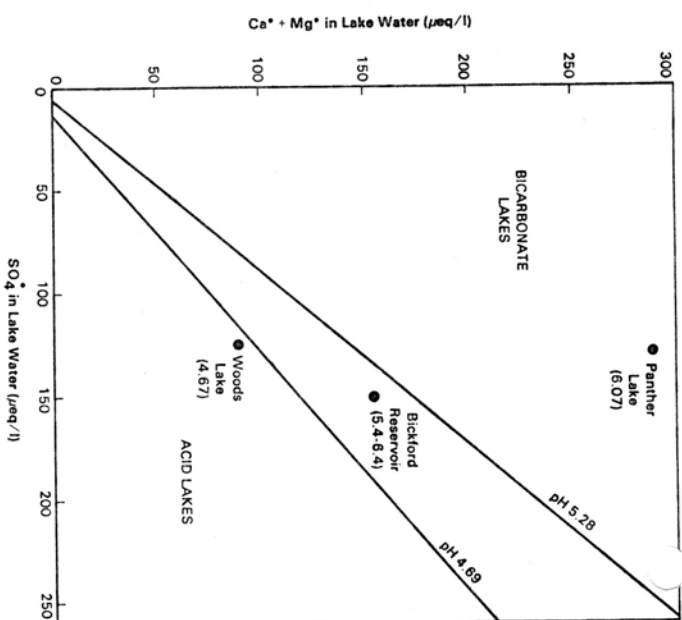


FIG. 2.—Application of Henriksen's ( $Ca^{2+} + Mg^{2+}$  versus  $SO_4^{2-}$ ) Plot to the Selected Lakes (Values in Parenthesis Represent Mean pH Level of Lake)

acidity in lakes. Second, the simplified models treat a lake as a completely mixed water body. This assumption is difficult to meet as many lakes are stratified during summer months and inversely stratified during winter months.

The simplified methods and empirical models as described are very easy-to-use tools to identify lake acidification and to estimate the degree of acidification. On the other hand, such graphs provide no analysis capability beyond the finding that many surface waters can be positioned on the same graph. Without additional information, their predictive capability is highly limited because inferring acidification or the reverse of acidification are not accounted for in the models (7). If significant decisions are to be made as to acidification control (e.g., seasonal liming), more quantitative analysis techniques than these simple models are required.

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#### APPENDIX.—REFERENCES

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