

## A REGIONAL pH-ALKALINITY RELATIONSHIP

M. J. SMALL and M. C. SUTTON

Departments of Civil Engineering and Engineering and Public Policy, Carnegie-Mellon University,  
Pittsburgh, PA 15213, U.S.A.

(Received August 1985)

**Abstract**—An explicit equation relating the pH and alkalinity of natural waters is derived as an inverse hyperbolic sine function. For the range of pH generally encountered in lake and stream acidification studies, the parameters of the equation are related to the dissolved CO<sub>2</sub> saturation relative to atmospheric CO<sub>2</sub> and the concentration of weak acid anions, though the relationship is approximate. The functional form allows for statistical parameter estimation given a regional or temporal pH-alkalinity data-set. The relationship simplifies pH estimation in regional aquatic acidification models where alkalinity is computed as the master variable.

**Key words**—acid deposition, alkalinity, lake acidification, pH, titration

### INTRODUCTION

A number of lake and stream acidification models have been developed to assess the effects of acid deposition on regional aquatic resources (e.g. Chen *et al.*, 1979; Henriksen, 1979; Jones *et al.*, 1982; Arp, 1983; Thompson, 1982; Wright, 1983, 1984; Schnoor *et al.*, 1984; and Schnoor and Stumm, 1984). The range of assumptions and model complexity are reviewed by Galloway *et al.* (1983). In most regional models, material balance calculations are made with titration endpoint alkalinity as the master variable, utilizing electroneutrality relationships and weathering factors. To directly assess biological impacts, however, pH predictions are required.

The pH-alkalinity relationship evolves from the definition of alkalinity which incorporates the hydrogen ion and pH-dependent species. The relationship may be solved analytically over a limited range with appropriate simplifying assumptions, approximated with an explicit empirical function, or solved directly using numerical techniques. In many studies of regional acidification, observations of pH and alkalinity from many lakes or streams are used as a basis for determining the relationship. Although the model is used in a "longitudinal" sense, i.e. to infer temporal changes in pH for individual lakes or streams, "cross-sectional" data are used for model estimation. The use of cross-sectional data to estimate parameters for longitudinal models is common in statistical studies where historical data are lacking. A problem in developing this relationship for regional pH-alkalinity data-sets has been the lack of a simple, yet flexible functional form for estimation. The function proposed in this paper should help to meet this need.

Analytical forms have been used in previous studies to represent regional pH-alkalinity relationships. Thompson (1982) approximates the pH-alkalinity relationship by equating alkalinity to the bicarbonate

ion and assuming equilibrium with a constant partial pressure of atmospheric CO<sub>2</sub>. Wright (1983) uses an empirical relationship between the pH and the logarithm of the bicarbonate ion. Both result in explicit relationships, but are limited in application to non-acid lakes with positive titration endpoint alkalinites. For lakes with negative alkalinity (i.e. negative acid neutralization capacity), the hydrogen ion concentration is estimated from electroneutrality and an assumed relationship between the pH and acid cations such as aluminum. Pfeiffer and Festa (1980) use a variation of the logarithmic relationship which allows for negative alkalinity, but as is the case with Wright, the form is empirical and allows no physical interpretation of parameters.

Jones *et al.* (1982) and Schnoor *et al.* (1984) use iterative numerical solutions of the alkalinity equation in the manner of Stumm and Morgan (1981). In these numerical solutions the carbonic acid is assumed to be in equilibrium with atmospheric CO<sub>2</sub>, and the effects of dissolved organic acids are included. Driscoll and Bisogni (1984) extend the solution method to include the aluminum acid-base system. Numerical solutions are applicable over the entire range of pH and are derived directly from physical and chemical parameters. However, parameter estimation from regional data-sets is difficult when the underlying equation is numerical. The implicit form of the equation (i.e. {H<sup>+</sup>} appears on both sides of the equal sign) is such that it is difficult to evaluate the derivatives of the hydrogen ion concentration with respect to the model parameters. These derivatives are required for many nonlinear estimation procedures. More sophisticated parameter estimation techniques are available, for example, using optimization methods. However, these are difficult to implement, particularly with large data-sets. In practice, numerical models are usually fit to observed data qualitatively, by trial and error.

In this paper we seek an improved, explicit form for the pH-alkalinity relationship. The proposed relationship is a generalized form of the inverse hyperbolic sine function. The function first attracted our attention as an empirical relationship; it appeared to have the proper shape, and could be closely matched to observed data-sets. The accurate fits encouraged us to pursue a more fundamental basis for the relationship—to derive the arcsinh function from the underlying alkalinity equation. As shown in the paper, the derivation does require simplifying assumptions, particularly as regards the effect of weak acids. The derivation is presented first, followed by tests of the relationship with simulated chemical data and application of the solution to temporal and regional data-sets.

#### DERIVATION

Following well established definitions and the notation of Schnoor *et al.* (1984), we begin with the alkalinity:

$$\{A\} = \{HCO_3^-\} + 2\{CO_3^{2-}\} + \{OH^-\} - \{H^+\} + \{B^-\} \quad (1)$$

where

$\{B^-\}$  = molar concentration of organic acid anions or generalized weak base.

The equation is simplified by noting that the concentration of carbonate ion is negligible over the range of pH considered ( $pH \cong 4-8$ ). The remaining pH dependent species are given by:

$$\{HCO_3^-\} = \frac{K_H K_1 p_{CO_2}}{\{H^+\}} \quad (2)$$

where

$K_H$  = Henry's law constant for  $CO_2$  ( $\cong 10^{-1.5}$ ),

$K_1$  = first ionization constant for carbonic acid ( $\cong 10^{-6.3}$ ),

$p_{CO_2}$  = partial pressure of  $CO_2$  ( $\cong 10^{-3.5}$  atm for equilibrium with respect to atmospheric  $CO_2$ ),

and

$$\{OH^-\} = \frac{K_w}{\{H^+\}} \quad (3)$$

where

$K_w$  = ionization constant of water ( $\cong 10^{-14.0}$ ),

and

$$\{B^-\} = \frac{K_A \{C_T\}}{\{H^+\} + K_A} \quad (4)$$

where

$K_A$  = ionization constant of the weak acid,  
 $\{C_T\} = \{HB\} + \{B^-\}$  = total concentration of weak acid.

In the ensuing derivation we assume that the weak acid anion remains unprotonated over the range of pH considered, so that  $\{B^-\}$  is constant. For a typical  $pK_a$  of organic acids equal to 4.4–4.5 (Driscoll, 1980; Schnoor *et al.*, 1984), this approximation is reasonable for most nonacid and slightly acid lakes. However, the assumption is somewhat unsatisfactory in that the fundamental reason for including organic acids in the pH-alkalinity relationship is that titration can occur. Also, as noted by Driscoll and Bisogni (1984), the aluminium acid-base system may play an important role in some lakes, and the appropriate value of  $pK_a$  for this system is probably higher ( $\cong 5.5$ ). As demonstrated later, the assumption does not reduce the flexibility of the resulting relationship for fitting observed temporal or regional data-sets, but limits the direct physical interpretation of estimated parameters. This limitation is further evaluated as the relationship is developed and applied.

Combining equations (1)–(3) and the assumptions that  $\{CO_3^{2-}\} = 0$  and  $\{B^-\}$  is constant, a quadratic equation is obtained for the hydrogen ion concentration:

$$\{H^+\}^2 + (\{A\} - \{B^-\})\{H^+\} - \alpha = 0 \quad (5)$$

where

$$\alpha = (K_H K_1 p_{CO_2} + K_w).$$

Solving for the positive root:

$$\{H^+\} = \frac{(-\{A\} + \{B^-\}) + [(\{A\} - \{B^-\})^2 + 4\alpha]^{1/2}}{2} \quad (6)$$

Equation (6) is not new. It is similar to the quadratic approximation for monoprotic acids given by Stumm and Morgan (1981, p. 141) and arises as a result of ignoring the carbonate ion. We manipulate the solution to a convenient functional form by solving for the pH:

$$pH = a + b \operatorname{arcsinh} \left[ \frac{\{A\} - d}{c} \right] \quad (7)$$

where

$$a = -\log_{10} (\alpha^{1/2}),$$

$$b = 1/\ln 10,$$

$$c = 2 \alpha^{1/2},$$

$$d = \{B^-\}.$$

The parameter  $b$  is constant while  $a$  and  $c$  are related to the  $CO_2$  saturation, and  $d$  is related to the quantity of weak acid.

The inverse hyperbolic sine function is defined as

$$\operatorname{arcsinh} (Z) = \ln [Z + (Z^2 + 1)^{1/2}] \quad (8)$$

and is plotted in Fig. 1. The arcsinh is monotonically increasing, odd [ $\operatorname{arcsinh} (-Z) = -\operatorname{arcsinh} (Z)$ ] and its derivative

$$\frac{d \operatorname{arcsinh} (Z)}{dZ} = \frac{1}{(1 + Z^2)^{1/2}} \quad (9)$$

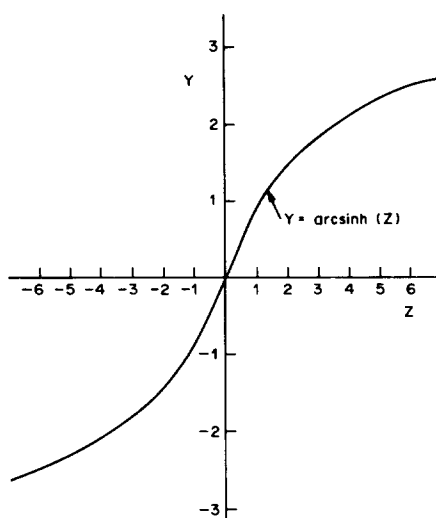


Fig. 1. The inverse hyperbolic sine function.

is maximum at  $Z = 0$ . As noted previously, functional derivatives are used in many nonlinear regression algorithms which are applied when fitting the equation to regional data.

Equations (6) and (7) are equivalent and are plotted for  $\{B^-\} = 0$  and  $p_{CO_2}$  equal to atmospheric

saturation ( $10^{-3.5}$ ) and ten times saturation ( $10^{-2.5}$ ) in Fig. 2(a); and for  $p_{CO_2}$  equal to atmospheric saturation and  $\{B^-\} = 0$  and  $30 \mu\text{equiv l}^{-1}$  in Fig. 2(b). The results with  $p_{CO_2} = 10^{-3.5}$  and  $\{B^-\} = 0$  are equivalent to numerical solutions of equation (1) reported in Stumm and Morgan (1981, p. 181) and Schnoor *et al.* (1984, p. 163) for pH below 8.2, where  $\{CO_3^{2-}\}$  is negligible. Note that if organic anion titration were properly included in Fig. 2(b), the dashed curve ( $\{B^-\} = 30 \mu\text{equiv l}^{-1}$ ) would be shifted to the left at low pH. The effect of this shift on parameter estimation is demonstrated later in the paper by testing the relationship with simulated chemical data.

The arcsinh relationship of equation (7) is preferable to equation (6) in that the arcsinh is easily visualized and nonlinear parameter estimation is more straightforward. In particular, the arcsinh relationship includes a logarithmic transformation of  $\{H^+\}$  to pH, so that regression results are not unduly biased by a few low pH observations. The bias arises from the fact that hydrogen ion concentrations are usually highly skewed, similar to a lognormal distribution. The distribution of pH is usually more symmetric, similar to a normal distribution. The use of a dependent variable with a symmetric normal shape is more consistent with the standard assumptions of statistical estimation.

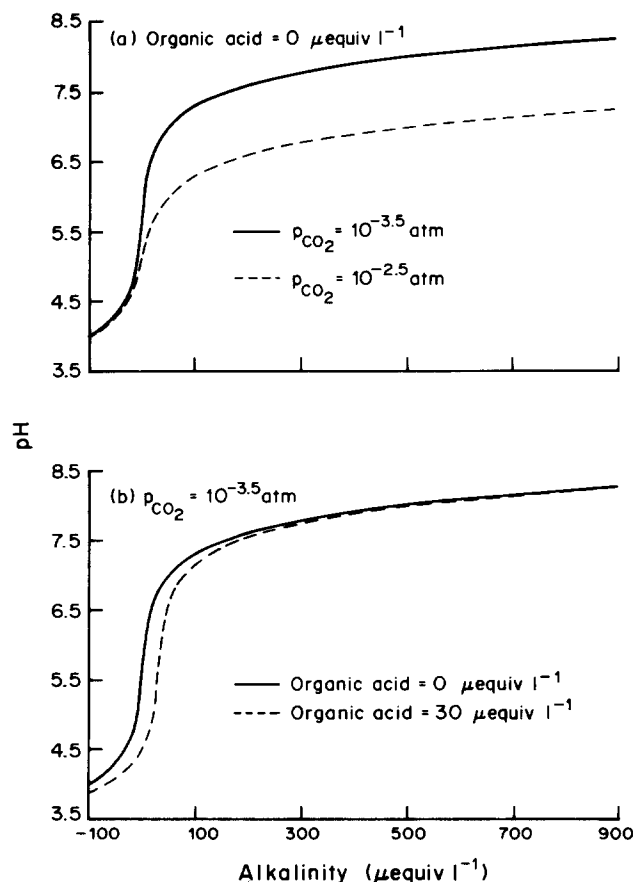


Fig. 2. Effect of  $CO_2$  and weak acid concentration on pH-alkalinity relationship.

### Parameter selection and estimation

Equation (7), as written, includes four parameters:  $a$ ,  $b$ ,  $c$  and  $d$ . Reference to the definitions associated with equation (7), however, indicates that  $b$  is a constant and two parameters,  $a$  and  $c$ , are related through  $\alpha$ . The relationship between  $a$  and  $c$  for units of  $\mu\text{equiv l}^{-1}$  for  $\{A\}$ ,  $c$  and  $d$  is:

$$a = -\log_{10} \left( \frac{c}{2 \times 10^6} \right). \quad (10)$$

As such, an equation can be formed with two physically-based parameters, which, within the limitations of the simplifying assumptions used in the derivation, can be related to  $p_{\text{CO}_2}$  and  $\{B^-\}$ . Combining equations (7) and (10) with the definition for  $b$ , the two parameter form for the relationship is:

$$\text{pH} = -\log_{10} \left( \frac{c}{2 \times 10^6} \right) + \frac{1}{\ln 10} \operatorname{arcsinh} \left[ \frac{\{A\} - d}{c} \right]. \quad (11)$$

The parameters  $c$  and  $d$  in equation (11) are determined from the observed pH-alkalinity data-set with nonlinear least-squares estimation, and  $p_{\text{CO}_2}$  and  $\{B^-\}$  calculated by

$$p_{\text{CO}_2} = \frac{(c \times 10^{-6}/2)^2 - K_w}{K_H K_1} \quad (12)$$

$$\{B^-\} = d. \quad (13)$$

To allow greater flexibility in fitting regional data-sets, a three parameter relationship is also tested. The three parameter equation permits  $a$  and  $c$  to be estimated independently, and is given by

$$\text{pH} = a + \frac{1}{\ln 10} \operatorname{arcsinh} \left[ \frac{\{A\} - d}{c} \right]. \quad (14)$$

The value of  $\{B^-\}$  is again calculated using equation (13), but the  $p_{\text{CO}_2}$  may now be estimated from either  $c$  in equation (12), or from  $a$ :

$$p_{\text{CO}_2} = \frac{10^{-2a} - K_w}{K_H K_1}. \quad (15)$$

As demonstrated in the following section, the three parameter form allows a more accurate empirical

representation of chemical data when an appreciable quantity of weak acid is present.

### Testing the relationships

Two factors are considered in evaluating the effectiveness of the pH-alkalinity relationship developed in this paper. First is the ability of the equations to represent actual chemical data. Second, is the accuracy of the physical parameters inferred from fitting the models. Both factors could be affected by the approximation used for weak acids. To explore the practical impact of the weak acid approximation, the relationships are tested using synthetic chemical data generated with different  $p_{\text{CO}_2}$  and weak acid concentrations.

Synthetic pH-alkalinity data were simulated using equations (1)–(4), for four cases with different values of  $p_{\text{CO}_2}$ ,  $\{C_T\}$  and  $pK_a$ . The two and three parameter forms of the arcsinh relationship were fit to the simulated data using the BMDP nonlinear regression program (Dixon, 1981), and values of  $p_{\text{CO}_2}$  and  $\{B^-\}$  estimated.

The chemical parameters for the four cases and results of the model estimation are summarized in Table 1. The corresponding pH-alkalinity relationships are compared to the simulated data in Fig. 3. Case 1 is a water solution in equilibrium with atmospheric  $p_{\text{CO}_2}$  with no weak acid. The estimated two and three parameter arcsinh relationships are equivalent, closely match the simulated data, and yield accurate estimates for  $p_{\text{CO}_2}$  and  $\{B^-\}$ . Case 2 is a similar example with  $p_{\text{CO}_2}$  equal to two times atmospheric saturation, and successful results are again obtained. The model is thus fully effective for the case where there is no weak acid; both for fitting observed data, and for estimating the value of  $p_{\text{CO}_2}$ .

Case 3 introduces weak acid at a concentration  $\{C_T\} = 30 \mu\text{equiv l}^{-1}$ . The  $pK_a$  is 4.5, representative of organic acids. As indicated in Fig. 3, the two-parameter equation no longer fits the simulated data over the entire range, though the three-parameter equation is accurate throughout. For the two parameter model, the value of  $\{B^-\}$  is slightly underestimated and the value of  $p_{\text{CO}_2}$  overestimated. This is due to the assumption that the weak acid anion

Table 1. Fitted parameters for simulated pH-alkalinity data

Case	True chemical parameters			Two parameter estimates				Three parameter estimates					
	$p_{\text{CO}_2}$ (atm)	$\{C_T\}$ ( $\mu\text{equiv l}^{-1}$ )	$pK_a$	$c^*$	$d^*$	$p_{\text{CO}_2}^\dagger$ (atm)	$\{B^-\}^\ddagger$ ( $\mu\text{equiv l}^{-1}$ )	$a^*$	$c^*$	$d^*$	$p_{\text{CO}_2}$ (atm) †	$\{B^-\}^\ddagger$ §	$\{B^-\}^\ddagger$ ( $\mu\text{equiv l}^{-1}$ )
1	$10^{-3.5}$	0	—	4.5 (0.0)	0.0 (0.0)	$10^{-3.5}$	0.0	5.7 (0.0)	4.5 (0.0)	0.0 (0.0)	$10^{-3.5}$	$10^{-3.5}$	0.0
2	$10^{-3.2}$	0	—	6.3 (0.0)	0.0 (0.0)	$10^{-3.2}$	0.0	5.5 (0.0)	6.3 (0.0)	0.0 (0.0)	$10^{-3.2}$	$10^{-3.2}$	0.0
3	$10^{-3.2}$	30	4.5	8.0 (1.0)	27.8 (2.2)	$10^{-3.0}$	27.8	5.6 (0.0)	7.9 (0.1)	29.0 (0.2)	$10^{-3.0}$	$10^{-3.4}$	29.0
4	$10^{-3.2}$	30	5.5	7.0 (1.0)	21.9 (3.0)	$10^{-2.8}$	21.9	5.6 (0.0)	9.5 (0.5)	18.6 (1.4)	$10^{-3.1}$	$10^{-3.4}$	18.6

\*Asymptotic standard deviations of parameters indicated in parentheses.

†Computed from  $c$  using equation (12).

‡Computed from  $d$  using equation (13).

§Computed from  $a$  using equation (15).

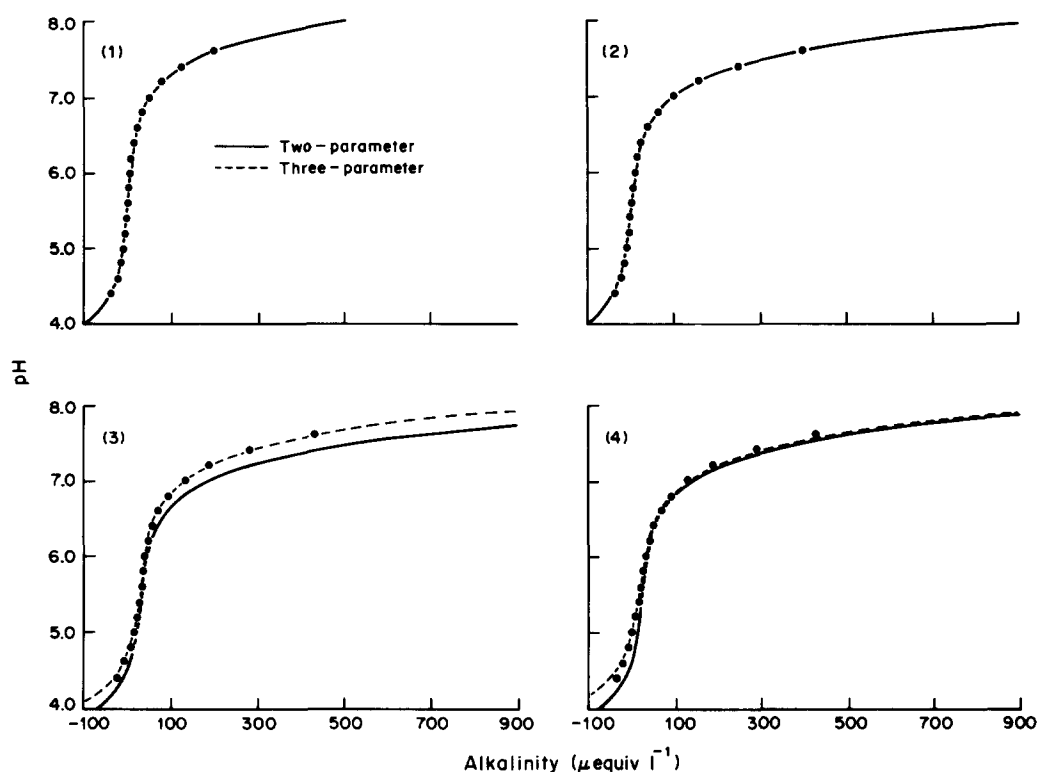


Fig. 3. Fit of pH-alkalinity relationship to simulated chemical data for case 1-4. (See Table 1 for description of cases.)

always remains unprotonated, which improperly ascribes some of the weak acid effect to an elevated value of  $p_{\text{CO}_2}$ . The three parameter model yields two estimates for  $p_{\text{CO}_2}$ , one higher than and one lower than the true value; and  $\{\text{B}^-\}$  is again slightly underestimated.

Case 4 incorporates weak acid with a  $pK_a = 5.5$ , representative of the aluminum acid-base system. The results of the estimations are similar to Case 3, but with more pronounced errors in the estimates of  $p_{\text{CO}_2}$  and  $\{\text{B}^-\}$ . However, as indicated in Fig. 3, the simulated data are still well represented by the fitted equations, particularly with the use of the three parameter model.

The results of these tests suggest that the arcsinh model does provide an effective method for fitting pH-alkalinity data, particularly with the extra degree of freedom provided by the three parameter estimation technique. However, the physical parameters inferred from the model are only approximate, due to the simplifying assumptions employed in the derivation. The quantity of weak acid is systematically underestimated, particularly for higher values of  $pK_a$ . As such, the model may best be classified as semi-empirical, capable of providing accurate fits to observed data, but linked only approximately to underlying physical parameters. The empirical utility of the arcsinh relationship is demonstrated in the following section using actual lake and stream data. The inferred values of  $p_{\text{CO}_2}$  and  $\{\text{B}^-\}$  are also presented, noting the approximate nature of these estimates.

#### APPLICATION TO REGIONAL PREDICTION

Aquatic acidification models are used to predict the change in lake or stream chemistry resulting from a change in acid deposition. The pH-alkalinity equation thus relates the temporal profile of pH to changes in alkalinity for an individual water body. As noted previously, we rely on a relationship determined from cross-sectional (regional) data to predict in a longitudinal (temporal) manner. To address this dual use of the relationship, application of equation (7) to both temporal and regional data-sets is demonstrated.

The chemical data-sets used in the study are summarized in Table 2. The temporal data are from four streams in the Adirondack region of New York sampled during 1980 and early 1981 (Colquhoun *et al.*, 1981). The regional data include observations from the Adirondacks, Denmark, New England and northcentral Wisconsin. The Adirondack and Denmark data were taken from the compilation of Wright (1983). The Adirondack data were originally collected in a June 1975 survey of lakes located above 610 m elevation (Schofield, 1977). The Denmark data were collected by Rebsdurf (1981) between 1977 and 1979. The New England survey was conducted from 1978 to 1981 using headwater sites selected to represent a range of bedrock and soil buffering conditions (Haines and Akielaszek, 1983). The Wisconsin lakes were sampled during the summer of 1979 and included observations from representative hydrologic lake types in the region (Eilers *et al.*, 1979).

Table 2. Data-set summaries

Location	Source	No. observations
<i>Temporal</i>		
Independence River (Grove Road)	Colquhoun <i>et al.</i> (1981)	7
Cold Stream (Arietta)	Colquhoun <i>et al.</i> (1981)	16
West Canada Creek (Upper Access)	Colquhoun <i>et al.</i> (1981)	10
Silver Run (Downstream, Bradley and Cellar Br.)	Colquhoun <i>et al.</i> (1981)	8
<i>Regional</i>		
Adirondacks	Schofield (1977); Wright (1983)	217
New England	Haines and Akielaszek (1983)	211
Denmark	Rebsdorf (1981); Wright (1983)	14
Northcentral Wisconsin	Eilers <i>et al.</i> (1983)	275

All reported alkalinity data used in this study were computed using the Gran titration method (Gran, 1952; Johansson, 1970). In this method, the alkalinity or acidity is determined by linearization of the titration curve. In recent years, the method has been extended to allow a separate identification of the strong and weak acid components of a sample (e.g. Glover and Webb, 1979; Henriksen and Seip, 1980). As noted by Molvaersmyr and Lund (1983), Barnard and Bisogni (1985) and Keene and Galloway (1985), however, this method is subject to error. In particular, the strong acid acidity is systematically overestimated relative to the weak acid acidity, and the total acidity may be overestimated due to the presence of unpurged CO<sub>2</sub> in the sample. It is interesting to note that the underestimation of the weak acid concentration which is inherent to the Gran plot method is also characteristic of the regional-statistical method presented in this paper. In addition, because the negative alkalinity data reported in this section are calculated from strong acidity measurements, the errors in this procedure can affect the results, and should be recognized.

The observed data-sets were fit with the two and three parameter forms of the inverse hyperbolic sine equation using the BMDP program (Dixon, 1981).

Estimated parameters are summarized in Tables 3 and 4 and the predicted equations are compared to the observed data in Figs 4 and 5. The two and three parameter relationships are similar in most cases, and both appear to provide a reasonable representation of the observed data. Significant differences between the two and three parameter predictions are apparent only in small data-sets, such as Silver Run and Denmark, where the three parameter equation generally provides a more accurate representation. Note the reduction in the root mean square error of predicted pH obtained when using the three parameter equation relative to the two parameter equation for the Silver Run and Denmark data-sets.

The values of  $p_{\text{CO}_2}$  and  $\{\text{B}^-\}$  associated with the estimated equations are also of interest. As noted previously, the estimated values of  $p_{\text{CO}_2}$  are likely to be high (particularly for the two parameter estimates in Table 3), and the estimated values of weak acid concentration are likely to be low. This is particularly true for the Independence River and West Canada Creek predictions, where a negative value of  $\{\text{B}^-\}$  is determined. Note that even if  $p_{\text{CO}_2}$  and weak acid activity could be properly estimated for a region, the physical interpretation of these values must be qualified. Values of CO<sub>2</sub> saturation and organic acid

Table 3. Parameters estimated for two parameter relationship

Data-set	$c^*$	$d^*$	RMS error of predicted pH	$p_{\text{CO}_2}$ (atm)	$\{\text{B}^-\}$ ( $\mu\text{equiv l}^{-1}$ )
Independence River	8.3 (0.17)	-3.1 (1.9)	0.006	$10^{-3.0}$	-3.1
Cold Stream	8.6 (0.24)	4.5 (1.9)	0.016	$10^{-2.9}$	4.5
West Canada Creek	10.32 (0.38)	-8.9 (3.7)	0.021	$10^{-2.8}$	-8.9
Silver Run	6.43 (0.59)	9.4 (5.1)	0.057	$10^{-3.2}$	9.4
Adirondacks	9.2 (0.11)	5.6 (1.0)	0.045	$10^{-2.9}$	5.6
New England	11.7 (0.12)	-0.1 (1.6)	0.086	$10^{-2.7}$	-0.1
Denmark	6.5 (0.24)	4.5 (2.1)	0.029	$10^{-3.2}$	4.5
Northcentral Wisconsin	7.1 (0.06)	1.2 (1.2)	0.096	$10^{-3.1}$	1.2

\*Asymptotic standard deviations of the parameters indicated in parentheses.

Table 4. Parameters estimated for three parameter relationship

Data-set	$a^*$	$c^*$	$d^*$	RMS error of predicted pH	$p_{\text{CO}_2}$ (atm)		$\{\text{B}^-\}$ ( $\mu\text{equiv l}^{-1}$ )
					†	‡	
Independence River	5.4 (0.06)	9.0 (0.76)	-1.7 (2.6)	0.006	$10^{-3.0}$	$10^{-2.9}$	-1.7
Cold Stream	5.4 (0.09)	9.2 (1.1)	5.8 (3.0)	0.017	$10^{-3.0}$	$10^{-2.9}$	5.8
West Canada Creek	5.4 (0.13)	11.6 (1.7)	-5.2 (5.5)	0.022	$10^{-3.0}$	$10^{-2.7}$	-5.2
Silver Run	5.8 (0.15)	8.6 (1.7)	17.8 (4.2)	0.015	$10^{-3.7}$	$10^{-2.9}$	17.8
Adirondacks	5.4 (0.03)	9.5 (0.42)	6.2 (1.3)	0.045	$10^{-3.0}$	$10^{-2.8}$	6.2
New England	5.2 (0.05)	10.9 (1.1)	-0.9 (2.0)	0.086	$10^{-2.6}$	$10^{-2.7}$	-0.9
Denmark	5.6 (0.05)	8.3 (0.60)	4.2 (1.4)	0.007	$10^{-3.4}$	$10^{-3.0}$	4.2
Northcentral Wisconsin	5.7 (0.08)	11.1 (1.7)	10.0 (2.5)	0.094	$10^{-3.6}$	$10^{-2.7}$	10.0

\*Asymptotic standard deviations of the parameters indicated in parentheses.

†Computed from  $a$  using equation (15).

‡Computed from  $c$  using equation (12).

activity are dependent on biological productivity, respiration, decomposition, etc. These are not constant over a region, and are expected to vary significantly over time, even at a single location. The same could be said for the activity of other weak bases such as aluminum. As such, the use of a single value of  $p_{\text{CO}_2}$  or  $\{\text{B}^-\}$  for a site or a region is primarily a conceptualization allowing for simplified computation. While it provides some indication of general chemical properties, the characterization is rough. The more important feature of the solution is its ability to match observed regional and temporal

data, and the effectiveness of the model is thus found primarily in its use as an empirical tool, providing simplified, yet accurate representation.

#### CONCLUSIONS

A new functional form is proposed to relate the pH and alkalinity of natural waters. The relationship is applicable to regional or single site data-sets and parameter estimation is relatively straightforward. Simplifications in the derivation limit the physical interpretation of estimated parameters; in particular,

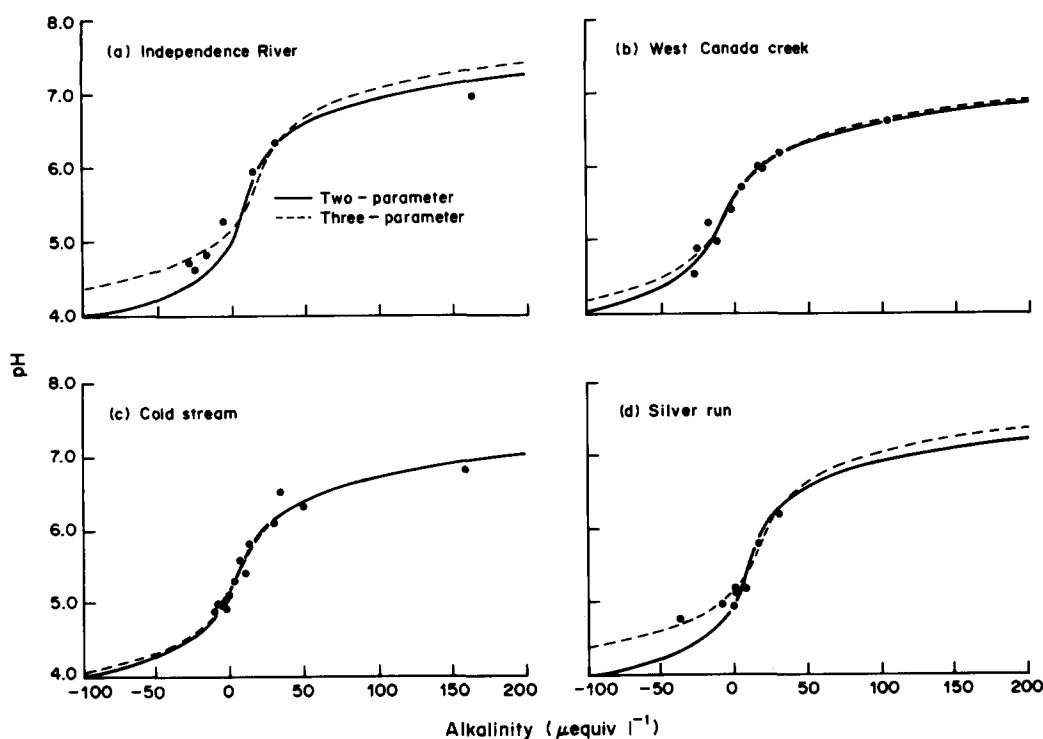


Fig. 4. Fit of pH-alkalinity relationship to temporal data-sets.

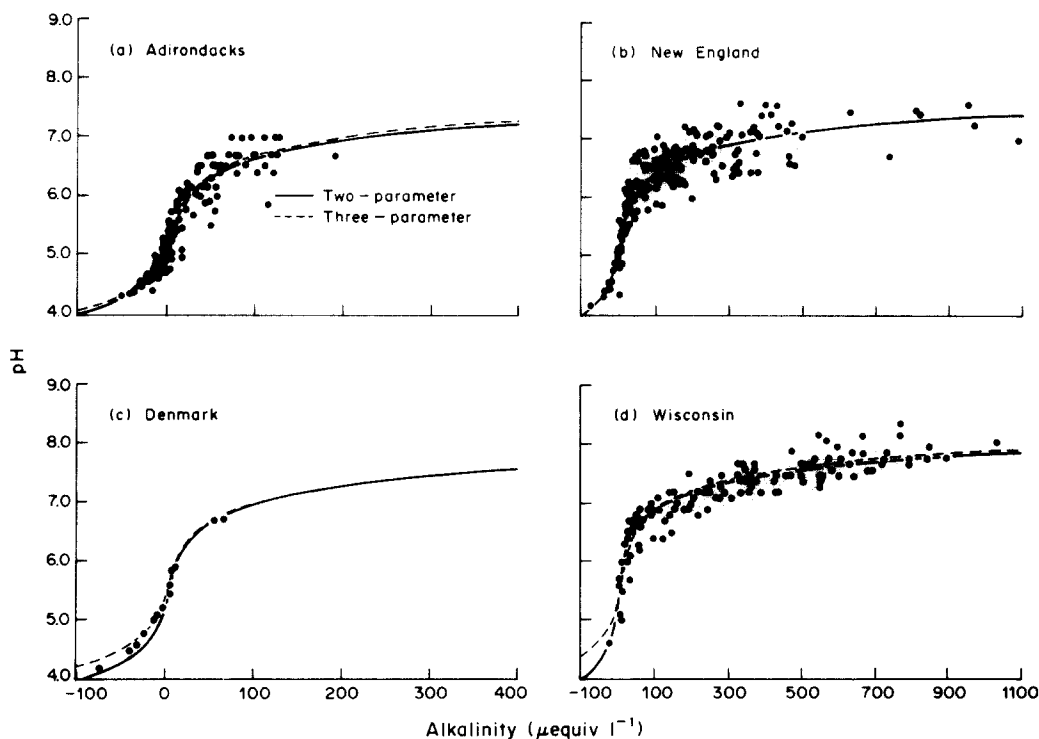


Fig. 5. Fit of pH-alkalinity relationship to regional data-sets.

weak acid concentrations are systematically underestimated. Physical interpretation of estimated parameters is also limited by the fact that the  $p_{\text{CO}_2}$  and weak acid concentration are spatially and temporally variable. However, accurate representations of the pH-alkalinity relationship are still obtained, particularly with the use of the three parameter estimation procedure. As such, the model is appropriate for use as a semiempirical relationship in regional acidification studies; given its origin in basic chemical principles, ease of use, and demonstrated ability to represent observed temporal and regional data-sets.

**Acknowledgements**—This research was supported in part by a grant from the U.S. Environmental Protection Agency as part of the National Acid Precipitation Assessment Program (NAPAP), and funds from the Claude Worthington Benedum Foundation. However, it has not been subjected to NAPAP's required peer and administrative review and therefore does not necessarily reflect the views of NAPAP, and no official endorsement should be inferred. Useful advice and review were provided by Richard G. Luthy. Gary E. Glass assisted in obtaining data for northcentral Wisconsin lakes, and provided helpful discussion. Suggestions provided by anonymous reviewers were also greatly beneficial.

#### REFERENCES

- Arp P. A. (1983) Modelling the effects of acid precipitation on soil leachates: a simple approach. *Ecol. Modell.* **19**, 105–117.
- Barnard T. E. and Bisogni J. J. (1985) Errors in Gran function analysis of titration data for dilute acidified water. *Water Res.* **19**, 393–399.
- Chen C. W., Gherini S. A. and Goldstein R. A. (1979) Modeling the lake acidification process. In *Ecological Effects of Acid Precipitation*, Central Electricity Research Lab, EA-79-6-LD, Electric Power Research Institute, Palo Alto, Calif.
- Colquhoun J. R., Symula K., Pfeiffer M. and Feurer J. (1981) Preliminary report of stream sampling for acidification studies—1980. NYSDEC Technical Report No. 81-2. Division of Fish and Wildlife, Albany, N.Y.
- Dixon W. J. (1981) BMDP Statistical Software, University of California Press, Berkeley, Calif.
- Driscoll C. T. (1980) Chemical characterization of some dilute streams and lakes in the Adirondack region of New York State. Ph.D. dissertation, Cornell University, Ithaca, N.Y.
- Driscoll C. T. and Bisogni J. J. (1984) Weak and acid/base systems in dilute acidified lakes and streams of the Adirondack Region of New York State. In *Modeling of Total Acid Precipitation Impacts* (Edited by Schnoor J. L.), p. 53. Butterworth, Boston.
- Eilers J. M., Glass G. E., Webster K. E. and Rogalla J. A. (1983) Hydrologic control of lake susceptibility to acidification. *Can. J. Fish. Aquat. Sci.*, **40**, 1896–1904.
- Galloway J. N., Norton S. A. and Church M. R. (1983) Freshwater acidification from atmospheric deposition of sulfuric acid: a conceptual model. *Envir. Sci. Technol.* **17**, 541A–545A.
- Glover G. M. and Webb A. H. (1979) Weak and strong acids in the surface waters of the Toval region in S. Norway. *Water Res.* **13**, 781–784.
- Gran G. (1952) Determination of the equivalent point in potentiometric titrations, Part II. *Analyst* **77**, 661–671.
- Haines T. A. and Akielaszek J. (1983) A regional survey of chemistry of headwater lakes and streams in New England: vulnerability to acidification. U.S. Fish and Wildlife Service Eastern Energy and Land Use Team, FWS/OBS-80/40.15.
- Henriksen A. (1979) A simple approach for identifying and measuring acidification of freshwater. *Nature* **278**, 542–545.



- Henriksen A. and Seip H. M. (1980) Strong and weak acids in surface waters of Southern Norway and Southwestern Scotland. *Water Res.* **14**, 809–813.
- Johansson A. (1970) Automatic titration by stepwise addition of equal volumes of titrant. *Analyst* **95**, 535–540.
- Jones M., Marmorek D. and Staley M. (1982) Acid precipitation in eastern Canada: an application of adaptive management to the problem of assessing and predicting impacts on an extensive basis. Report for Canada Department of Fisheries and Oceans by ESSA Ltd, Vancouver, B.C.
- Keene W. C. and Galloway J. N. (1985) Gran's titrations: inherent errors in measuring the acidity of precipitation. *Atmos. Envir.* **19**, 199–202.
- Molvaersmyr K. and Lund W. (1983) Acids and bases in fresh-water. Interpretation of results from Gran plots. *Water Res.* **17**, 303–307.
- Pfeiffer M. and Festa P. J. (1980) Acidity status of lakes in the Adirondack region of New York in relation to fish resources. NYSDEC publication, Albany, N.Y.
- Rebsdorf A. (1981) Danish lakes threatened by acidification, Report 38, Denmark Ministry of Environment, Copenhagen, Denmark.
- Schnoor J. L. and Stumm W. (1984) Acidification of aquatic and terrestrial systems. In *Chemical Processes in Lakes* (Edited by Stumm W.). Wiley-Interscience, New York.
- Schnoor J. L., Palmer W. D. Jr and Glass G. E. (1984) Modeling impacts of acid precipitation for northeastern Minnesota. In *Modeling of Total Acid Precipitation Impacts* (Edited by Schnoor J. L.), p. 155. Butterworth, Boston.
- Schofield C. L. (1977) Acidification of Adirondack lakes by acid precipitation: extent and magnitude of the problem. U.S. Fish and Wildlife Service, Fed. Aid Fish Restoration Project F-28-R.
- Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry*, 2nd edition. Wiley-Interscience, New York.
- Thompson M. E. (1982) The cation denudation rate as a quantitative index of sensitivity of eastern Canadian rivers to acidic atmospheric precipitation. *Wat. Air Soil Pollut.* **18**, 215–226.
- Wright R. F. (1983) Predicting acidification of North American lakes. Norwegian Institute for Water Research, Acid Rain Research Report 3/1983, Oslo, Norway.
- Wright R. F. (1984) Norwegian models for surface water chemistry: an overview. In *Modeling of Total Acid Precipitation Impacts* (Edited by Schnoor J. L.), p. 73. Butterworth, Boston.