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Analysis of Historic Lake Alkalinity and pH Data: An Application of Chemical Adjustment Techniques[†]

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The relationship between acid loading and lake pH or alkalinity response is exceedingly difficult to quantify *a priori*. One method is obviously the comparison of data taken in the 1920's or 1930's. Changing analytical methods, however, dictates that older data must be examined in detail. In this work we briefly review chemical principles that should be applied when "redundant" data is available, that is, pH, alkalinity, and acidity. These techniques are applied to water quality data collected during 1925–1941 for low conductivity lakes in northern Wisconsin, U.S.A. The magnitude of corrections is also discussed.

KEY WORDS: Alkalinity, acidity, water quality data, pH-measurements, lake water.

INTRODUCTION

While there still is considerable uncertainty about the absolute magnitude, most investigations clearly show that anthropogenic

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emissions of SO_x and NO_x contribute to excess acidity in precipitation in many regions of eastern North America.^{1, 2, 3, 4, 5} The decreased pH in precipitation in New England and New York, for example, seems to have occurred before the mid-1950's since no significant change is evident after this time period.⁵ Such observations seem to be in reasonable accord with trends in SO_x and NO_x emission patterns in north eastern U.S. Historical data on pH in precipitation for the southeastern, midwestern, and western parts of the U.S. give a picture which is more ambiguous. However, Turk⁵ concludes "...available data indicate that precipitation at individual sites has been acidified by anthropogenic emissions".

Several reports now also exist which attempt to demonstrate that lakes and rivers in areas receiving low pH precipitation have been acidified.^{3, 4, 5} The degree of surface water acidification as it relates to acid loading has, however, been difficult to quantify. A common approach has been to use conceptual geochemical models such as those of Henriksen,^{6, 7} Dickson,⁸ Galloway *et al.*⁹ The complexity of geochemical, biological, and hydrological processes, however, dictates that these models should only serve as a "first-cut" evaluation step.⁴ Kramer and Tessier¹⁰ have argued that it is exceedingly difficult to provide unambiguous and quantitative acid impact assessments with conceptual models.

Perhaps the most straightforward impact assessment procedure is afforded by trend analysis of appropriate chemical indicators, i.e. pH and alkalinity. Such attempts have been published by for example, Schoefield¹¹ and Smith and Alexander.¹² These procedures also have inherent problems due to changing analysis techniques and, most importantly, lack of appropriate data bases. Any interpretation as to causes must also involve such factors as length of records, natural variability of chemicals, watershed land use changes, and climatic and hydrologic variations.

Kramer and Tessier¹⁰ have recently discussed how to circumvent some of the methodological problems, given redundant data, i.e. alkalinity, acidity, and pH. Very few pre-1950's data bases seem to be available containing all three measurements. We have recently completed an examination of historic lake chemistry data stored in University of Wisconsin Archives. During the 1925-1941 period Birge, Juday, and their co-workers collected water quality data for over 600 northern Wisconsin lakes. A large number of these lakes

have low conductivity waters of low buffering capacity (less than $100 \mu\text{eq/L}$) and may thus be sensitive to acid loadings because the present annual average precipitation pH is 4.6–4.8.¹³

In this work we briefly review the principles for correcting old alkalinity and colorimetric pH data. We then describe the data base and discuss how the parameters were determined. Our final discussion deals with an analysis of the type and magnitude of corrections that must be applied to these data before they can be compared with present day electrometric determinations.

THEORY

The fundamental principles involved in understanding the inorganic carbon cycles in natural waters have been reviewed in detail by, for example, Stumm and Morgan¹⁴ and Kramer and Tessier.¹⁰

Alkalinity is defined from the ion balance condition on H_2CO_3 and its hydrolysis products:

$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]. \quad (1)$$

Acidity may also be defined from the ion balance condition of the neutral bicarbonate salt:

$$[\text{CO}_2 - \text{Acy}] = [\text{H}_2\text{CO}_3] + [\text{H}^+] - [\text{CO}_3^{2-}] - [\text{OH}^-]. \quad (2)$$

The addition of (1) and (2) gives the total inorganic carbon concentration $-C_T$:

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = [\text{Alk}] + [\text{CO}_2 - \text{Acy}]. \quad (3)$$

For pH-values less than 7 Eqs. (1), (2) and (3) may be simplified to:

$$[\text{Alk}] = [\text{HCO}_3^-] - [\text{H}^+] \quad (4)$$

$$[\text{CO}_2 - \text{Acy}] = [\text{H}_2\text{CO}_3] + [\text{H}^+] \quad (5)$$

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-]. \quad (6)$$

With appropriate substitutions and elimination of negligible terms, Kramer and Tessier¹⁰ show that, at the respective equivalence points of $[\text{H}^+]_a$ and $[\text{H}^+]_b$, one obtains:

$$[\text{H}^+]_a = \sqrt{C_T K_1} - K_1/2 \quad (7)$$

$$[\text{H}^+]_b = \sqrt{K_1(K_2 + K_w/C_T)}. \quad (8)$$

In practice, the equivalent endpoints where alkalinity and CO_2 -acidity equal zero, are obtained by titration. Alkalinity is obtained by titrating a sample of volume V_s with v_a ml of strong acid of concentration C_a eq/L. CO_2 -acidity is similarly determined by titrating V_b ml of strong base of concentration C_b eq/L to $[\text{H}^+]_b$.

Modern alkalinity and acidities are usually obtained via the Gran method, whereas older determinations were accomplished with indicators, such as methyl orange (MO) and phenolphthalein. Such indicators imparted their own contributions to the hydrogen ion balance and "true" $[\text{H}^+]_a$ and $[\text{H}^+]_b$ endpoints were often not measured. Alkalinity and CO_2 -acidity measured to a different endpoint, $[\text{H}^+]_x$, may be corrected to the correct endpoints via:

$$[\text{Alk}] = [\text{Alk}]_x + [\text{HCO}_3^-] - [\text{H}^+]_x \quad (9)$$

$$[\text{CO}_2 - \text{Acy}] = [\text{CO}_2 - \text{Acy}]_x + [\text{H}^+]_x + [\text{H}_2\text{CO}_3]_x \quad (10)$$

where the subscript x indicates the concentration at $[\text{H}^+]_x$. Kramer and Tessier¹⁰ have shown that Eqs. (9) and (10) may be expressed as:

$$[\text{Alk}] = \text{Alk}_{\text{MO}} + \frac{C_t([\text{H}^+]_{\text{MO}}K_1 + 2K_1K_2)}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_2} + \frac{K_w}{[\text{H}^+]_{\text{MO}}} - [\text{H}^+]_{\text{MO}} \quad (11)$$

and

$$\begin{aligned} [\text{CO}_2 - \text{Acy}] = & [\text{CO}_2 - \text{Acy}]_p + \frac{C_t([\text{H}^+]_p^2 - K_1K_2)}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2} \\ & + [\text{H}^+]_p - \frac{K_w}{[\text{H}^+]_p} \end{aligned} \quad (12)$$

where C_t = total carbonate, Alk_{MO} = alkalinity determined by MO-titration, K_1 and K_2 are first and second carbonic acid dissociation constants, and $[\text{CO}_2 - \text{Acy}]_p$ = acidity determined using the phenolphthalein indicator. $[\text{Alk}]$, $[\text{CO}_2 - \text{Acy}]$, and C_t may then be calculated in an iterative fashion using Eqs. (3), (11) and (12). These authors also recommend values of $10^{-6.34}$, $10^{-10.33}$, $10^{-14.00}$, $10^{-4.04}$ and $10^{-8.25}$ for K_1 , K_2 , K_w , $[\text{H}^+]_{\text{MO}}$ and $[\text{H}^+]_p$, respectively. Indications for our historic data base indicate that an appropriate value for $[\text{H}^+]_{\text{MO}}$ is $10^{-4.2}$.

While modern pH data usually are determined with electrometric techniques, historic data was determined with indicators. These dyes also influence the $[\text{H}^+]$ and procedures must be developed that take into account the dissociation constant of the indicator, K_c , concentration and volume of indicator, as well as volume of sample. If $[\text{H}^+]$ is the "true" value and $[\text{H}^+]_c$ is the colorimetric value, Kramer and Tessier¹⁰ showed that, if one assumes that addition of indicator does not change C_t , a quadratic equation may be derived. That is:

$$\begin{aligned} &[\text{H}^+]^2 + ([\text{Alk}] + K_1)[\text{H}^+] - ([\text{H}^+]_c + K_1)/V[\text{H}^+]_c(V_1 + v_1) \\ &\quad - V_1 K_c [\text{Alk}] / ([\text{H}^+]_c + K_1) + V[\text{Alk}] \\ &\quad + C_1 v_1 [\text{H}^+]_c / ([\text{H}^+]_c + k_c) = 0 \end{aligned} \quad (13)$$

where V = volume of sample, v_1 = volume of indicator added, C_1 = concentration of indicator solution, and K_c = dissociation constant for indicator. Data for these parameters were readily available in laboratory and field notebooks.^{14, 15}

Thus the pH_c/Alk couple may be used, together with the appropriate dissociation constants and methods to obtain a "corrected" pH. Using similar arguments, it is also possible to derive equations for the $\text{Alk}/\text{CO}_2 - \text{Acy}$ and $\text{pH}_c/\text{CO}_2 - \text{Acy}$ couples, i.e. for $\text{Alk}/\text{CO}_2 - \text{Acy}$:

$$[\text{H}^+]^2 + (K_1 + [\text{Alk}])[\text{H}^+] - K_1[\text{Acy}] = 0 \quad (14)$$

and for $\text{pH}_c/\text{CO}_2 - \text{Acy}$:

$$[\text{H}^+]^2 + [\text{H}^+]([\text{Acy}]K_1/[\text{H}^+]_c - (V + v_c)([\text{H}^+]_c + K_1)/V - C_c v_c) \\ ([\text{H}^+]_c + K_1)/V([\text{H}^+]_c + K_c) + K_1 - [\text{Acy}]K_1 = 0 \quad (15)$$

These equations are easily solved with microcomputers with appropriate data input.

MATERIALS AND METHODS

The data base has already been described in some detail by Eilers *et al.*¹³ and Juday *et al.*¹⁶ One hundred and sixty-one lakes were chosen because of good data bases and because they were of the seepage type or possessed waters of low conductivity. According to archived records,¹⁵ nearly all samples were collected with a Kemmerer water sampler during summer seasons (1925–1941). Soda pop bottles were used for storage and pH and alkalinity were usually determined within 24 hrs. Alkalinity was determined by titrating a 100 ml water sample with 1/44 N HCl with methyl orange to a faint pink end point. Recent duplications of the above method¹³ indicate that a correction of 63 $\mu\text{eq/L}$ must be made on these alkalinity measurements. This is a smaller correction than that recommended by Kramer and Tessier¹⁰ (81 $\mu\text{eq/L}$). This is mainly due to the different endpoints used by Birge and co-workers.¹⁵

The pH was measured using a LaMotte colorimeter for data presented here. The indicators most commonly used were cresol red, bromothymol blue, chlorophenol red, and methyl red. Solution concentrations and dissociation constants for these dyes are shown in Table I.

In our analysis of 161 lakes, we first computed the alkalinity by using $[\text{H}^+]_a = 10^{-4.2}$ M for each sample (all in all about 500 measurements). The acidity was calculated assuming a phenolphthalein $[\text{H}^+]$ endpoint of $10^{-8.25}$. The corrected alkalinity and acidity data were then used with Eqs. (14) and (15). Following Kramer's¹⁷ scheme historical data is considered superior if the standard deviation on alkalinity measurements are better than 50 $\mu\text{eq/L}$ and if pH agrees within 0.2 pH units for $\text{pH} < 5$ and with

TABLE I
Properties of dyes used in pH comparators^a

Dye	Comparator range	Conc. (mmol)	pH _c
Cresol red	7.2–8.8	1.13	8.3
Bromothymol blue	6.0–7.6	0.64	7.0
Chlorophenol red	4.8–6.4	0.95	5.98
Methyl red	4.2–6.3	0.19	5.05

^aFrom Kramer¹⁷

0.5 for pH > 5. For the purpose of presentation and discussion each corrected alkalinity and pH are then averaged for each lake.

RESULTS AND DISCUSSION

The corrections applied in this procedure apply only if no other protolytes are important. The historic data base does not contain information on other protolytes. Kramer¹⁷ has discussed the relative effects of typical monoprotic organic acids and concluded that the total concentration must approach C_T if an effect is to be observed. In the lakes chosen for this study recent data indicate that organic anion concentrations are low. We thus assume that the chemical principles derived above describe the system.

A preliminary analysis of the data set indicate that, of the 161 lakes considered, approximately 129 lakes possess "superior" quality data. Most of the rejection of the pH was due to problems with pH_c.

Perhaps of most interest is the magnitude of pH corrections. These are exhibited in histogram form in Figure 1. Both positive and negative corrections in the pH data result. Corrections range from +0.60 to -1.26 pH units. Haines *et al.*¹⁸ report that the best precision one can expect with colorimetric techniques is about ±0.2 pH units. This precision is achieved if the determination is made at the midpoint of indicator ranges shown in Table I.

We conclude that colorimetric pH and alkalinity data must be corrected before comparisons with recent data can be made. Our

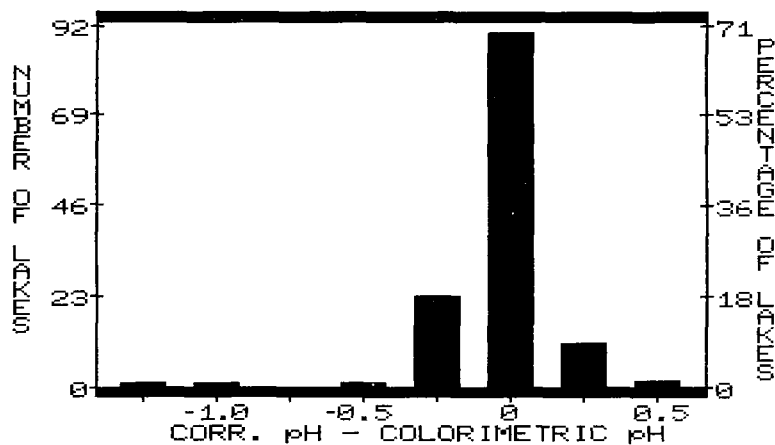


FIGURE 1 Histogram of pH corrections versus number of lakes (0.25pH unit intervals).

analysis indicate that corrections due to indicator H^+ -ion contributions may be larger (>1 pH unit) than the analytical precision reported for colorimetric pH techniques.¹⁸ Depending upon titration endpoint, alkalinity adjustments of between 51 and 79 $\mu\text{eq/L}$ should also be made.

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