

Acid Neutralizing Capacity, Alkalinity, and Acid-Base Status of Natural Waters Containing Organic Acids

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■ The terms acid neutralizing capacity (ANC) and alkalinity (Alk) are extensively employed in the characterization of natural waters, including soft circumneutral or acidic waters. However, in the presence of organic acids, ANC measurements are inconsistent with many conceptual definitions of ANC or Alk and do not provide an adequate characterization of the acid-base chemistry of water. Knowledge of Gran ANC and inorganic carbon concentrations does not by itself allow calculation of the pH of a water containing organic acids. Neither is measured ANC invariant upon changes in organic acid concentration. The result is a significant, but hidden, problem for policy makers and regulators, since ANC is considered a fundamental index of natural water acid-base status. ANC is the main output of many of the watershed simulation models now used in acid precipitation assessment programs, and considerations of present or expected ANCs apparently will play a major role in regulatory decisions. It is proposed to model such natural waters by (1) independently specifying the organic acid concentration and (2) adopting a definition of alkalinity that is invariant with changes of organic acid concentrations. Alkalinity, when so defined, can be both measurable and useful and possesses the conservative chemical properties commonly attributed to the term. A simple computational scheme, amenable to graphical presentation, is proposed to express the relationship between alkalinity, pH, organic acid concentration and inorganic carbon content.

Introduction

Acid neutralizing capacity (ANC) or alkalinity (Alk) of natural waters is widely measured as a key water quality parameter in both regional water quality surveys and intensive watershed studies. ANC (or Alk) is the primary output of several watershed acidification models (1). Both terms are widely used as indexes of the extent of acidification or the susceptibility of a natural water to acidification. ANC (or Alk) is generally regarded as a more suitable index of a natural water's acid-base status than pH because it is considered not to vary with transient (e.g., diurnal) changes in total inorganic carbon content (C_T). Taken together, C_T and Alk (or ANC) are sufficient to completely determine the pH of simple, organic-acid-free natural waters. This relationship can be expressed in the useful, graphical form of the Deffeyes diagram (2).

Many soft natural waters, for which knowledge of acid-base status is most needed, contain concentrations of organic acids sufficient to contribute significantly to the ionic balance of the water, or even to dominate the water's acid-base status in some ecosystems (3, 4). Moreover, the acidity constant distribution of natural acids includes a significant fraction with pK_a 's of ≤ 3.5 . The strength of these acids raises questions about the definition and utility of existing ANC and alkalinity concepts in the presence of such acids, which are neither fully ionized nor fully protonated at any pH normally attained either in natural ecosystems or in alkalinity titrations.

Background

Definitions. Because of the differing usages prevailing in the literature, it is necessary to define terms prior to

considering the measurement and the computational utility of ANC or Alk. Table I summarizes several conceptual definitions of ANC or Alk. Definition 2 essentially equates ANC and Alk in natural waters; other definitions ascribe to Alk only carbonate species (definition 7; see also ref 1, p XV). Differences in assumed water compositions account for some differences (e.g., the inclusion of borate, silicate, and sulfide in definition 4). The definitions that do consider organic acids (4, 6, 8, 9) include an organic anion term together with the sum of other weak acid anions (HCO_3^- , CO_3^{2-}). Definitions 6 and 9 also indicate that the ANC or Alk expression is equal to $C_B - C_A$, the sum of strong base cations minus strong acid anions. Application of the electroneutrality principle to definitions 4 and 8 also yields the conceptual result that $\text{Alk} = C_B - C_A$.

Most of the conceptual definitions of Table I (except 7, 9, and an alternate analytical measurement of $C_B - C_A$ for 6) are coupled to an operational, titration-based definition. However, it will be shown in the following section that the result of the Gran alkalinity titration (a) does not correspond to the conceptual definitions of Alk (or ANC) and (b) does not, even in conjunction with C_T , describe the acid-base chemistry of water. Gran Alk is specifically examined because of its near-universal usage in present-day acid deposition studies. However, it can be shown that, in the presence of organic acids, alternative titration procedures are equally problematic, because the broad pK_a spectrum and surprising strength of natural organic acids thwart efforts at defining a unique, logical, and practical titration end point.

Methods

Computations for the following sections and Appendix were performed in BASIC on a COMPAQ Plus PC, using equilibrium constants for carbonate species at 15 °C and zero ionic strength (2). Iterative calculations were carried to an accuracy of $\pm 1 \mu\text{equiv/L}$. Ionic activity coefficients were taken as unity. Organic acid is modeled by the empirical equation of Oliver et al. (10). In recognition of variability in natural organic acids, it is emphasized that the approach used here could be used, unchanged, with any other model in which the degree to which Org_T ionizes to produce H^+ and organic anions is determined by pH. (For convenience, Org_T is expressed in units of milligrams per liter and is equal to total dissolved organic carbon (DOC). Thus, the degree of ionization must have units of equivalents per milligram.) Simulated Gran titration plots (Figure 1) were created by plotting calculated $[\text{H}^+]$ against added strong acid in 10 $\mu\text{equiv/L}$ increments (assuming acid volumes caused negligible dilution) and fitting a least-squares straight line to the data points for which $[\text{H}^+]$ exceeded 300 $\mu\text{equiv/L}$.

Discussion

(I) What Does Gran ANC Actually Measure? Figure 1 presents the Gran plots for simulated titrations of water containing 0, 10, 20, and 30 mg/L Org_T . Several observations are noteworthy:

(1) Although the organic acids are *not* fully protonated in these simulated titrations, the data for $[\text{H}^+] > 300$

Table I. Representative Definitions of ANC and Alkalinity Appearing in Recent Literature

quantity	definition	measurement	ref
(1) ANC	titration with strong acid to preselected equivalence point (equiv pt)	same as definition	2, p 163
(2) Alk	ANC of natural or carbonate water	same as definition 1	2, p 166
(3) Alk	$-[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$	titration to CO ₂ equiv pt	2
(4) total alkalinity	$[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [HS^-] + [H_2SiO_4^-] + [Org^-] + [OH^-] - [H^+]$	titration to pH known to be close to the correct end point	5
(5) Alk	-TOTH	titration to CO ₂ equiv pt	6
(6) ANC	$C_B - C_A = Alk + \sum[Ot]_i$	analytical measurement of C _B and C _A , or Gran titration	7
(7) Alk	$-[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$	from DIC - pH data	7
(8) H - Aci (≡ -Alk)	$[H^+] - [OH^-] - [HCO_3^-] - \sum n[Org^n^-]$	alkalimetric Gran titration	8
(9) Alk	$-[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [Org^-] = C_B - C_A$	not given	9

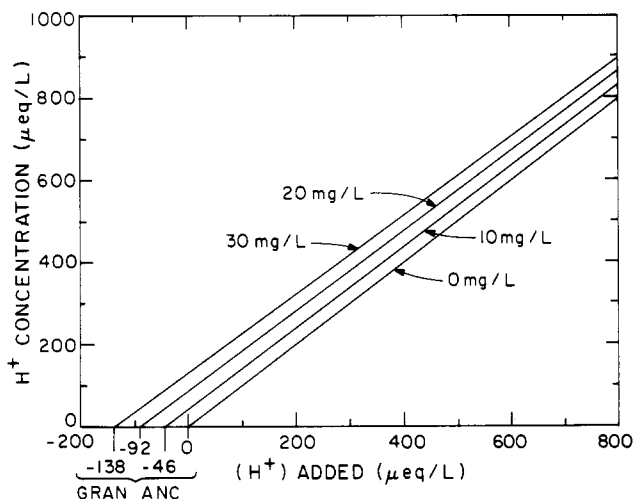


Figure 1. Simulated Gran plots for waters containing different concentrations of natural organic acid. For each water, Gran ANC is numerically equal to the X intercept of the best-fit line to all titration points for which $[H^+] > 300 \mu\text{equiv/L}$. For every line shown, $R^2 > 0.9999$; slopes are 1.000, 0.980, 0.971, and 0.958 for waters containing 0, 10, 20, and 30 mg/L organic acid, respectively.

$\mu\text{equiv/L}$ fit straight lines with an error unmeasurable in practice ($r^2 = 1.0000$).

(2) As Org_T increases, the slope of the plots decreases slightly. (The slope is 95.8% for $Org_T = 30 \text{ mg/L}$.) Such small differences from unity could easily be mimicked by minor errors in pH meter offset or minor departures from the theoretical Nernstian electrode response.

(3) Gran Alk is only equal to alkalinity defined as $Alk \equiv C_B - C_A \equiv -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [Org^-]$ when $Org_T = 0$.

(4) Each milligram of Org_T per liter lowers Gran ANC by 4.6 $\mu\text{equiv/L}$. This value is quite constant over the range of Org_T from 0 to 30 mg/L (and perhaps beyond).

(5) As a consequence of observation 4, Gran Alk is essentially conserved upon the mixing of two waters.

It is most important to observe that the pH of two waters of identical Gran ANC and C_T need not be equal. As an example, compare water A having $Org_T = 20 \text{ mg/L}$ and Gran ANC = $-92 \mu\text{equiv/L}$ with water B having $Org_T = 0$ and an identical Gran Alk. Initially the pH values are 3.97 and 4.04, respectively. If the Gran Alk of each is raised by 80 $\mu\text{equiv/L}$ by adding strong base (perhaps modeling an effect of acid source reduction on a catchment), the pH values rise to 4.36 and 4.94, respectively. A further increase of 80 $\mu\text{equiv/L}$ in Gran Alk of each water brings the pH values to 5.3 and 7.1, respectively, while Gran Alk remains identical for each water.

One must conclude that Gran ANC is affected by, but does not properly represent, the acid-base effects of organic acids. It is, therefore, an inadequate measure of the acid-base condition of natural waters containing appre-

ciable Org_T . Errors in calculated ionic concentrations of the order of several microequivalents per milligram of Org_T may be anticipated. This error is significant, especially around the pH range of roughly 5–5.5, where absolute differences of a few tens of microequivalents per liter in $[H^+]$ can make a large difference in the viability of an aquatic habitat.

(II) A Practical Model for Soft Waters Containing Organic Acids. That humic substances confound the conventional $Alk-C_T$ -pH model, which has otherwise proven successful for natural carbonate waters, should not be surprising. Organic acids defy any effort to satisfactorily lump their influence with that of other ionic species in a single ANC or Alk term. They must simply be recognized with another term, such as Org_T , which in general must be specified or measured. Complete specification of the chemical equilibrium system requires knowledge of the pK_a spectrum of Org_T (as well as some model for competitive interactions between H^+ and other cations if this is to be considered. In the present discussion, we set aside the latter concern, an action probably justifiable in many soft waters).

For practical as well as theoretical reasons, it is best to sever the primary definition of alkalinity from the problem of an operational definition based on titration. A primary definition based on $C_B - C_A$ does not suffer such problems. Of course, any definition using C_B and C_A is implicitly restricted to a range of pH over which it is possible to unequivocally identify “strong” and “weak” acid or base species. If no such pH restriction is applied, even conventionally “strong” acids such as sulfuric acid (second $pK_a = 1.7$; ref 11) must be considered “weak”. In practice, there is no major problem. The pH range of, say, 3.5–8 encompasses most fresh waters of concern with respect to acidification, while restricting the list of protolytic species to organic acids and carbonate species (and aluminum species where they must be considered). Ammonium appears only as NH_4^+ , and silica is essentially unchanged. [We assume waters are oxidic, and $[Fe(II)]_T$ and $[S(-II)]_T$ are negligible.]

Using the expression CBALK (“charge balance alkalinity”) to emphasize our primary definition of alkalinity

$$CBALK \equiv C_B - C_A \quad (1)$$

CBALK is unambiguously defined and is conservative with respect to both CO₂ and organic acid addition. CBALK is thus distinguished from titration-based alkalinity definitions, which might best be left with the name “ANC”. CBALK could be measured by direct analysis of a water for $C_B - C_A$; this would typically include the ions Ca²⁺, Na⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻, NO₃⁻, and NH₄⁺. In a water containing C_A , C_B , H^+ , OH^- , carbonate species, and Org_T , which fits the Oliver model, CBALK could also be estimated (in units of microequivalents per liter for CBALK

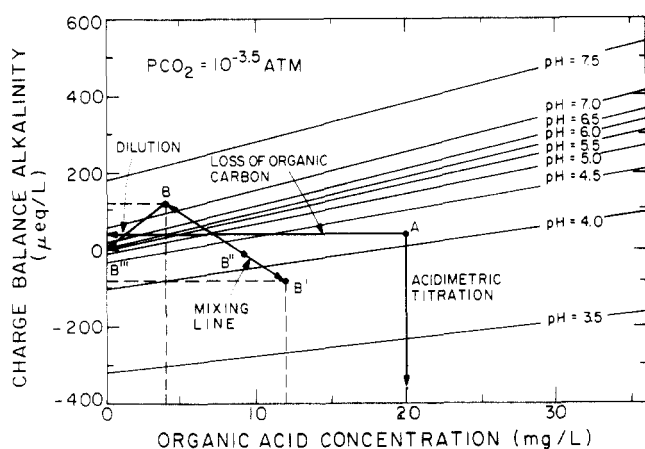


Figure 2. CBALK-pH-Or_T plot for fixed $P_{\text{CO}_2} = 10^{-3.5}$ atm. This plot, and similar plots constructed for different values of P_{CO_2} , or C_T , provide graphical solutions to a variety of chemical problems in waters containing natural organic acids.

and Gran ANC, milligrams per liter for Or_T, where Or_T = DOC) as

$$\text{CBALK} = \text{Gran ANC} + 4.6\text{Or}_T \quad (2)$$

(III) A Graphical Technique Using CBALK To Solve Chemical Equilibria. The usefulness of Alk as a chemical concept is illustrated by the widely used Deffeyes diagram (described in ref 1), on which knowledge of two of the three quantities, Alk, C_T , and pH, suffices to determine the third. The definition of Alk as CBALK permits a useful extension of the Deffeyes diagram, in which any three of CBALK, pH, C_T , and Or_T will determine the fourth. Electroneutrality of water requires that

$$C_B - C_A = -[\text{H}^+] + [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{Org}^-] \quad (3)$$

This may be rewritten as

$$\text{CBALK} = f_1 + f_2 C_T + f_3 \text{Or}_T \quad (4)$$

where f_1 , f_2 , and f_3 are functions of pH only. Function $f_1 = -[\text{H}^+] + [\text{OH}^-]$; f_2 equals $\alpha + 2\alpha_2$, where α_1 and α_2 are ionization fractions such that $[\text{HCO}_3^-] = \alpha_1 C_T$ and $[\text{CO}_3^{2-}] = \alpha_2 C_T$; f_3 equals the ionization fraction of Or_T (expressed in units of equivalents per milligram if Or_T is in milligrams per liter). Then CBALK is of the form

$$\text{CBALK} = K_1 + K_2 C_T + K_3 \text{Or}_T \quad (5)$$

where K_1 , K_2 , and K_3 are constant at any given pH. Equation 5 defines a plane of constant pH in a coordinate system of CBALK, C_T , and Or_T. This 3-D graph can be represented as a series of 2-D plots of CBALK vs Or_T (or CBALK vs C_T) at different values of C_T (or Or_T) for each plot.

For a water in equilibrium with a given partial pressure of CO_2 (P_{CO_2}), C_T is a function of pH only. It is therefore possible to write an equation analogous to (5) in terms of P_{CO_2} instead of C_T . Thus, one can construct a 2-D graph showing the relationship of Or_T, pH, and CBALK at either fixed P_{CO_2} or fixed C_T . Figure 2 is an example for the condition $P_{\text{CO}_2} = 10^{-3.5}$ atm, corresponding to water equilibrated with the atmosphere. Higher P_{CO_2} values would correspond, for example, to soil waters or sediment porewaters. More extensive tables, for several conditions of C_T and of P_{CO_2} , are given in the supplementary material.

Figure 2 (or a similar figure constructed by use of a different organic acid model) can be a practical tool for estimating the composition of a surface water. The quantitative importance of Or_T in influencing pH is immediately evident by inspection in such a figure. Since

both Or_T and CBALK are conservative upon changes in C_T or the mixing of waters, the effects of additions of Or_T, or addition of strong base/acid, can be immediately determined by graphical methods.

Examples: (1) Acidimetric titration of a natural water. Acidimetric titration of a water sample corresponds to a vertical downward movement on the CBALK - Or_T graph (volume corrections are assumed negligible). In Figure 2, water "A" containing 20 mg/L Or_T (DOC) and initial CBALK = +40 μequiv/L is titrated with strong acid in equilibrium with the atmosphere. Following this procedure, one can generate Gran titration curves such as are plotted in Figure 1.

(2) Mixing of natural waters. Natural processes can result in the mixing of two (or more) parcels of water having rather different characteristics. Confluence of two surface streams is an obvious example; mixing of "old" soil water with "new" precipitation water is another example of a mixing problem when the conservative behavior of solutes must be maintained in a chemical mixing model.

Assuming equilibrium with the atmosphere, line B-B' of Figure 2 represents a mixing line for water "B" having CBALK = +120 μequiv/L and Or_T = 4 mg/L, and water B' having CBALK = -80 μequiv/L and Or_T = 12 mg/L. Point B'' along line B-B' will represent the composition (including pH) of the mix; if the mix is 67% water B, B'' is located 67% of the distance from B' to B. Note that dilution can be modeled; water B is diluted along line B-B'', causing (in this case) a near-neutral water to become acidic.

(3) Photooxidation or other degradation of Or_T. Removal of organic carbon by oxidation to CO_2 , at constant P_{CO_2} , corresponds to displacement to the left in Figure 2. The pH of water A, upon loss of the organic carbon, rises from 4.2 to 6.8. This may happen in laboratory procedures such as photooxidation (12) as well as in nature. This also illustrates another reason that waters containing organic acids must not be biogeochemically equated to waters having the same Gran ANC but no organic carbon. In nature, the pH of the former may rise, perhaps sharply, upon degradation of the organic carbon by photochemical or microbial processes. (In some cases, nitrogen, sulfur, or other elements may also be mineralized in sufficient quantity to affect final pH and CBALK.)

Supporting Data from Empirical Studies. The observation that Gran Alk changes by 4.6 μequiv/mg of an organic acid conforming to the model of ref 10 is reflected in the construction of Figure 2 (although the validity and general form of the Or_T-Alk-pH- C_T graph does not depend on any specific model of organic acid). Recent data from lakes in the Adirondacks region (ref 13, Figure 6b) have shown a systematic difference between $C_B - C_A$ and Gran Alk that is strongly correlated to DOC (Or_T); $C_B - C_A$ exceeds Gran ANC by an amount averaging 5.4 μequiv/mg of DOC, a result predicted both qualitatively and quantitatively by the preceding analysis and model. The difference of 0.8 μequiv/mg between prediction and observation is quite small in view of the natural variability of organic acids.

Other Protolytic Species. In general, it appears that addition of important amounts of any additional chemical species, such as hydrolyzable metals, which will complex or release H^+ or OH^- over a pH range of interest, requires the addition of another axis if this graphical model is to be employed. Some species that might become important under certain conditions are those of Al, Fe, S(-II), or Mn.

Aluminum presents the same problems that humic substances do because the equilibrium between species of

different proton levels shifts over any plausible range of titration end points, or range of zero proton level specifications. By use of stability constants from ref 6, the dominant inorganic, monomeric aluminum species can be shown to be Al^{3+} below pH 4.7, $\text{Al}(\text{OH})_2^+$ from pH 4.7 to 5.7, and $\text{Al}(\text{OH})_3$ from pH 5.7 to over 8. (The real-world problem is further complicated by gibbsite precipitation/dissolution. The likelihood of Al^- -organic complex formation must also be considered.) Incorporating aluminum into the alkalinity expression is thus subject to the same problems as organic acids. Defining alkalinity as $\text{CBALK} \equiv C_B - C_A$ provides a resolution of the ambiguity. Explicit specification of aluminum ($[\text{Al}]_T$), in addition to three of the quantities CBALK, Org_T , C_T , and pH, is necessary to accurately model the acid-base behavior of the water.

Summary

Natural waters containing organic acids defy accurate categorization on the basis of ANC (or Alk) and C_T alone. When such acids are present, alkalinity and ANC may lose the desirable properties of uniqueness and computational utility under definitions based on titration end points, equivalence points, or zero proton reference levels.

One consequence is that assessments of acid deposition effects that rely on classical ANC concepts or Gran ANC may be substantially in error for natural waters containing appreciable levels of organic acids. The definition, $\text{CBALK} \equiv (C_B - C_A)$, preserves the uniqueness and computational utility of alkalinity. However, the presence of organic acids requires that additional parameters be specified or measured. If an acceptable model for the acid-base properties of the organic acids is available (e.g., an empirical ionization model), simply specifying Org_T provides all the additional data that are required, and a useful graphical representation of the system becomes feasible. Such a graphical model is presented here and is used to solve problems of titration, organic acid degradations, and mixing of natural waters containing DOC.

Acknowledgments

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Appendix

Tables A1-A7 (supplementary material) contain entries corresponding to the pH of a water for a given CBALK and organic acid content Org_T , under several conditions of fixed C_T or fixed P_{CO_2} . Calculations are for 15 °C, no

ionic strength corrections, and are to an accuracy of ± 0.1 $\mu\text{equiv/L}$. For $\text{CBALK} < -200$ $\mu\text{equiv/L}$, the tables become independent of C_T or P_{CO_2} over the range considered; thus, only Table 1A extends below $\text{CBALK} = -200$ $\mu\text{equiv/L}$. Note that straight lines of constant pH may be drawn through these tables, yielding pH- Org_T -CBALK graphs identical in concept with Figure 2.

Supplementary Material Available

Tables of fixed values of C_T (Tables I-IV) and of fixed P_{CO_2} (9 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, authors' names, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$19.00 for photocopy (\$21.00 foreign) or \$10.00 for microfiche (\$11.00 foreign), are required.

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