Wat. Res. Vol. 25, No. 2, pp. 185–190, 1991
Printed in Great Britain. All rights reserved

0043-1354/91 $3.00 + 0.00
Copyright © 1991 Pergamon Press plc

THE EFFECT OF CARBON DIOXIDE EQUILIBRIUM ON pH IN DILUTE LAKES

JAMES J. BISOGNI JR[1]Ⓜ and SHARI L. ARROYO[2]

[1]School of Civil and Environmental Engineering, Cornell University, Ithaca, NY 14853 and
[2]JMM Consulting Engineers Inc., Walnut Creek, CA 94598, U.S.A.

(First received February 1990; accepted in revised form August 1990)

Abstract—Difficulties in measuring *in situ* pH in dilute acidified lakes have often resulted in an assumption of atmospheric carbon dioxide equilibrium to compute this pH. Unfortunately, the sensitivity of pH to carbon dioxide content of dilute waters is high. The results of our experimental study show the carbon dioxide equilibrium is seldom attained in a dilute lake. As a result, invoking an atmospheric equilibrium assumption can lead to pH estimation errors of greater than one (1) pH unit at pH = 6. A more accurate method to estimate *in situ* pH is presented. The method uses measured acid neutralizing capacity and total inorganic carbon. Contribution of humic substances to acid neutralizing capacity is taken into account.

Key words—carbon dioxide, pH, chemical equilibrium, acid lakes, acid neutralizing capacity

INTRODUCTION

Models which have been used to assess the impact of acid precipitation on freshwater lakes often assume equilibrium between the lake water and atmospheric carbon dioxide (Nikolaidis *et al.*, 1989; Lin and Schnoor, 1986; Chen *et al.*, 1982; Schindler *et al.*, 1989). It is well known, however, that CO_2 equilibrium is seldom attained particularly in the hypolimnion of thermally stratified lakes (Hutchinson, 1957; Kratz *et al.*, 1987).

Even lakewater samples taken at shallow depths (1.5 and 0.5 m) during the National Surface Water Survey (NSWS) were supersaturated with CO_2 (Linthurst *et al.*, 1986). Softwater lakes are poorly buffered and, thus, even small changes in CO_2 concentration can significantly affect pH. The NSWS recognized the probable differences in measured pH for open and closed systems and therefore reported pH data for both atmospheric CO_2 equilibrated and closed samples (Hillman *et al.*, 1986). Metcalf *et al.* (1989) suggest closed system pH values more closely represent actual (*in situ*) lake pH.

pH predictions made using mathematical models should be verified with *in situ* pH measurements. However, accurate *in situ* pH measurements are difficult to obtain for softwater lakes due to atmospheric CO_2 exchange during sampling and analysis, and low ionic strength and subsequent reference electrode junction potential problems. These problems have been acknowledged by many researchers (Herzceg and Hesslein, 1984; Kratz *et al.*, 1987; Metcalf *et al.*, 1989, McQuaker *et al.*, 1983). In addition, CO_2 variations due to diurnal and seasonal changes in biological activity can significantly affect pH measurements (Lung, 1984). These difficulties have prompted substitutions for direct *in situ* pH measurements with indirect calculation procedures.

In this paper we report on an experimental study in which CO_2 equilibrium and its effect on pH was evaluated for Wolf Pond, a thermally stratified softwater lake. A procedure to account for the contribution of fulvic and humic substances to acid neutralizing capacity, ANC, is also presented.

THEORETICAL CONSIDERATIONS

ANC is an important parameter for lake samples which are not at equilibrium with atmospheric CO_2, since gains or losses of CO_2 do not affect sample ANC. ANC can be used to compute sample pH from ANC–pH relationships presented in detail by Morel (1983) and Stumm and Morgan (1981). Those relationships pertinent to this study are presented in this section.

The ANC of a sample which contains bicarbonate, carbonate and other protolytic ions can be defined by equation (1). Typical "other" protolytic ions for softwater lakes include humates, fulvates and perhaps aluminum hydroxy species (Pavlova and Wedborg, 1988).

$$\mathrm{ANC} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + \sum_{i=1}^{i=N} [A_i] \quad (1)$$

where $[HCO_3^-]$ = molar concentration of bicarbonate; $[CO_3^{2-}]$ = molar concentration of carbonate; $[OH^-]$, $[H^+]$ = molar concentrations of hydroxide ion and hydrogen ion, respectively, $[A_i]$ = equivalent concentration of protolytic ion, A_i, excluding inorganic carbon species and; N = total number of different non-inorganic carbon protolytic species.

For a closed system (non-volatile CO_2) and an open system (atmospheric CO_2 equilibrated) the total inorganic carbon concentration (TIC) is given by equation (2).

$$TIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]. \quad (2)$$

For a closed system:

$$[H_2CO_3] = TIC \cdot \left\{1 + \frac{K_1}{[H^+]} + \frac{K_1 \cdot K_2}{[H^+]^2}\right\}^{-1} \quad (3)$$

$$[HCO_3^-] = TIC \cdot \left\{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right\}^{-1} \quad (4)$$

$$[CO_3^{-2}] = TIC \cdot \left\{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 \cdot K_2}\right\}^{-1} \quad (5)$$

where K_1, K_2 = the first and second dissociation constants for carbonic acid.

If the system is at equilibrium with atmospheric carbon dioxide (volatile CO_2 system) the concentrations of $[H_2CO_3]$, $[HCO_3^{-1}]$ and $[CO_3^{2-}]$ are functions of pH and the partial pressure of atmospheric CO_2 (P_{CO_2}):

$$[H_2CO_3] = P_{CO_2} \cdot K_H \quad (6)$$

$$[HCO_3^-] = \frac{P_{CO_2} \cdot K_H \cdot K_1}{[H^+]} \quad (7)$$

$$[CO_3^{2-}] = \frac{P_{CO_2} \cdot K_H \cdot K_1 \cdot K_2}{[H^+]^2} \quad (8)$$

where K_H = Henry's constant for CO_2 (mol/l-atm); and P_{CO_2} = partial pressure of CO_2 (atm).

The acid neutralizing capacity expression for an open system can be rewritten as:

$$ANC = \frac{P_{CO_2} \cdot K_H \cdot K_1}{[H^+]} + 2\frac{P_{CO_2} \cdot K_H \cdot K_1 \cdot K_2}{[H^+]^2} + [OH^-] - [H^+] + \sum_{i=1}^{i=N} [A_i]. \quad (9)$$

Bisogni (1988) and Arroyo (1989) have shown that inorganic carbon species, humates and fulvates are the only acid neutralizing capacity components of significance in Wolf Pond so that $\Sigma[A_i]$ can be replaced with the equivalent concentration of humates and fulvates, $[A_{org}]$. The functional relationship between pH and $[A_{org}]$ is complicated. These organic acids are polyprotic acids which have dissociation coefficients which vary in magnitude according to the level of protonation of the whole acid molecule. In other words, the dissociation coefficients as well as the degree of dissociation for these organic acids are a function of pH. Oliver *et al.* (1983) and Kramer and Davies (1988) present convenient methods to quantitatively describe humic and fulvic acid dissociation. We chose to use the method of Oliver *et al.* (1983) who correlated $p\bar{K}$, the negative logarithm of the acid dissociation coefficient, with pH for a wide variety of aquatic humic substances. This correlation is given as:

$$p\bar{K} = 0.96 + 0.90\,pH - 0.039\,(pH)^2. \quad (10)$$

With this correlation and a mass action quotient it is then possible to write $[A_{org}]$ as a function of pH:

$$[A_{org}] = C_{org} \cdot \frac{10^{-p\bar{K}}}{[H^+] + 10^{-p\bar{K}}} \quad (11)$$

where C_{org} is the concentration of humic and fulvic acid proton sites expressed in equivalents per liter.

Oliver *et al.* (1983) report a mean of 10 microequivalents of titratable proton sites per mg of organic carbon for a variety of freshwater sources. Assuming this value for titratable protons, C_{org} in equiv/l can be estimated by multiplying measured total organic carbon concentration (TOC) in mg/l by 10^{-5}

$$C_{org} = 10^{-5} \cdot TOC. \quad (12)$$

In writing equation (12) it is assumed that total organic carbon consists primarily of dissolved organic carbon and that this carbon is mainly humic and fulvic acid. Aiken *et al.* (1985) report that 80% of lakewater dissolved organic carbon is in the form of humic substances. Morel (1983) reports that 40–99% of dissolved organic carbon in natural aquatic systems may be in the form of humic material. The possible propagation of errors caused by inaccurate assumption of titratable protons sites per mg of carbon is discussed under Experimental Results.

A number of important calculations can be performed using equations (1)–(12). In an open system, for example, equilibrium pH can be calculated if ANC and TOC are known. If the system is closed to the atmosphere ANC, TIC and TOC must be known to calculate equilibrium pH. All of these parameters have been measured for Wolf Pond samples. TOC and TIC measurements are straightforward, but ANC measurements are difficult for dilute samples such as those from Wolf Pond. The Gran plot procedure is the most common method for ANC determination for dilute samples. Inorganic carbon species contribution to ANC can accurately be determined by the Gran plot method. However, the Gran plot procedure gives erroneous results if the sample contains very weak acids such as fulvic and humic acids (Barnard and Bisogni, 1985). This problem is confounded by the presence of pH-dependent dissociation coefficients of humic and fulvic acids. For titrations with endpoints in the pH range of 3.2–4 the Gran plot error due to the presence of humic and fulvic acids is a constant fraction of the theoretical humic and fulvic ANC. Using the humic acid model of Oliver *et al.* (1983), this error is 54%, i.e. only 46% of the fulvic and humic ANC is measured (Arroyo, 1989). Assuming that this humic substance model is representative, measured acid neutralizing capacity, ANC_m, for a closed system [using equations (2)–(5) for carbonate species] and open system [using equations (6)–(8)] can then be described by:

$$ANC_m = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + 0.46 \cdot [A_{org}]. \quad (13)$$

To compute equilibrium pH using acid neutralizing capacity it is first necessary to determine whether a particular sample is in equilibrium with atmospheric carbon dioxide. To do this it is first assumed that a sample is in atmospheric equilibrium. Then, using measured values of ANC and TOC equation (13) is solved for $[H^+]$. This equilibrium $[H^+]$ can then be used to solve equations (2), (5), (6) and (7) for TIC. This calculated total inorganic carbon concentration, TIC_c, can then be compared to measured total inorganic carbon concentration, TIC_m. The difference between TIC_m and TIC_c (ΔTIC) is a measure of the degree of super- or undersaturation of carbon dioxide with respect to the atmosphere. Values of TIC_m are, of course, subject to CO_2 loss or gain during sampling. ΔTIC may, therefore, be underestimated for supersaturated samples and overestimated for undersaturated samples.

METHODS

The lake used in this study, Wolf Pond, is located in Franklin County, N.Y. It has a surface area of 21 ha, an estimated volume of 894,000 m^3 and is thermally stratified for most of the summer period (June–October). Wolf Pond was monitored regularly from July 1984 until October 1988. The lake had a surface pH of approx. 4.5 at the beginning of the study. Wolf Pond was neutralized with $NaHCO_3$ in July 1984 (Bisogni, 1988) and again in September 1987 to maintain positive ANC values.

During the monitoring period (7/84 to 10/88) surface and depth samples from Wolf Pond were analyzed for acid neutralizing capacity, pH, total aluminum, calcium, sodium, total organic carbon, total inorganic carbon, temperature and dissolved oxygen. ANC was measured using the method of Bisogni and Barnard (1987). Total aluminum, calcium and sodium were measured using atomic absorption spectrophotometry (Perkin–Elmer Model 460). Total inorganic and organic carbon were measured using an O.I.C. Model 700 Total Organic Carbon Analyzer. pH was measured with a Corning Model 150 pH meter and a Corning General Purpose combination electrode or a Corning Reverse Sleeve electrode with a silver/silver chloride reference electrode. Dissolved oxygen and temperature were measured using a YSI Model 57 Dissolved Oxygen meter.

For the first 2 years of the study samples were taken from the surface and near the bottom at three sites. The locations of these sites were at the three deepest parts of the lake. Samples were collected in a PVC submersible sampler. In the last 2 years sampling continued in the same locations but sampling depth intervals were decreased to approximately every 10 ft. Samples during this period were collected using a Wildco Instruments Vertical Alpha Bottle Sampler. Samples were stored in 1-liter LDPE bottles at approx. 4°C for usually less than 1 week prior to analysis.

EXPERIMENTAL RESULTS

Figures 1, 2 and 3 present the results of ΔTIC computations for the three Wolf Pond sampling sites. ΔTIC data for the earliest samples are presented in Table 1 because only surface and bottom samples were collected for these dates. Partial pressure of carbon dioxide was assumed to be $10^{-3.46}$ atm for these calculations (Lerman and Stumm, 1989). Thermodynamic coefficients were corrected for temperature using the correlations given by Pearson and McDonnell (1975).

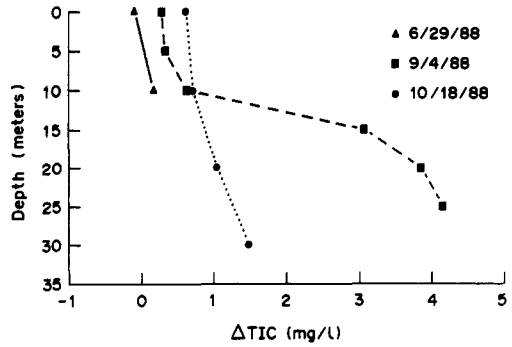

Fig. 1. ΔTIC vs depth—Site 1.

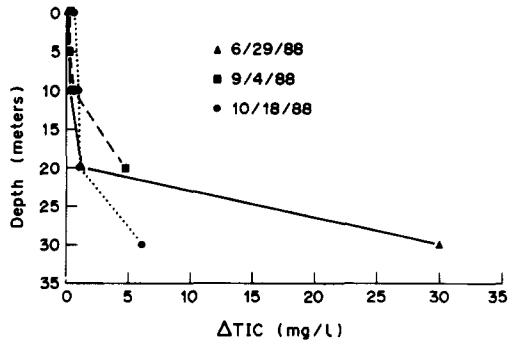

Fig. 2. ΔTIC vs depth—Site 2.

It is apparent that supersaturation of CO_2 is a depth-related phenomenon. One possible cause of CO_2 supersaturation at depth is the bicarbonate ion added during neutralization. Sodium concentrations averaged over depth for the period 8/23/84 to 8/12/85 show uniform spatial distribution (Bisogni, 1988). Sodium depth profiles for the remainder of the study period for Sites 1 and 3, (see Table 2), also show a high degree of homogeneity. Therefore, assuming sodium and the added bicarbonate ion are subject to the same diffusion rate, increases in ΔTIC with depth should not be due to bicarbonate addition for these sites. On the other hand, a sodium profile for Site 2 revealed a significant accumulation of sodium at the bottom of this site. This accumulation was undoubtedly due to the fact that most of the added sodium

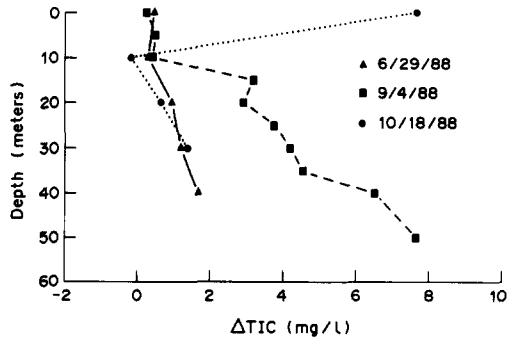

Fig. 3. ΔTIC vs depth—Site 3.

Table 1. Wolf Pond ΔTIC data: 8/23/84–4/15/85

Date	Site (depth, m)	ΔTIC (mg/l)
	1 (0)	−0.24
	1 (13)	8.48
8/23/84	2 (0)	2.53
	3 (0)	2.67
	3 (18)	7.82
	1 (0)	2.92
	1 (12)	6.72
9/28/84	2 (0)	4.06
	2 (9)	10.3
	3 (0)	3.68
	3 (18)	18.1
	1 (3)	0.08
4/15/85	1 (9)	4.77
	2 (2)	0.66
	2 (7)	2.67

Table 2. Depth averaged sodium concentration: Sites 1 and 3 6/29/88–10/18/88

Date	Na (mg/l) Site 1	Na (mg/l) Site 3
6/29/88	4.3 ± 0 (2 samples)	4.2 ± 0.11
9/4/88	4.3 ± 0.07	4.1 ± 0.03
10/18/88	4.8 ± 0.06	4.4 ± 0.07

bicarbonate was placed in the lake near Site 2. Therefore, ΔTIC data for this site are considered anomalous and high ΔTIC values at depth are attributed to added bicarbonate.

For Sites 1 and 3, the likely cause of CO_2 supersaturation at depth is the production of CO_2 by sediment microbial respiration. During periods of thermal stratification the thermocline prevents escape of respiration CO_2 and atmospheric replenishment of respired O_2. Dissolved oxygen profiles for all three sites were measured on 6/29/88 to confirm this. These profiles are shown in Fig. 4. The profiles show a depletion of O_2 with depth and confirm the presence of sediment respiration. DO and TIC data for Site 3 on 6/29/88 were compared in an attempt to estimate a respiratory quotient (ratio of moles CO_2 produced to moles O_2 utilized). For depths between 30 and 55 ft the respiratory quotient averaged 0.8 ± 0.25. This value is well within the expected range (Hutchinson, 1957; Kratz *et al.*, 1987) and confirms the respiration hypothesis.

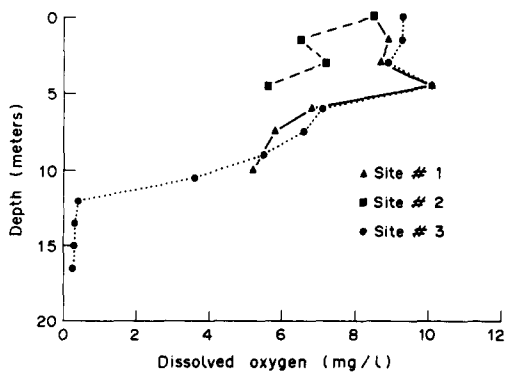

Fig. 4. Dissolved oxygen profile—6/29/88.

Table 3. Estimated *in situ* pH—Site 1

Depth (m)	Estimated *in situ* pH (pH_c) 6/29/88	9/4/88	10/18/88
0	7.41	6.55	6.59
1.5	—	6.53	—
3	6.77	6.43	6.55
4.5	—	5.96	—
6	—	5.95	6.44
7.6	—	5.91	—
9.1	—	—	6.29

Table 4. Estimated *in situ* pH—Site 2

Depth (m)	Estimated *in situ* pH (pH_c) 6/29/88	9/4/88	10/18/88
0	6.97	6.60	6.61
1.5	—	6.65	—
3	6.65	6.41	6.54
6	7.19	6.82	6.55
9.1	7.32	—	8.69

ΔTIC data show that Wolf Pond behaves as a closed, rather than an open, system. Therefore, the closed system model [equation (13)] can be invoked to estimate *in situ* pH, pH_c, of the Wolf Pond samples. pH ($[H^+]$) can be solved for by substituting measured TOC, TIC_m and ANC_m into equation (13). The results of these calculations are shown in Tables 3, 4 and 5. Sites 1 and 3 show marked declines in pH_c with depth as a result of benthic respiration. Site 2, however, shows an increase in pH_c with depth because of the large increase of ANC with depth. Although O_2 depletion data suggests benthic respiration of the same magnitude for all sites, elevated ANC for Site 2 masked any CO_2–pH effects. Conditions in Site 2 are aberrant in the sense that added bicarbonate accumulated in this site due to poor mixing and stable thermal stratification. Conditions in Sites 1 and 3 are, however, typical for dilute or softwater lakes.

The impact of CO_2 disequilibrium on pH in Wolf Pond is illustrated in Figs 5, 6 and 7. The difference between open system pH (pH_o) and calculated closed system pH (pH_c) is plotted in these figures. The assignment of titratable proton site numbers for organic matter influences the result of this study. Error propagation calculations were done using 2 and 20 μequiv/mg C. If the titratable proton site number was 2 instead of the assumed value of 10, mean errors for all data of −17.1 and −1.1% for ΔTIC and pH_c

Table 5. Estimated *in situ* pH—Site 3

Depth (m)	Estimated *in situ* pH (pH_c) 6/29/88	9/4/88	10/18/88
0	6.54	6.70	7.92
1.5	—	6.46	—
3	6.60	6.52	6.51
4.5	—	5.85	—
6	6.38	6.01	6.22
7.6	—	5.91	—
9.1	6.29	5.82	6.27
10.7	—	5.89	—
12.2	6.28	5.90	—
15.2	—	5.86	—

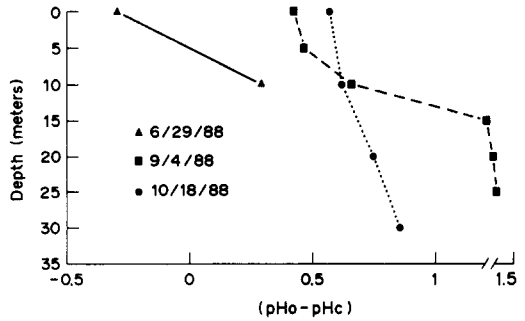

Fig. 5. ($pH_o - pH_c$) vs depth—Site 1.

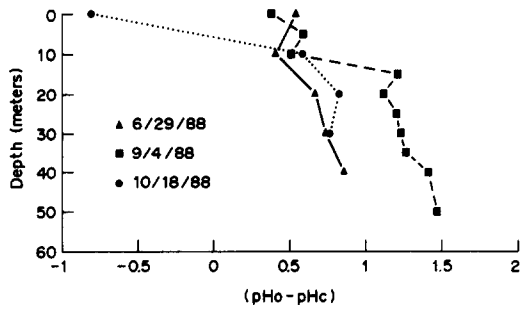

Fig. 7. ($pH_o - pH_c$) vs depth—Site 3.

would be propagated. If the titratable proton number site was 20 instead of the assumed value of 10, mean errors of 21.0 and 1.9% for ΔTIC and pH_c would be propagated.

In situ pH measurements were taken on 6/12/85. The *in situ* pH readings were clearly unstable with drift of about ±0.2 pH units at pH of approx. 5.5. However, it was useful to compare the difference between measured *in situ* pH and atmospheric equilibrated pH (pH_o) to the difference $pH_c - pH_o$. For five samples taken at several different depths at Sites 1, 2 and 3 measured $pH - pH_o$ had a mean of 1.52 ($\sigma = 0.22$). These pH differences were correlated with depth ($r^2 = 0.75$) and compare well with $pH_c - pH_o$ as shown in Figs 5, 6 and 7. Except for an occasional random sample, *in situ* pH readings were not taken for any other sampling period.

For a system in which TIC changes are due only to removal or addition of CO_2, the ratio of CO_2 increments or decrements to pH increments or decrements ($\partial pH/\partial TIC$) is of interest. Incremental removal or addition of carbon dioxide has no effect on ANC. Acidity or base neutralizing capacity (BNC) as defined by equation (14) is, however, affected by carbon dioxide removal or addition.

$$BNC = 2[H_2CO_3] + [HCO_3^-] - [OH^-] + [H^+] + [HA_{org}] \quad (14)$$

where $[HA_{org}]$ is the concentration of protonated humic substances.

$\partial pH/\partial TIC$ is found by differentiating equation (14) with respect to pH while maintaining constant ANC. Talling (1973) derived similar differentials without incorporating the effect of humic substances. To differentiate equation (14) the following relationship between ANC, BNC, TIC and C_{org} must be invoked:

$$ANC + BNC = 2 \cdot TIC + C_{org}. \quad (15)$$

Rearranging equation (15) and differentiating with respect to pH yields:

$$2 \cdot \frac{\partial TIC}{\partial pH} = \frac{\partial BNC}{\partial pH} + \frac{\partial ANC}{\partial pH} - \frac{\partial C_{org}}{\partial pH}. \quad (16)$$

For system changes which involve only CO_2 exchange the last two terms in equation (16) are zero. Therefore:

$$2 \cdot \frac{\partial TIC}{\partial pH} = \frac{\partial BNC}{\partial pH}. \quad (17)$$

$\partial pH/\partial TIC$ is, of course, found by inverting equation (17). The partial differentials of equation (17) are straightforward, even if the model of Oliver *et al.* (1983) is used to describe the $[HA_{org}]$ term in the BNC expression.

Figure 8, a plot of $\partial pH/\partial TIC$ vs pH, is a convenient way to demonstrate the pH sensitivity of dilute lakes to CO_2 changes. In this figure $\partial pH/\partial TIC$ is plotted for three typical softwater lake TIC values with an assumed C_{org} value of 50 μequiv/l. These plots show that as acid lakes are neutralized pH become more sensitive to CO_2 perturbations. This fact exacerbates the problem of predicting and attaining target pH when neutralizing acid lakes.

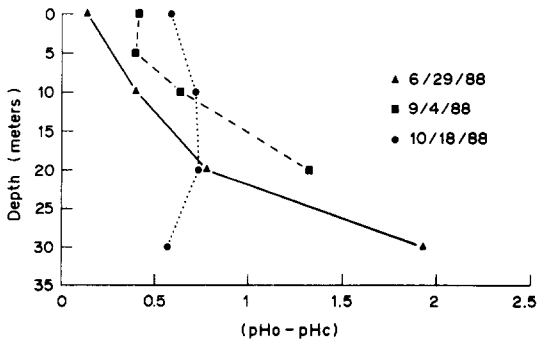

Fig. 6. ($pH_o - pH_c$) vs depth—Site 2.

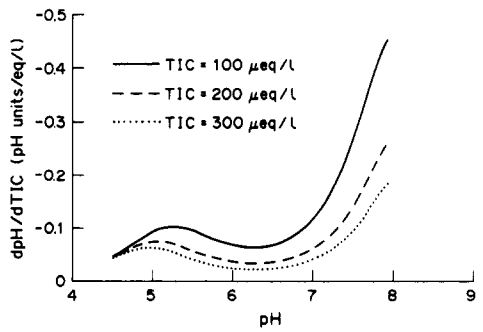

Fig. 8. dpH/dTIC vs pH.

CONCLUSIONS

The results of the observations and calculations done in this study demonstrate that CO_2 disequilibrium is likely in dilute lakes and that this disequilibrium has a profound effect on *in situ* pH. This effect is most significant in hypolimnetic regions. For example, a pH error of one unit at pH = 6 is possible for the hypolimnion if the *in situ* pH is approximated by an atmospheric equilibrated pH measurement. Also these observations show that *in situ* pH varies considerably with depth. Therefore, it is not sufficient to use a single depth pH measurement as representative of the whole lake pH. Further, atmospheric equilibrated pH measurements should not be used to represent actual (*in situ*) pH in dilute lakes. It is more accurate to estimate *in situ* pH by calculation using measured ANC and TIC in a closed environment. Humic and fulvic acid contributions to ANC are small but can be significant for these dilute waters. Measurement of humic substance ANC by Gran plot analysis results in fractional values of the theoretical ANC.

Acknowledgements—We thank Church and Dwight Co., Inc. and The National Consortium for Graduate Degrees for Minorities in Engineering, Inc. for financial support.

REFERENCES

Aiken G. R., McKnight D. M., Wershaw R. L. and MacCarthy P. (1985) *Humic Substances in Soil, Sediment and Water*. Wiley–Interscience, New York.

Arroyo S. L. (1989) Carbon dioxide equilibria of a neutralized lake. M.S. thesis, Cornell University, Ithaca, N.Y.

Barnard T. E. and Bisogni J. J. Jr (1985) Errors in Gran function analysis of titration data for dilute acidified water. *Wat. Res.* **19,** 393–399.

Bisogni J. J. Jr (1988) Fate of added alkalinity during neutralization of acid lake. *J. envir. Engng Am. Soc. civ. Engrs* **114,** 1219–1224.

Bisogni J. J. Jr and Barnard T. E. (1987) Numerical technique to correct for weak acid errors in Gran function analysis of titration data. *Wat. Res.* **21,** 1207–1216.

Chen C. W., Dean J. D., Gherini S. A. and Goldstein R. A. (1982) Acid rain model: hyrologic module. *J. envir. Engng Am. Soc. civ. Engrs* **108,** 455–472.

Herczeg A. L. and Hesslein R. H. (1984) Determination of hydrogen ion concentration in softwater lakes using carbon dioxide equilibria. *Geochim. cosmochim. Acta* **98,** 837–845.

Hillman D. C., Potter J. F. and Simon S. J. (1986) National surface water survey, Eastern Lake survey—phase I, analytical methods manual. EPA/600/4-86/009, U.S. EPA, Las Vegas, Nev.

Hutchinson G. E. (1957) *A Treatise on Limnology*, Vol. 1. Wiley, New York.

Kramer J. R. and Davies S. S. (1988) Estimation of non-carbonate protolyses for selected lakes in the eastern lakes survey. *Envir. Sci. Technol.* **22,** 182–185.

Kratz T. K., Cook R. B., Bowser C. J. and Brezonik P. L. (1987) Winter and spring pH depressions in northern Wisconsin lakes caused by increases in pCO_2. *Can. J. Fish. Aquat. Sci.* **44,** 1082–1088.

Lerman A. and Stumm W. (1989) CO_2 storage and alkalinity trends in lakes. *Wat. Res.* **23,** 139–146.

Lin J. C. and Schnoor J. L. (1986) Acid precipitation model for seepage lakes. *J. envir. Engng Am. Soc. civ. Engr* **112,** 677–694.

Linthurst R. A., Landers D. H., Eilers J. M., Brakke D. F., Overton W. S., Meier E. P. and Crowe R. E. (1986) Characteristics of lakes in the eastern United States. Vol. 1: population descriptions and physico-chemical relationships. EPA/600/4-86/007a, U.S. EPA, Washington, D.C.

Lung W-S. (1984) Understanding simplified lake acidification models. *J. envir. Engng Am. Soc. civ. Engrs* **110,** 997–1002.

McQuaker N. R., Kluckner P. D. and Sandberg D. K. (1983) Chemical analysis of acid precipitation: pH and acidity determination. *Envir. Sci. Technol.* **17,** 431–435.

Metcalf R. C., Peck D. V. and Arent L. J. (1989) The influence of dissolved organic carbon on pH measurements of low solute content waters. *Geochim. cosmochim. Acta* **53,** 773–784.

Morel F. M. M. (1983) *Principles of Aquatic Chemistry*. Wiley–Interscience, New York.

Nikolaidis N. P., Schnoor J. L. and Georgakakos K. P. (1989) Modeling of long-term lake alkalinity responses to acid precipitation. *J. Wat. Pollut. Control Fed.* **61,** 188–199.

Oliver B. G., Thurman E. M. and Malcolm R. L. (1983) The contribution of humic substances to the acidity of colored natural waters. *Geochim. cosmochim. Acta* **47,** 2031–2035.

Pavlova V. and Wedborg M. (1988) Model calculations on the alkalinity titration of lake water. *Wat. Res.* **22,** 497–501.

Pearson F. H. and McDonnell A. J. (1975) Use of crushed limestone to neutralize acid wastes. *J. envir. Engng Am. Soc. civ. Engrs* **101,** 139–158.

Schindler D. W., Kasian S. E. M. and Hesslein R. H. (1989) Biological impoverishment in lakes of the midwestern and northeastern United States from acid rain. *Envir. Sci. Technol.* **23,** 573–580.

Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry*. Wiley–Interscience, New York.

Talling J. F. (1973) The application of some electrochemical methods to the measurement of photosynthesis and respiration in fresh waters. *Freshwat. Biol.* **3,** 335–362.