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A Model of Calcium Carbonate Precipitation in Onondaga Lake

Dominic M. Di Toro
James J. Fitzpatrick
A.K.M. Quamrul Ahsan
Nico deRooij

HydroQual Inc.
1 Lethbridge Plaza
Mahwah, NJ

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INTRODUCTION

The precipitation of calcium carbonate in lakes has been studied for many years (1,2). A number of laboratory studies on the kinetics of formation and dissolution of calcium carbonate are also available (3). However, models that attempt to predict, or at least mimic, the behavior of calcium carbonate in lakes are less common (4,5). This paper presents a steady state model for the concentration of calcium carbonate in a lake. The model includes the exchange of carbon dioxide with the atmosphere and the loss of calcium carbonate to the sediments. The kinetics of calcium carbonate are included. The model is applied to the last 21 years of data from Onondaga Lake. During this time there has been dramatic changes in calcium discharged to the lake, which have influenced the formation and deposition of calcium carbonate in unexpected ways. The purpose of this paper is to elucidate the factors that control its behavior.

The paper begins with a presentation of the conventional model for carbon dioxide and alkalinity in natural waters. The results are used to estimate the concentration of calcium carbonate that is present in Onondaga Lake water. The observation that dissolved calcium and carbonate are not in equilibrium with calcium carbonate indicates that precipitation kinetics are important.

Models of calcium carbonate formation are formulated for a completely mixed volume which is either in equilibrium with the atmosphere or which is closed. The results suggest the definition of excess concentrations and clarify the importance of whether calcium or alkalinity are in excess. The importance of excess inorganic carbon is also apparent in determining the concentration of calcium carbonate that forms.

For a lake, models are formulated in which calcium carbonate is at equilibrium and in which precipiitation kinetics are included. Inputs of calcium, alkalinity, and inorganic carbon; loss by outflow; carbon dioxide exchange with the atmosphere; and calcium carbonate sedimentation are included. Remarkably, the equations that result are quite similar to the closed system model. The non-equilibrium lake model is applied to Onondaga Lake, first for the period when loading data are available for all the variables. Then the loading data are estimated and a 21 year period is simulated. The results are interpreted using the insights gained from the modeling analysis.

CARBON DIOXIDE AND ALKALINITY EQUILIBRIUM

The chemistry of carbon dioxide and alkalinity in natural waters is well understood (6-9). The major species are dissolved carbon dioxide (CO_2); carbonic acid (H_2CO_3), which can be neglected because its concentration is small relative to carbon dioxide; and the bicarbonate

(HCO_3^-) and carbonate (CO_3^{2-}) ions. The nomenclature for all the symbols introduced below is summarized in Table A1 in the Appendix. The following mass action equations determine the relative concentrations of these species:

$$\frac{\{H^+\}\gamma_1[HCO_3^-]}{[CO_2]} = K_1$$

$$\frac{\{H^+\}\gamma_2[CO_3^{2-}]}{\gamma_1[HCO_3^-]} = K_2$$

where $\{H^+\}$ is the activity of the hydrogen ion, the brackets denote molar concentrations and the γ's are activity coefficients. The activity coefficient for carbon dioxide (γ_0) is approximately one except in very concentrated solutions. The mass balance equations for dissolved alkalinity (Alk_d) and dissolved total inorganic carbon (TIC_d) are as follows:

$$Alk_d = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

$$TIC_d = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

The awkward nomenclature "dissolved total inorganic carbon" is adopted to conform with the usual definition of "total inorganic carbon", eq.(4), and the need to distinguish between the sum of the dissolved species of inorganic carbon, and total inorganic carbon which includes particulate calcium carbonate. The solution of these equations, together with the mass action equation for hydroxide, $\{H^+\}\{OH^-\} = K_w$, determines the concentrations of the species and, in particular, the pH.

1. Approximate Solution

For a pH range of 5–10 and dissolved alkalinity (Alk_d) greater than 0.1 meq/L, the concentrations of H^+ and OH^- are small relative to the other terms in the alkalinity mass balance, eq.(3), so that:

$$Alk_d \approx HCO_3^- + 2CO_3^{2-}$$

$$= HCO_3^-\left(1 + \frac{2K_2'}{H^+}\right)$$

where eq.(2) has been used to obtain the second equation. The square brackets have been eliminated to simplify the notation and $K_2' = K_2\gamma_1/\gamma_2$. The dissolved TIC mass balance equation (4) can be written as:

$$TIC_d = HCO_3\left(\frac{H^+}{K_1'} + 1 + \frac{K_2'}{H^+}\right)$$

using eqs.(1-2), where $K_1' = K_1 \gamma_0 / \gamma_1$. Dividing eq.(5) by eq.(6) yields:

$$\frac{Alk_d}{TIC_d} = \frac{\left(1 + \frac{2K_2'}{H^+}\right)}{\left(\frac{H^+}{K_1'} + 1 + \frac{K_2'}{H^+}\right)} \equiv r(H^+)$$

The final equality defines the function $r(H^+)$ which determines the pH, given the ratio Alk_d/TIC_d. This equation indicates that for the usual pH range and for alkaline waters, the pH is determined only by the ratio of dissolved alkalinity and dissolved inorganic carbon, and not their individual concentrations. This finding is important in understanding the factors that determine the pH in natural waters (10).

The predictions based on eq.(7) are compared to observations from synthetic solutions and two lakes (Fig.1, which is adopted from Talling [11] and Wood [12]). A similar analysis is available for seawater (13). The deviation between observations and predictions for pH greater than 9 in lake water in contrast to synthetic solutions, may be caused by the formation of calcium carbonate as discussed below. However, for pH less than 9, eq.(7), which is used in the next section, is confirmed.

2. Estimating the Concentration of Calcium Carbonate

The relationship between pH and Alk_d/TIC_d, eq.(7), applies to dissolved alkalinity and dissolved inorganic carbon. A comparison of pH to the ratio of total alkalinity and total inorganic carbon from Onondaga Lake is shown in Fig.2. The data are from a unified database that was recently prepared (14). Fig.2A presents the pH calculated from eq.(7) for the appropriate temperature and ionic strength for each observation. The formulas for the chemical parameters that are used for this and all the subsequent calculations are listed in Table 1. Fig.2B presents the corresponding observed pH from the unified database. The observed pHs in Fig.2B bare no relationship to the calculated pHs in Fig.2A as indicated by the completely different patterns. The reason for the lack of agreement is that, whereas eq.(7) is valid for dissolved alkalinity and dissolved inorganic carbon, it is not true if particulate alkalinity and inorganic carbon are present in the form of calcium carbonate particles. The measurements in the unified database for Onondaga Lake are for total alkalinity and total inorganic carbon.

In fact, this discrepancy can be used to estimate the quantity of calcium carbonate that must be present in each sample. The dissolved and total concentrations are related as follows:

$$Alk_T = Alk_d + 2CaCO_3(s)$$

Table 1
Chemical Constants (7)

$$
\begin{aligned}
T &= \text{Temperature} \quad (^\circ\text{C}) \\
T_K &= T + 273.15 \quad (^\circ\text{K}) \\
CO_{2,atm} &= 3.3 \times 10^{-4} \quad (\text{atm}) \\
[\text{Cl}] &= \text{Chloride Concentration} \quad (\text{mg/L}) \\
I &= 3.38979 \times 10^{-5} [\text{Cl}] + 0.0077 \quad (\text{M}) \\
\log_{10}(\gamma_1) &= -0.5 \left(\frac{\sqrt{I}}{\sqrt{I} + 1.0} - 0.2\, I \right) \frac{298.15}{T_K} \\
\log_{10}(\gamma_2) &= 4 \log_{10}(\gamma_1) \\
\text{pK}_1 &= 93.4657 \log_{10}(T_K) - 0.12675\, T_K + \frac{17052}{T_K} - 545.56 \\
\text{pK}_2 &= 0.02379\, T_K + \frac{2902.39}{T_K} - 6.498 \\
\text{pK}_{sp} &= 8.50 + 0.01183\, (T - 25.0) \\
\text{pK}_{CO_2} &= 0.0138\, T + 1.12 \\
CO_{2,sat} &= \frac{10^3\, CO_{2,atm}}{10^{\text{pK}_{CO_2}}} \quad (\text{mM}) \\
&= \frac{10^3}{10^{\text{pK}_1}\, \gamma_1} \quad (\text{mM}) \\
K_2' &= \frac{10^3\, \gamma_1}{10^{\text{pK}_2}\, \gamma_2} \quad (\text{mM}) \\
&= \frac{10^6}{\gamma_2^2\, 10^{\text{pK}_{sp}}} \quad (\text{mM})^2 \\
&= 10^{-3}\, H_1\, \gamma_2^2\, K_p \quad (\text{L/mmol-d})
\end{aligned}
$$

Carbon Dioxide Equilibria

$Alk_d/TIC_d = r(H^+)$

● Data

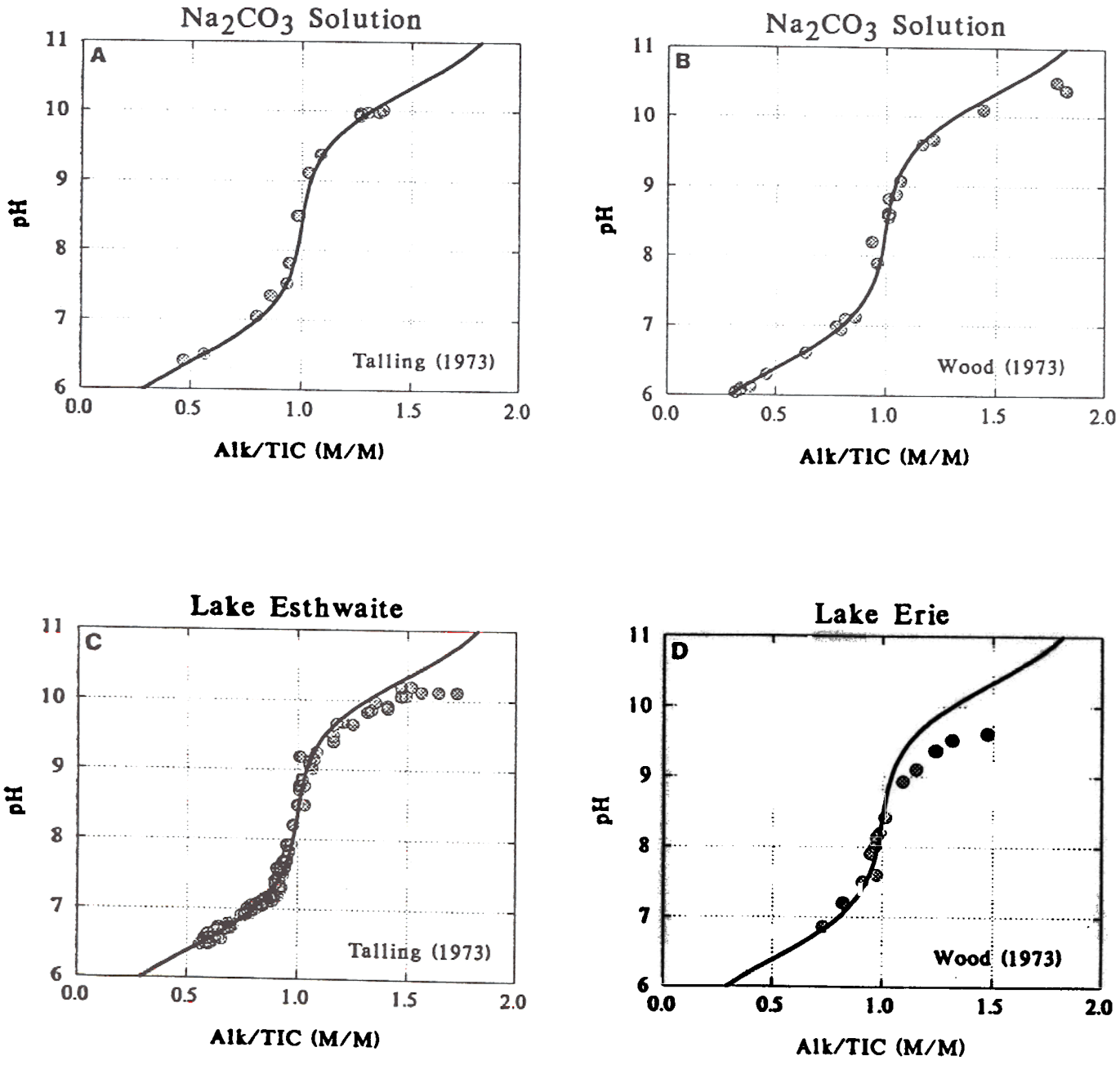


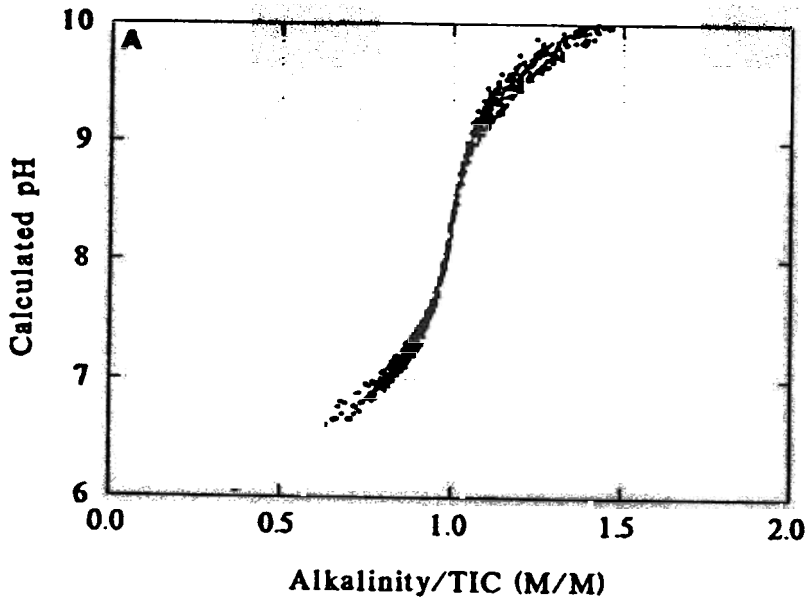
Figure 1

ALKTICP2

Onondaga Lake

Alkalinity, Total Inorganic Carbon, and pH

Theoretical Relationship



Observed Relationship

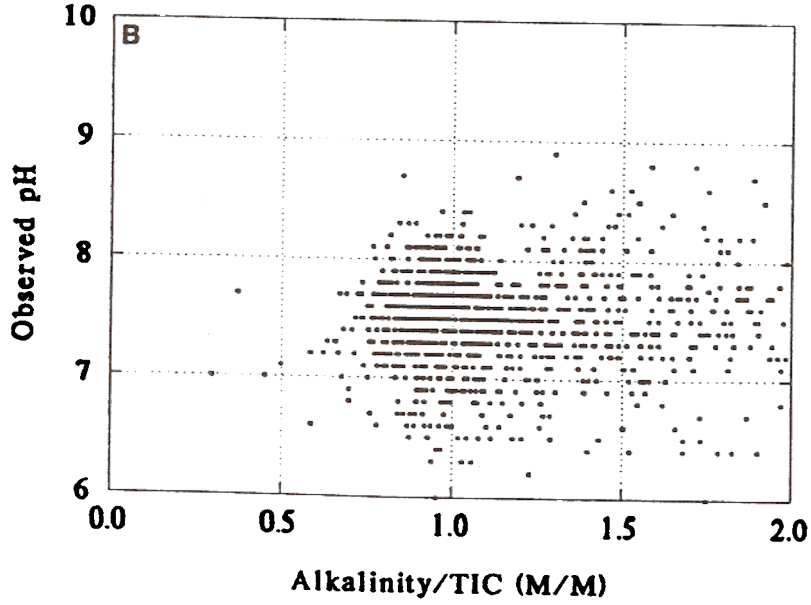


Figure 2

$$TIC_T = TIC_d + CaCO_3(s)$$

where $CaCO_3(s)$ is the molar (not equivalent) concentration of calcium carbonate. The factor of two in the alkalinity equation converts one mole of $CaCO_3(s)$ to two equivalents of alkalinity. Substituting these relationships into eq.(7) yields:

$$\frac{(Alk_T - 2CaCO_3(s))}{(TIC_T - CaCO_3(s))} = r(H^+)$$

from which it follows that:

$$CaCO_3(s) = \frac{(Alk_T - TIC_T r(H^+))}{(2 - r(H^+))}$$

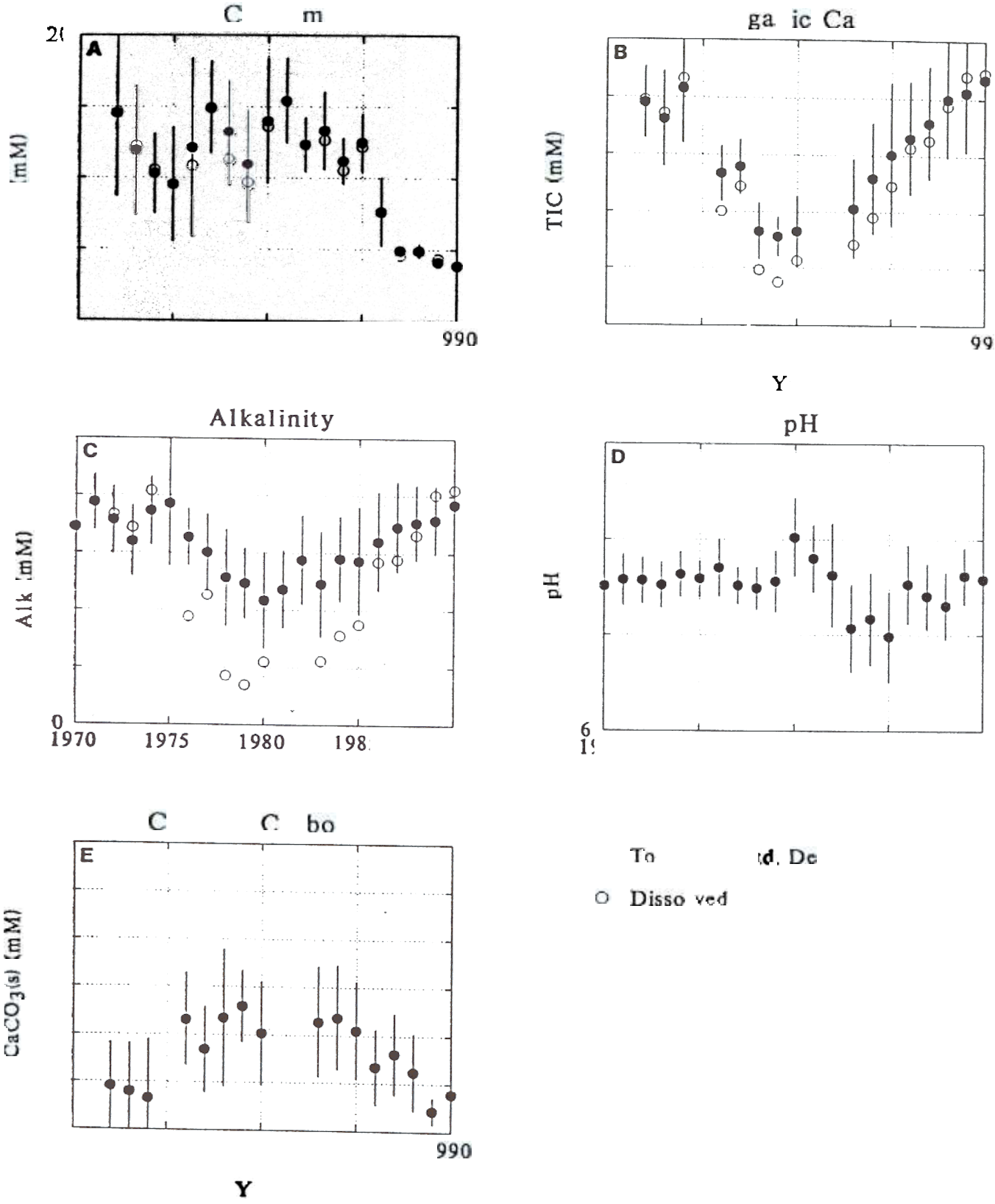
Fig.3 presents the yearly average of observed total and computed dissolved concentrations of calcium, inorganic carbon, and alkalinity; observed pH; and calculated calcium carbonate. The calcium carbonate and the dissolved TIC and dissolved alkalinity concentrations are calculated using eq.(8,9,11) for every observation in the unified database for which total inorganic carbon, total alkaliinity, temperature, chloride (to compute ionic strength - see Table 1), and pH are available. The yearly average concentrations and standard deviations are then computed and shown in Fig.3.

The computed calcium carbonate, Fig.3E, is slightly negative for 1972 and 1974 and for 1989-1990. This is due, presumably, to inaccuracies in the measurements and/or the model assumptions. For the other years, the concentration is positive and follows a fairly regular pattern. Because calcium is in excess relative to calcium carbonate, the differences between total and dissolved calcium are not large (Fig.3A, compare the filled and open symbols). However, substantial fractions of alkalinity (Fig.3C) and, to a lesser extent, inorganic carbon (Fig.3B) are particulate (the difference between the filled and open symbols), especially during the years around 1980. The calcium carbonate concentration peaks during this period. The sharp drop in the calcium concentration after 1985 is due in part to the termination of the AlliedSignal discharge to the lake as discussed below. However, there appears to be no apparent correlation between the calcium concentration (Fig.3A) and the increasing concentration of calcium carbonate from 1970 to 1978 and its decrease from 1978 until 1985 (Fig.3E). One purpose of the model described below is to understand this and the other features of the observations.

CALCIUM CARBONATE EQUILIBRIUM

The solubility of calcium carbonate at equilibrium is determined by the following mass action equation:

Ononda a Lake



Figure

$$\{Ca^{2+}\}\{CO_3^{2-}\} = K_{sp} \tag{12}$$

where K_{sp} is the equilibrium constant for calcium carbonate. A convenient way to examine the departure from equilibrium is to compute the apparent ion activity product (IAP) which is defined as:

$$IAP = \{Ca^{2+}\}\{CO_3^{2-}\} = \gamma_2[Ca^{2+}]\frac{\gamma_1[HCO_3^-]K_2'}{\{H^+\}} \approx \frac{\gamma_1\gamma_2[Ca_d][Alk_d]K_2'}{10^{-pH}} \tag{13}$$

and should be equal to K_{sp} if the solution is in equilibrium with calcium carbonate. The final equality in eq.(13) is obtained using the mass action eq.(2) for CO_3^{2-} and the approximation $Alk_d \approx HCO_3^-$. The pIAP, which (by analogy to pH) is defined as $pIAP = -\log_{10}(IAP)$, would be approximately 8.5 for a solution in equilibrium with calcium carbonate at 25 °C and zero ionic strength, (see pK_{sp} in Table 1).

Many data sets have been used to examine the variation of IAP with respect to environmental variables such as temperature in as attempt to understand the factors that influence the degree to which calcium carbonate equilibrium is achieved in natural waters. We have found a most striking regular variation with respect to pH. Fig.4 presents pIAP versus pH plots for Onondaga Lake and three other lakes (15,16,17). The inverse relationship is apparent. The line is included for visual reference. If the kinetics of precipitation were rapid, the pIAP would level out at approximately 8.5 and stay approximately constant as pH increases. Instead, what is observed is that the pIAP continues to decrease, suggesting that calcium carbonate is failing to form rapidly enough to compensate for the increasing pH.

The reason for the inverse relationship can be seen by examining the last approximate equality in eq.(13). As the pH increases, the denominator decreases. For the solution to remain in equilibrium the numerator must decrease as well. This would occur if calcium carbonate formed since that would decrease the dissolved calcium and alkalinity. Apparently, this does not occur rapidly enough. The result is that the numerator stays approximately constant, IAP increases and $pIAP$ decreases as pH increases. This suggests that the formation of calcium carbonate in lakes is slow enough so that equilibrium is not attained. This further suggests that the kinetics of formation need to be considered in an analysis of the behavior of calcium carbonate in lakes.

It is interesting to note that the inverse relationship between pIAP and pH has a similar slope in each case (-1), but different intercepts. This is indicated by the displacement relative to the sloping line. Lake Erie has the largest intercept, followed by Canadarago, Ijssel, and Onondaga Lakes. It remains to be determined if this observation can be explained using the model developed below.

Calcium Carbonate Ion Activity Product

pH Variation

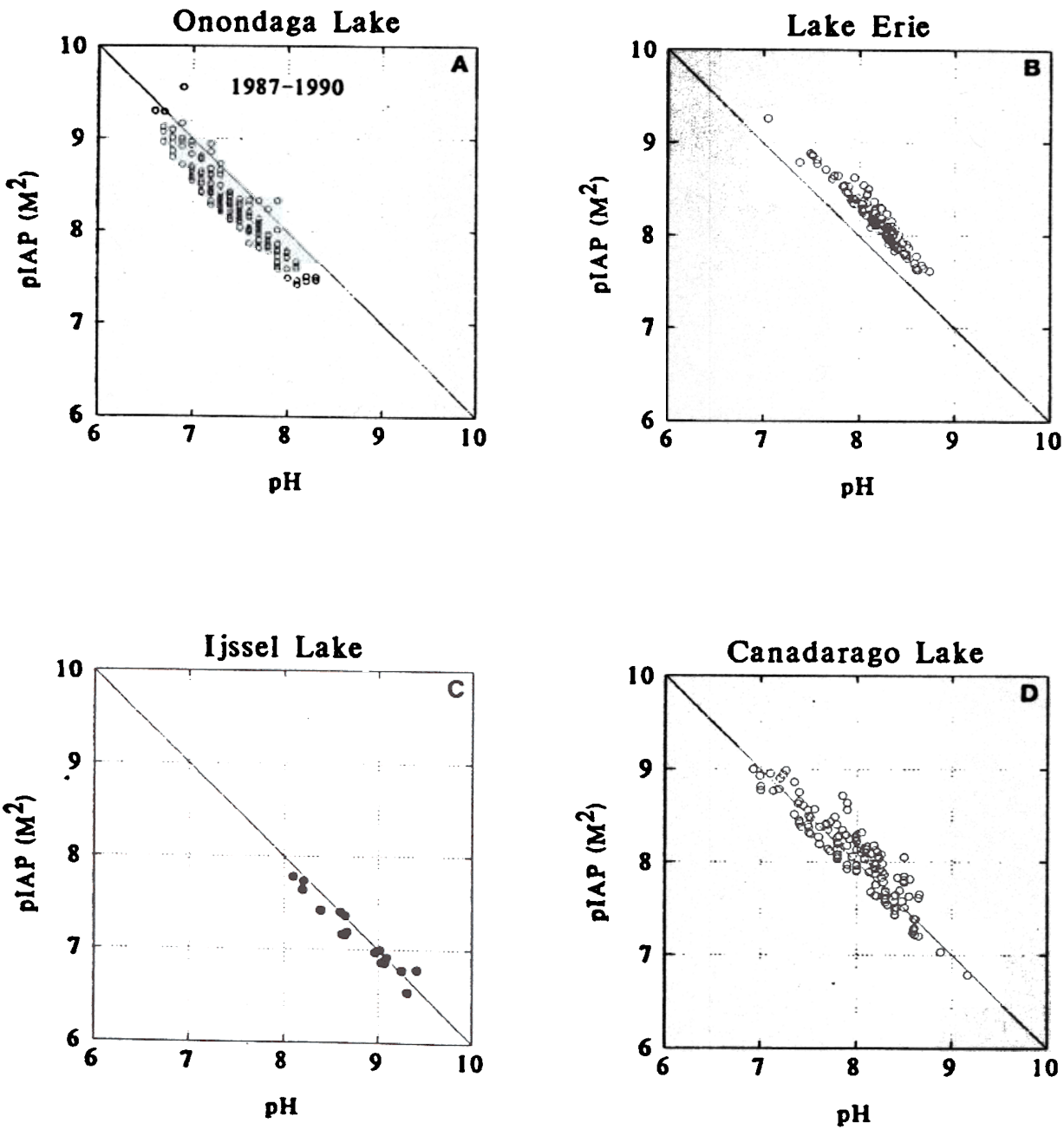


Figure 4

1. Kinetics of Calcium Carbonate Precipitation

A model for the kinetics of precipitation and dissolution of calcium carbonate has been formulated based on an extensive evaluation of laboratory data (3). The rate of dissolution, R (mol/L-day), is postulated to be:

$$R = k_1\{H^+\} + k_2\{CO_2\} + k_3\{H_2O\} - k_4\{Ca^{2+}\}\{CO_3^{2-}\}$$

At alkaline pHs, this equation becomes:

$$R \approx k_3\{H_2O\}\left(1 - \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{K_{sp}}\right)$$

$$-K_p(\{Ca^{2+}\}\{CO_3^{2-}\} - K_{sp})$$

where $K_p = k_3 / K_{sp}$. The rate of formation and dissolution of calcium carbonate is linearly proportional to the degree of over or under saturation. This formulation will be employed below.

MODELS OF CALCIUM CARBONATE CONCENTRATION

The purpose of this section is to elucidate the factors that control the quantity of calcium carbonate that forms. This is best accomplished by analyzing a series of models that gradually approach the most realistic formulations. The analysis begins with models in which calcium carbonate is at equilibrium, after which a non-equilibrium model is examined.

1. Completely Mixed Volume at Atmospheric Equilibrium

The simplest situation is a completely mixed volume of water that is in equilibrium with the carbon dioxide in the atmosphere and with calcium carbonate. The pH that results is well known (18). The mass action equations are as follows:

$$\frac{\{H^+\}[HCO_3^-]}{[CO_2]} = K_1'$$

$$\frac{\{H^+\}[CO_3^{2-}]}{[HCO_3^-]} = K_2$$

and the equilibrium condition for calcium carbonate is:

$$[Ca^{2+}][CO_3^{2-}] = \frac{K_{sp}}{\gamma_2^2} = K_{sp} \tag{18}$$

where the prime denotes that the activity coefficients are included in the equilibrium constants (see Table A1). The mass balance equations are as follows:

$$Alk_T = [HCO_3^-] + 2[CaCO_3(s)]$$

$$Ca_T = [Ca^{2+}] + [CaCO_3(s)]$$

where Alk_T is the total alkalinity, and Ca_T is the total calcium concentrations. Instead of a mass balance for total inorganic carbon, the condition is that carbon dioxide be at atmospheric equilibrium:

$$[CO_2] = [CO_{2,sat}]$$

where $[CO_{2,sat}]$ is the concentration of carbon dioxide in equilibrium with the atmosphere.

Unlike the usual formulation (e.g. refs. 6,7,9), the concentration of calcium carbonate is explicitly included in the mass balance eqs. (19-20). The reason is that, in addition to computing the resulting pH, which is the usual goal of the analysis, the concentration of calcium carbonate is required. The carbonate ion concentration (CO_3^{2-}) has been left out of the alkalinity mass balance equation (20). This considerably simplifies the resulting equations but restricts the validity of these equations to pH less than about 8.3.

The equations (16-21) can be reduced to the following cubic equation in dissolved alkalinity, $Alk_d = [HCO_3^-]$:

$$Alk_d^3 + 2\left(Ca_T - \frac{1}{2}Alk_T\right)Alk_d^2 - 2\alpha[CO_{2,sat}] = 0$$

where:

$$\alpha = \frac{K_1' K_{sp}'}{K_2'}$$

There are two interesting features of eq.(21). The first feature is that all the chemistry parameters occur as one group: $\alpha[CO_{2,sat}]$. Thus, the variation of the solution with respect to any factors that influence the equilibrium constants, such as temperature and ionic strength, occurs only through this group. The second feature is that calcium and alkalinity occur as a difference ($Ca_T - 1/2 Alk_T$) rather than as separate quantities. This has an important chemical meaning, which is discussed in the next section.

2. Defining Excess Calcium

The difference term in eq.(22) prompts the definition of "excess calcium" as follows:

$$Ca_x = Ca_T - \frac{1}{2} Alk_T \tag{24}$$

so that eq.(22) becomes:

$$Alk_d^3 + 2[Ca_x] Alk_d^2 - 2\alpha[CO_{2,sat}] = 0 \tag{25}$$

To understand why the concentration of dissolved alkalinity is a function only of excess calcium, substitute the mass balance equations (20-21) into the definition of excess calcium:

$$\begin{aligned} Ca_x &= Ca_T - \frac{1}{2} Alk_T \\ &= Ca^{2+} + CaCO_3(s) - \frac{1}{2}(HCO_3^- + 2CaCO_3(s)) \\ &= Ca^{2+} - \frac{1}{2} HCO_3^- \\ &= Ca_d - \frac{1}{2} Alk_d \end{aligned} \tag{26}$$

The critical observation is that excess calcium (eq.24) is *independent* of the calcium carbonate concentration. Therefore, so also is the dissolved alkalinity that results from the solution of eq.(25).

The above observation reflects an important chemical fact. Imagine that a completely mixed volume of water has come into equilibrium with the atmosphere and with some quantity of calcium carbonate which is present in the volume. Now imagine that additional calcium carbonate is added to the volume. Because there is already calcium carbonate present, the addition has no effect on the chemistry of the dissolved species. The solution was at equilibrium and remains in equilibrium with calcium carbonate. Thus, the concentrations of the aqueous species are not a function of the quantity of calcium carbonate that is present. The only requirement is that calcium carbonate be present in some amount so that the solution is saturated and at equilibrium.

3. Solution for the Solubility Limit

The factors that control the quantity of calcium carbonate are determined by the solution of the cubic eq.(25). The solution is more easily analyzed if it is assumed that the term $\alpha[CO_{2,sat}]$ is small relative to the other terms. This corresponds, for example, to a very insoluble calcium carbonate. In fact, calcium carbonate is not very insoluble. Nevertheless, it is instructive to examine the results in the limit as as $K_{sp}' \rightarrow 0$. The cubic equation for Alk_d becomes:

$$Alk_d^2(Alk_d + 2Ca_x) = 0$$

Because dissolved alkalinity must be positive or zero (a zero concentration is allowed in the limit as $K_{sp}' \rightarrow 0$) the following two solutions are possible, depending on the sign of excess calcium. If excess calcium is positive then:

$$Ca_x > 0 \qquad Alk_d = 0$$

because the term in parenthesis is positive and only zero dissolved alkalinity can satisfy eq.(27). For negative excess calcium the term in parenthesis can be equal to zero for a positive dissolved alkalinity as follows:

$$Ca_x < 0 \qquad Alk_d = -2Ca_x$$

The solutions for the remaining species are listed in Table 2. They follow from the mass balance equations. Each equation in the Table is referred to by the letter (2a), (2b), and so on.

Table 2

Solutions for Solubility Limit

	$Ca_x > 0$		$Ca_x < 0$	
	(a)	0	(d)	$Alk_T - 2Ca_T$
	(b)	$Ca_T - \frac{1}{2}Alk_T$	(e)	0
$CaCO_3(s)$	(c)	$\frac{1}{2}Alk_T$	(f)	Ca_T

Consider the case for which there is excess calcium, $Ca_x > 0$, and the left hand side of Table 2 applies. Then $Alk_d = 0$ (2a). Therefore, all the alkalinity in the system is calcium carbonate (2c). The dissolved calcium is that which remains after that utilized for the formation of $CaCO_3(s)$ (2b). This result is simply the consequence of the stoichiometry of the formation of a very insoluble calcium carbonate when calcium is in excess:

$$\nu_1 CaCl_2 + \nu_2 Na_2CO_3 \rightarrow \nu_2 CaCO_3(s) + 2\nu_2 NaCl + (\nu_1 - \nu_2) CaCl_2 \qquad (30)$$

where ν_1 and ν_2 are the amounts of calcium chloride and sodium carbonate that are added to form calcium carbonate. The excess calcium insures that $\nu_1 - \nu_2 > 0$. No sodium carbonate remains. Adding alkalinity by adding Na_2CO_3 to the system increases ν_2 which will form additional calcium carbonate (eq.30 and 2c). But adding additional calcium by adding $CaCl_2$, which increases ν_1, will not increase calcium carbonate. The reason is that there is no more available sodium carbonate and, therefore, available alkalinity to form calcium carbonate because it is already zero (eq.30 and 2a).

Alternately, if alkalinity is in excess and $Ca_x < 0$, then the right hand side of Table 2 applies. In this case, $Ca_d = 0$ (2e), and all the calcium in the system is calcium carbonate (2f). Adding additional alkalinity will not form additional calcium carbonate, but rather will increase the dissolved alkalinity (2d) because there is no more calcium available to form calcium carbonate. Again, this result is simply the consequence of the stoichiometry of the formation of a very insoluble calcium carbonate when alkalinity is in excess:

$$v_1 CaCl_2 + v_2 Na_2CO_3 \rightarrow v_1 CaCO_3(s) + 2v_1 NaCl + (v_2 - v_1) Na_2CO_3 \qquad (31)$$

No calcium chloride remains. The excess alkalinity insures that $v_2 - v_1 > 0$ Adding alkalinity, Na_2CO_3, increases v_2, but it does not increase calcium carbonate. However, adding $CaCl_2$ and increasing v_1 does increase calcium carbonate.

The conclusion of this analysis is that if calcium is in excess (left hand side of Table 2), then the quantity of calcium carbonate present is determined by the alkalinity and not the calcium. Conversely, if the alkalinity is in excess, then the quantity of calcium carbonate is determined by the calcium concentration, not the alkalinity. Simply stated, the quantity that is in excess does not determine the concentration of calcium carbonate. Rather, it is the quantity that is in short supply.

The behavior of calcium carbonate in the solubility limit is, of course, an approximation. As shown in the next section, however, the actual behavior is quite similar.

4. Numerical Solutions

The results of numerical solutions (19) of the complete equations (1-4) that are valid over the indicated pH range are illustrated in Fig.5. Consider the case for which $CO_2 = 1.0 \times CO_{2,sat}$ (i.e. the solution is in equilibrium with the atmosphere). Table 3 gives the results and the equations that relate the species to the total concentrations.

Table 3
Numerical Solutions

	$Ca_x > 0$	$Ca_x < 0$
	(a) Small & constant	(d) $Alk_T - 2(Ca_T - Ca_d)$
	(b) $Ca_T - \frac{1}{2}(Alk_T - Alk_d)$	(e) Very small
$CaCO_3(s)$	(c) $\frac{1}{2}(Alk_T - Alk_d)$	(f) $Ca_T - Ca_d$

In the previous analysis, when calcium is in excess (left hand side of the table), the dissolved alkalinity is zero. For the finite solubility case, the dissolved alkalinity, Alk_d, is not zero, but it is small and does not change very much with a change in excess calcium (Fig.5A). Therefore, it does

Excess Calcium Titration

- 0.1 x CO_{2sat}
— 10.0 x CO_{2sat}
— 1.0 x CO_{2sat}

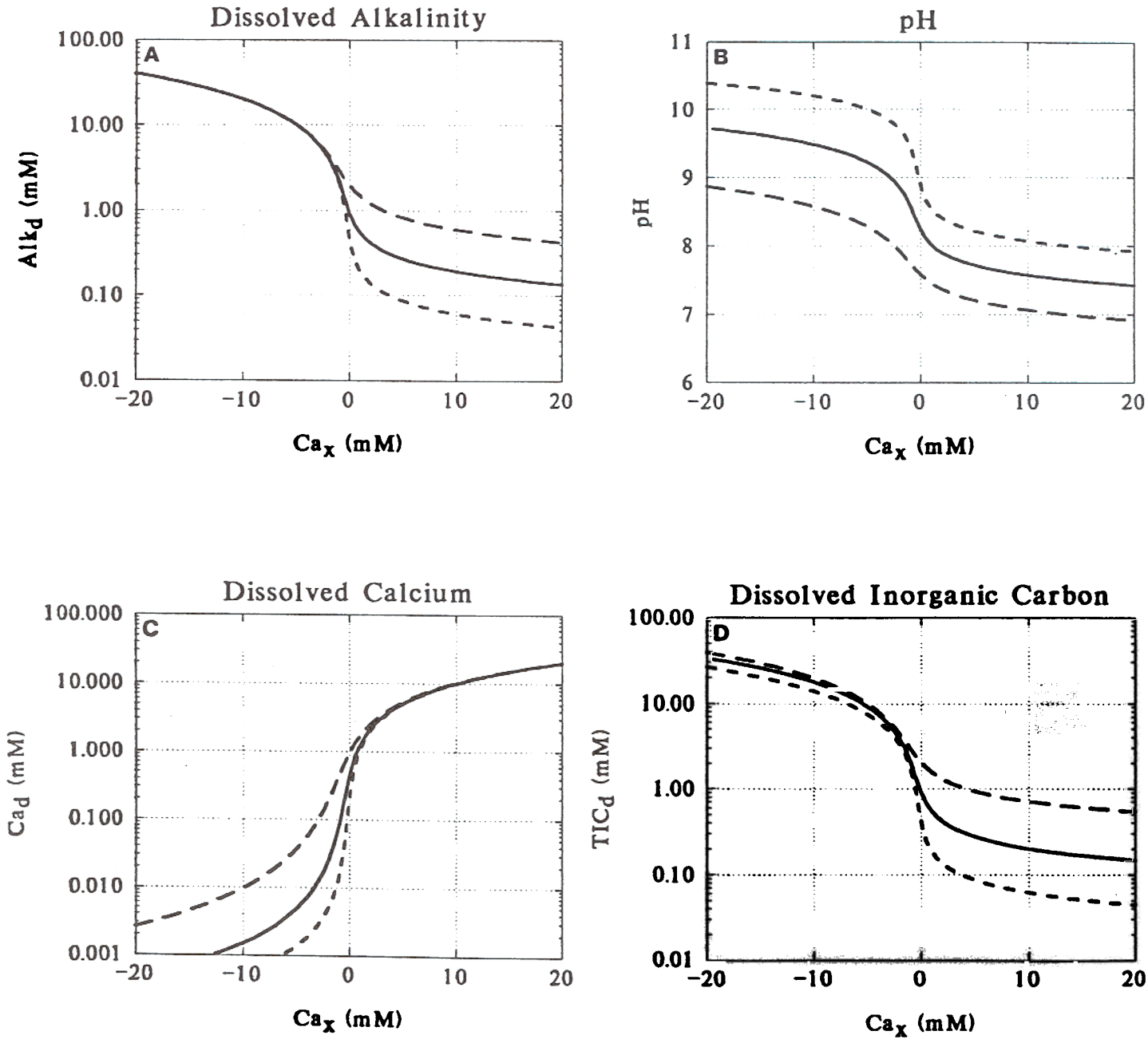


Figure 5

CO2ATMPG

not change very much with a change in either total calcium or total alkalinity because $Ca_x = Ca_T - 1/2\,Alk_T$. As a consequence, any change in total alkalinity causes a change in calcium carbonate (3c) because it does not cause a change in dissolved alkalinity (3a).

By contrast, any change in total calcium causes a change in dissolved calcium (3b) because the calcium carbonate concentration cannot change. This is so because the total alkalinity is not changed and the dissolved alkalinity does not change very much (3a).

Hence, the results are very much like the solubility limit considered above. When calcium is in excess, only an increase in alkalinity will increase calcium carbonate. Adding calcium does not. When alkalinity is in excess adding calcium increases calcium carbonate, but adding calcium does not.

There is, however, a new feature of the solution which is related to the finite solubility of calcium carbonate. The concentration of dissolved alkalinity is now a function of inorganic carbon as well. This can be seen in Fig.5A. As the concentration of $CO_2(aq)$ increases, in response to the increase in $CO_{2,sat}$, the dissolved alkalinity increases and the calcium carbonate decreases. This is the second important factor that determines the concentration of calcium carbonate.

5. Solubility Constraint

The results described above may be somewhat counter intuitive. One might expect that increasing *either* calcium or alkalinity would cause calcium carbonate to form. This intuition is based on the solubility product constraint, eq.(18), which forces the product of calcium and carbonate to be constant.

In fact, the solutions given above do indeed satisfy eq.(18). Adding calcium to the system causes $[Ca^{2+}]$ to increase. The solubility requirement is that: $[Ca^{2+}][CO_3^{2-}] = K_{sp}'$. One might expect that in response to the increase in $[Ca^{2+}]$ calcium carbonate would increase so that both dissolved calcium and carbonate decrease. However, it is also possible that the carbonate ion concentration decreases due to a decrease in pH. This is, in fact, what happens as shown in Fig.5B. As calcium is added, the pH decreases, thereby lowering the concentration of carbonate ion sufficiently to maintain calcium carbonate saturation.

Therefore, it is the relative amounts of calcium and alkalinity that are present that determine the concentration of calcium carbonate that forms. The solubility requirement determines the pH that results.

6. Completely Mixed Volume - Closed to the Atmosphere

The mass balance equations that describe a closed volume include an equation for total inorganic carbon, TIC_T, which replaces the atmospheric equilibrium condition, eq.(19), as well as the equations for total alkalinity and calcium:

$$TIC_T = [CO_2] + [HCO_3^-] + [CaCO_3(s)] \tag{32}$$

$$Alk_T = [HCO_3^-] + 2[CaCO_3(s)] \tag{33}$$

$$Ca_T = [Ca^{2+}] + [CaCO_3(s)] \tag{34}$$

These equations, together with the mass action equations, can be solved for dissolved alkalinity:

$$Alk_d^3 + 2[Ca_x]Alk_d^2 + \alpha Alk_d - 2\alpha[TIC_x] = 0$$

where:

$$\alpha = \frac{K_1' K_{sp}'}{K_2'}$$

and

$$Ca_x = Ca_T - \frac{1}{2}Alk_T$$

An analogous excess quantity for total inorganic carbon, namely excess total inorganic carbon, TIC_x, is defined as:

$$TIC_x = TIC_T - \frac{1}{2}Alk_T \tag{38}$$

The 1/2 in this equation arises from the 2 in eq.(33).

The equation for dissolved alkalinity, eq.(35), is also a cubic equation in terms of excess calcium and excess inorganic carbon. The solution depends only on the excess quantities and not on the individual total concentrations. The reasoning is similar to that given above. The solubility limit equation for which $\alpha \to 0$ is the same as that for the atmospheric equilibrium case, eq.(27). Therefore, the same stoichiometric arguments apply.

7. Numerical Solutions

The concentrations of dissolved alkalinity and the other species for various concentrations of excess TIC are computed (19) and displayed in Fig.6. For positive excess calcium and for

Excess Calcium Titration

- TIC_x = 10 mM
- TIC_x = 3.0 mM
- TIC_x = 1.0 mM
- TIC_x = 0.3 mM
- TIC_x = 0.1 mM

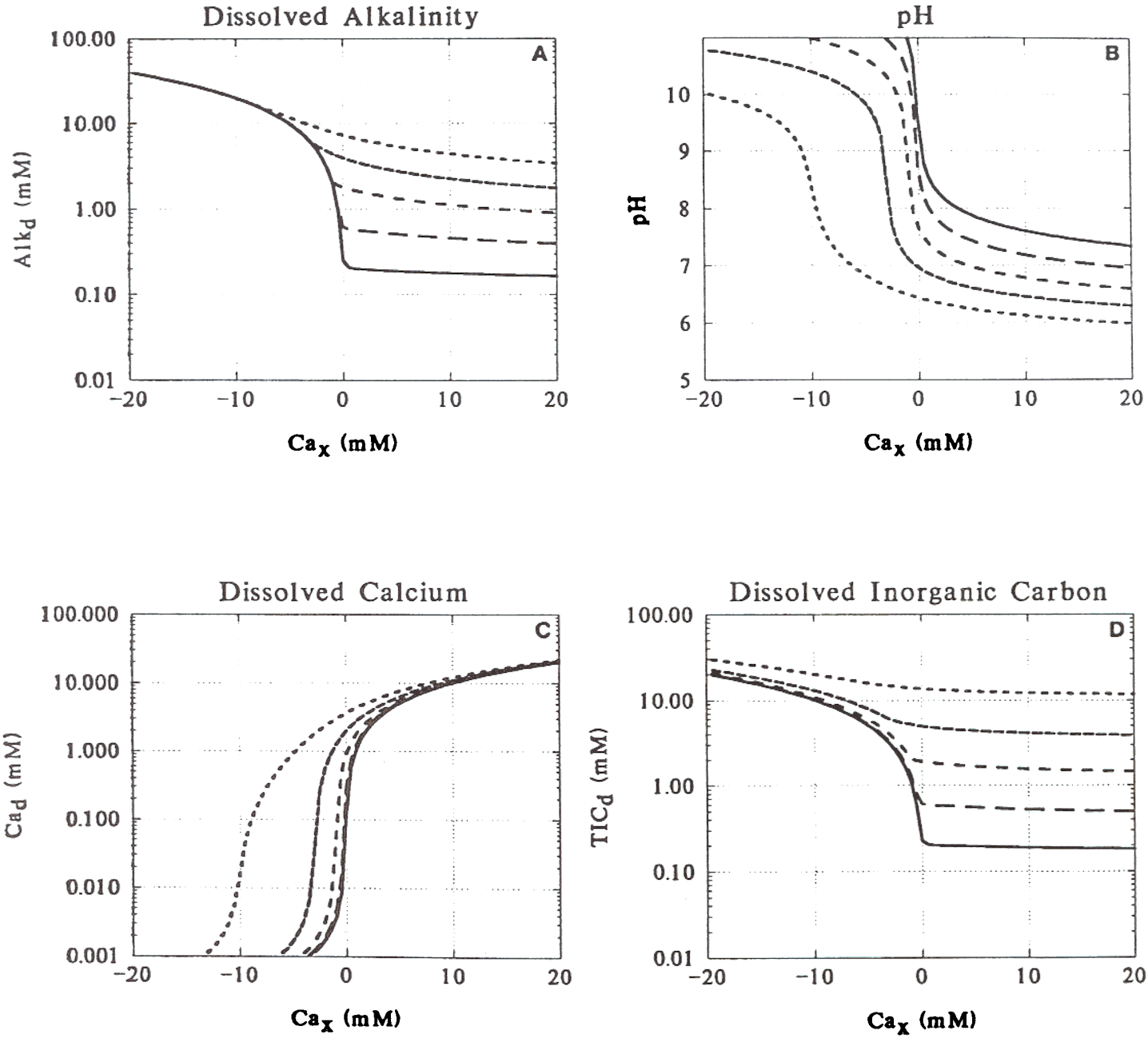


Figure 6

concentrations of excess inorganic carbon less than 1 mM, the dissolved alkalinity (Fig.6A) is small and approximately constant. Therefore, the relationships discussed above apply to this case. However, for TIC_X > 1 mM, the variation in dissolved alkalinity can be large enough so the changes in calcium can influence the formation of calcium carbonate to some extent.

For negative excess calcium, the dissolved calcium is small for TIC_X < 1 mM, and the results obtained from the atmospheric equilibrium case apply as well.

It is clear from the results in Fig.6 that the absolute amount of excess total inorganic carbon, TIC_X, affects the quantity of calcium carbonate that forms. For a constant positive concentration of excess calcium, increasing the TIC_X increases the dissolved alkalinity (Fig.6A) and, therefore, decreases the quantity of calcium carbonate. The same is true for negative excess calcium (the excess alkalinity case), but the effect is much less dramatic. The relationship between TIC_x and the quantity of calcium carbonate that forms is shown below to be important in understanding the behavior of calcium carbonate in Onondaga Lake.

8. Lines of Constant Dissolved Alkalinity

An important and simple relationship is implied by eq.(35). Although the equation is cubic in Alk_d, it is linear in the excess quantities, TIC_X and Ca_X. Therefore, for a constant dissolved alkalinity concentration, the relationship between TIC_X and Ca_X is a straight line. Fig.7 compares a contour plot of numerical computations (Fig.7A) used to construct Fig.6 (with more detail in the quadrant of interest) to the relationship derived from eq.(35), namely:

$$TIC_x = \frac{2Alk_d^2 Ca_x + Alk_d(\alpha + Alk_d^2)}{2\alpha} \tag{39}$$

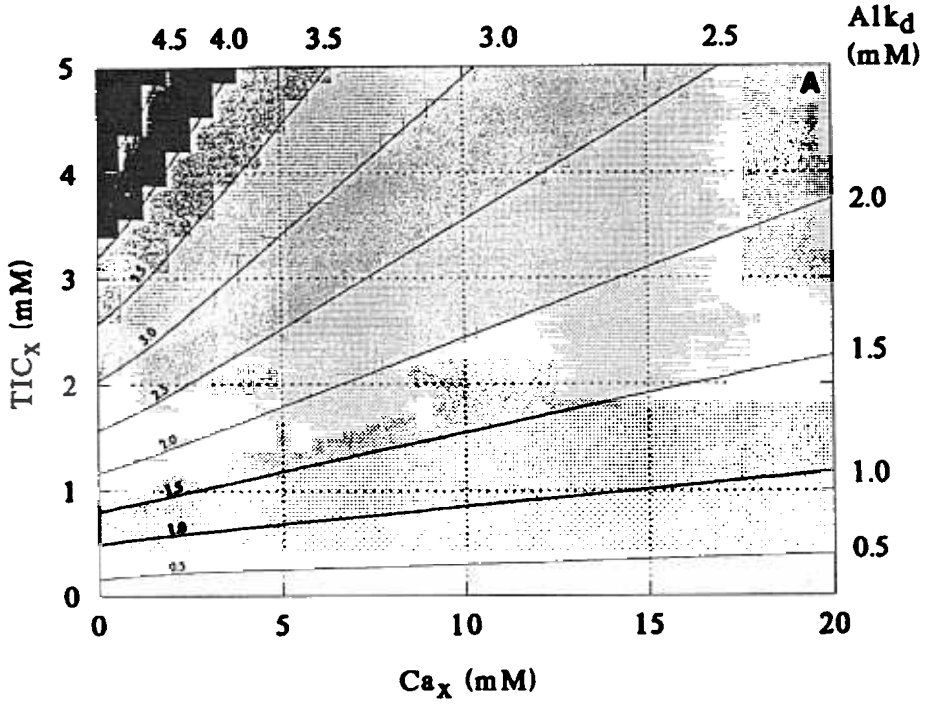
in Fig.7B. The results are in very close agreement. Therefore, Fig.7B can be used to understand what controls the quantity of calcium carbonate that forms. Knowing TIC_X and Ca_X, the dissolved alkalinity can be obtained by approximate interpolation. Then the calcium carbonate is given by the difference between the total and dissolved alkalinity. This representation is related to the modified Caldwell-Lawrence diagram (7).

MODELS OF CALCIUM CARBONATE CONCENTRATION IN LAKES

Lakes differ from closed volumes in one important respect: they are open systems. Whereas the concentrations in closed systems are specified by the total concentrations of the components (TIC_T, Ca_T, and Alk_T) that make up the chemical system, open systems are

Dissolved Alkalinity

Numerical Calculations



Linear Approximation

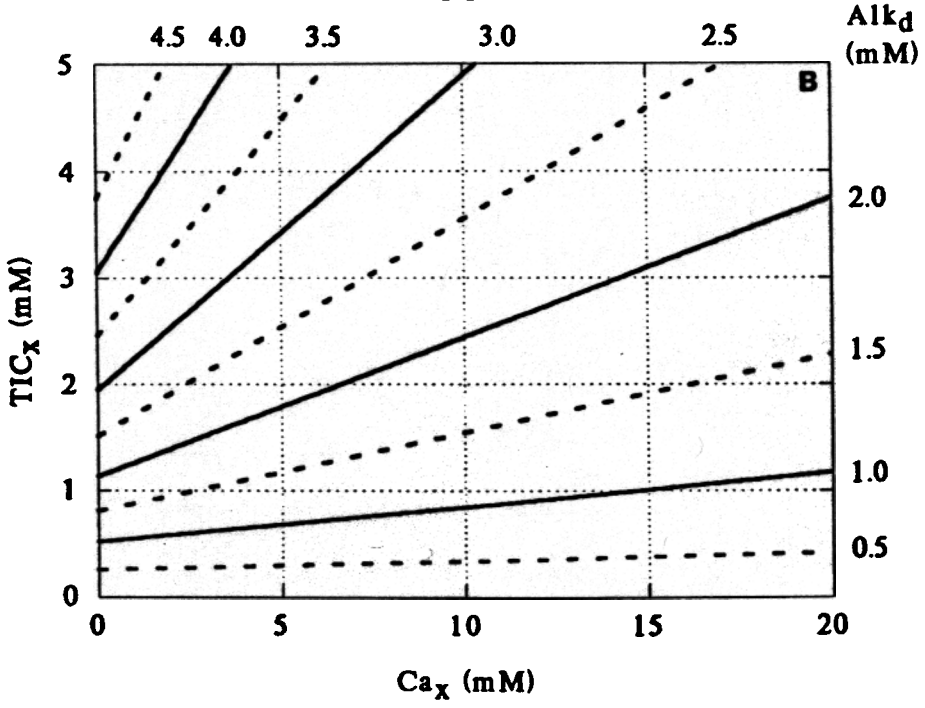


Figure 7

LOADP10

characterized by continuous inputs and outputs of the chemical species. This is illustrated in Fig.8, which shows the inputs and outputs of total inorganic carbon, alkalinity, and calcium. One would expect, therefore, that an open system would have a fundamentally different mathematical structure and solutions for the closed systems considered above. Surprisingly, this is not the case. Essentially all that has been learned from the previous models applies to the open system.

1. Calcium Carbonate Equilibrium

It is convenient to use the definitions of total quantities defined above, eqs(32 - 34), with the same approximation, namely not including the concentration of CO_3^{2-} in the alkalinity equation. This limits the applicability of the solution to pH < 8.3 as before.

The mass balance equations are constructed to account for the sources and sinks illustrated in Fig.8. The equations are formulated in terms of areally normalized loading rates and outflow from the lake. These variables are convenient when dealing with removal processes that are specified as settling velocities and mass transfer coefficients, both of which have units of length/time. The sources (external loading and atmospheric source) enter as positive terms and the sinks (outflow, settling and loss to the atmosphere) are negative terms. The equations are as follows:

$$J_{TIC} - q[TIC] - w_s[CaCO_3(s)] + K_{LOI}([CO_{2,sat}] - [CO_2]) = 0 \tag{40}$$

$$J_{Alk} - q[Alk_T] - 2w_s[CaCO_3(s \quad = 0 \tag{41}$$

$$J_{Ca} - q[Ca_T] - w_s[CaCO_3(s)] = 0 \tag{42}$$

where:

J_{TIC} = areal total inorganic carbon loading (mol/m^2-d)

J_{Alk} = areal total alkalinity loading (mol/m^2-d)

J_{Ca} = areal total calcium loading (mol/m^2-d)

q = overflow rate (m/d)

w_s = calcium carbonate sedimentation velocity (m/d)

K_{LOI} = air - water mass transfer coefficient (m/d)

The solution to these equations is a cubic equation in dissolved alkalinity, $Alk_d = [HCO_3^-]$:

$$Alk_d^3 + 2\left(\frac{J_{Ca_x}}{q}\right)Alk_d^2 + \left(\alpha\frac{q}{q+K_{LOI}}\right)Alk_d - 2\left(\alpha\frac{q}{q+K_{LOI}}\right)\left(\frac{J_{TIC_{xs}}}{q}\right) = 0 \tag{43}$$

where excess calcium and excess total inorganic carbon loadings are defined as:

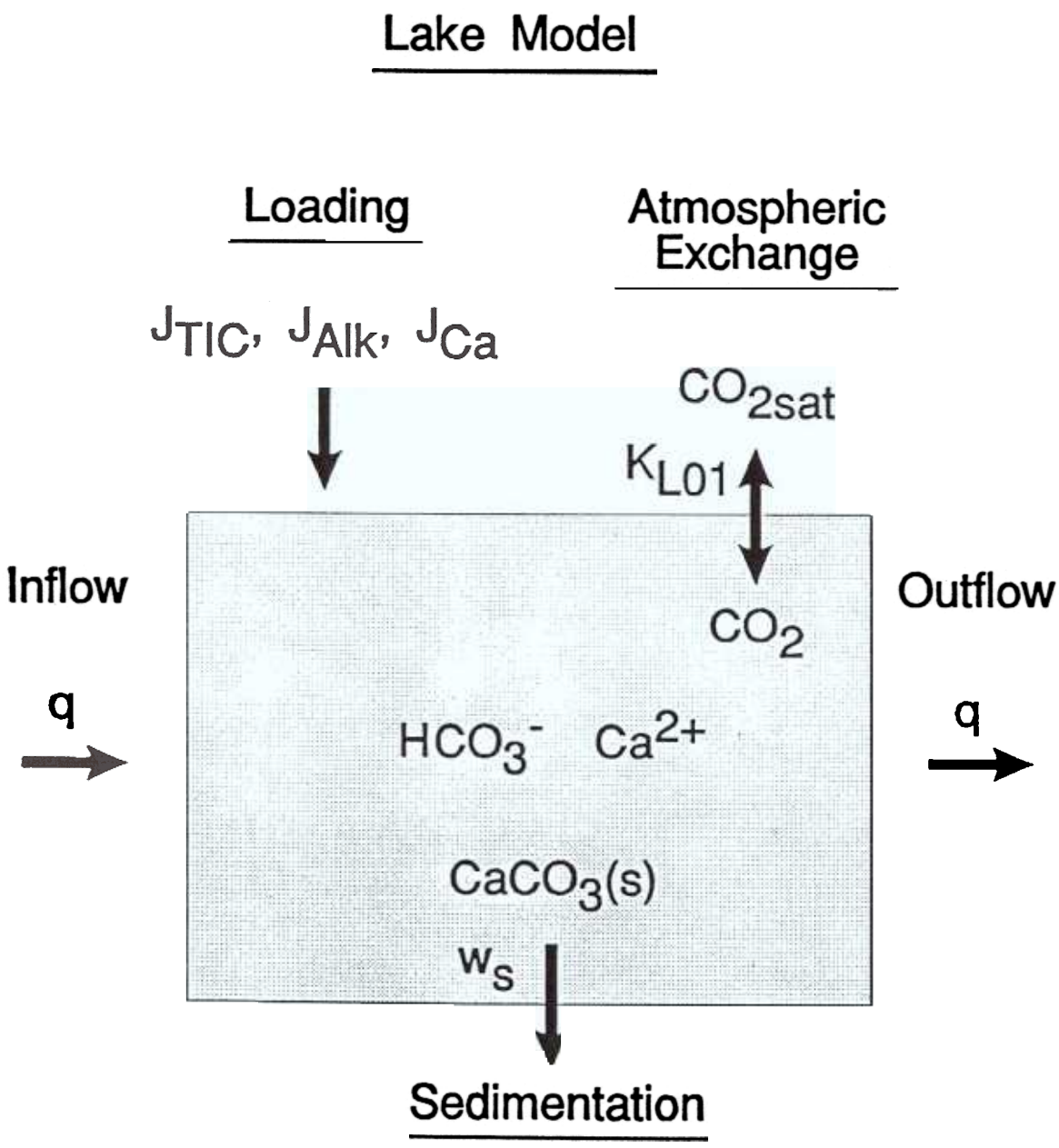


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Figure 8

$$J_{Ca_x} = J_{Ca} - \frac{1}{2} J_{Alk}$$

$$J_{TIC_x} = J_{TIC} - \frac{1}{2} J_{Alk}$$

An additional excess quantity is required to include the source of CO_2 to the lake from the atmosphere:

$$J_{TIC_{xs}} = J_{TIC_x} + K_{LOI}[CO_{2,sat}]$$

The remarkable result is that the equation for dissolved alkalinity for the open lake model is very similar to the closed volume model. The relationships are listed in Table 4.

Table 4
Comparison of Closed and Open Models

Coefficient	Closed	Open
Excess Calcium	Ca_x	$\frac{J_{Ca_x}}{q}$
Excess Inorganic Carbon	TIC_x	$\frac{J_{TIC_{xs}}}{q}$
Chemical Parameter	α	$\alpha\left(\frac{q}{q+K_{LOI}}\right)$

The concentrations of total excess calcium and total excess inorganic carbon in the closed volume case are replaced by the ratio of the loading rates to the overflow rates. But this is just the concentrations of excess quantities that would exist if excess calcium and inorganic carbon were removed only by outflow and by no other processes. This behavior is typical of what are termed conservative quantities, for example chloride ion (26).

The chemical ratio, α, is modified by a ratio involving the overflow rate, q, and the air-water mass transfer coefficient, K_{LOI}. If the mass transfer coefficient is zero, $K_{LOI} = 0$, then the system is closed to the atmosphere and the two expressions are the same. By contrast, if $K_{LOI} \rightarrow \infty$, then the first order term in the cubic equation goes to zero and the constant term becomes equal to the atmospheric equilibrium case, eq.(22).

What is initially surprising is that the sedimentation velocity of calcium carbonate, w_s, is *not* in the equations. This is because removing calcium carbonate from a saturated solution does not affect the concentrations of the dissolved species. This is also the reason that the excess quantities appear as conservative quantities. It is also the reason that solving eqs.(40-42) for the dissolved alkalinity, rather than for calcium carbonate, yields the simplest equation.

The flux of calcium carbonate to the sediment is found from the mass balance for alkalinity, eq.(33):

$$J[CaCO_3(s)] = \frac{1}{2}\left(\frac{w_s}{w_s + q}\right)(J_{Alk} - q[Alk_d])$$

and it is a function of the sedimentation velocity. The flux is equal to the loading flux of alkalinity to the lake (J_{Alk}) minus the loss of dissolved alkalinity to outflow ($q[Alk_d]$) modified by the ratio of the sedimentation velocity (w_s) to the total removal rate ($w_s + q$). At low sedimentation velocity ($w_s \ll q$) the flux is small, and calcium carbonate flows out of the lake. At high sedimentation velocity ($w_s \gg q$) all the available calcium carbonate settles to the sediment and none is left in the water column.

2. Precipitation Kinetics

The analysis of the observed ion activity product of calcium carbonate in lakes (Fig.4) clearly indicates that precipitation kinetics are important. The inclusion of precipitation kinetics into the mass balance equations requires that the equilibrium condition for calcium carbonate, eq(18), be replaced with a mass balance equation for calcium carbonate:

$$K_p' H_1([Ca^{2+}][CO_3^{2+}] - K_{sp}') - (q + w_s)[CaCO_3(s)] = 0$$

where $K_p' = K_p/\gamma_2^2$ is the rate of calcium carbonate formation and H_1 is the depth of the lake. The mass balance equation equates the rate of formation of calcium carbonate, the first term, to the losses via outflow and sedimentation. Solving for dissolved alkalinity yields a cubic equation:

$$Alk_d^3 + a_0 Alk_d^2 + a_1 Alk_d + a_2 = 0$$

where:

$$a_0 = -\frac{J_{TIC_{xs}}(2\beta_0 + \beta_1 J_{Alk})}{q + K_{LOI}}$$

$$a_1 = \frac{q}{\quad}[2\beta_0 + \beta_1(2J_{TIC_{xs}} + J_{Alk})$$

$$a_2 = \frac{4J_{Ca_x}(q + K_{LOI}) - \beta_1 q^3}{2q(q + K_{LOI})} \tag{52}$$

and:

$$\beta_0 = \frac{K_1' K_{sp}' H_1}{K_2'} \qquad \beta_1 = \frac{K_1}{K_2' K_p' H_1}$$

It is surprising that the governing equation (49) is still a cubic, despite the additional complexity of a mass balance equation for calcium carbonate. However, the coefficients have become more complicated. The concentration of dissolved alkalinity is no longer a function only of the excess quantities. This is indicated by the explicit appearance of the alkalinity loading, J_{Alk}, in the coefficients (eqs.50-51). The reason is that the calcium carbonate concentration now affects the concentrations of the dissolved species. The mass balance equation (48) for calcium carbonate is an explicit function of the calcium carbonate concentration. Therefore, so also is the dissolved calcium and carbonate concentrations. Because the concentration of calcium carbonate is a function of the alkalinity loading, see eq.(41), so also is the dissolved alkalinity. Of course the dependency disappears as the rate of calcium carbonate formation increases ($K_p' \to \infty$ and $\beta_1 \to 0$) and equilibrium is reached.

3. Lines of Constant Dissolved Alkalinity

For this model, a linear relationship exists between excess total inorganic carbon, TIC_{xs}, and excess calcium, Ca_x, for a constant dissolved alkalinity concentration, Alk_d. This can be seen from eqs.(49-52), which can be solved for excess TIC as follows:

$$TIC_{xs} = \frac{4Alk_d^2(q + K_{LOI})Ca_x + Alk_d q(\beta_1 Alk_T + 2\beta_0) + 2Alk_d^3(q + K_{LOI}) - Alk_d^2\beta_1 q}{2q(\beta_1(Alk_T - Alk_d) + 2\beta_0)}$$

where:

$$TIC_{xs} = \frac{J_{TIC_{xs}}}{q}$$

$$Ca_x = \frac{J_{Ca_x}}{q}$$

$$Alk_T = \frac{J_{Alk}}{q}$$

This important relationship is the key to the quantitative understanding of the quantity of calcium carbonate that forms in the lake model. Its use is illustrated below.

APPLICATION TO ONONDAGA LAKE

The model developed above for calcium carbonate precipitation in lakes is applied below to Onondaga Lake, a small dimictic lake located in metropolitan Syracuse, New York. The characteristics of the lake are listed in Table 5.

Table 5
Lake Characteristics

Volume	=	0.136 (km^3)
Surface Area	=	12.0 (km^2)
Mean Depth	=	11.3 (m)
Mean Hydraulic Residence Time	=	101 (days)
Mean Overflow Rate	=	0.119 (m/d)
Mean Temperature	=	12.5 (^oC)

There are six tributaries to the lake. The three largest, Ninemile Creek, Onondaga Creek, and Ley Creek contribute 90 - 98% of the combined inflow. In addition, the Syracuse Metropolitan Sewage Treatment Plant (Metro) and AlliedSignal until its closure in 1986, discharged to the lake. The lake outflow discharges to the Seneca River.

Onondaga Lake has been the focus of intensive research over the years (20). These data have been collected by various agencies and research institutes including Onondaga County Department of Drainage and Sanitation (D&S) (21), the Onondaga County Department of Health (DOH), the Upstate Freshwater Institute (UFI), and the U.S. Geological Survey (USGS). Walker (14) has documented and compiled these data into a unified database which is used for the present study.

D&S and UFI have collected data principally in two locations in the lake: one in the northern basin and the other in the southern basin. The conditions in the southern basin station have been found to represent the average lake concentrations (22,23). An analysis of the unified database confirms this observation.

1. Comparison to Model Calculation

Measurements of calcium and alkalinity concentrations in the tributaries and point sources exist from 1970 to 1990 from which the mass discharge rates to the lake can be calculated. However, total inorganic carbon tributary data are available only for 1983 - 1990 (14). Therefore, the latter period is analyzed initially.

The model was applied to each year as a steady state calculation. Because the detention time is approximately 100 days, the steady state calculation for the yearly average condition should be a reasonable approximation. The relevant loading data are listed in Table 6, and the overflow

Table 6

Observed and Estimated Annual Average Loadings

Year	Calcium		Alkalinity		Total Inorganic Carbon	
	(mol/m^2-d)		(meq/m^2-d)		(mol/m^2-d)	
	Obs.	Est.	Obs.	Est.	Obs.	Est.
1970	5.161	4.462	0.925	0.668	.	0.795
1971	4.399	2.632	0.512	0.486	.	0.540
1972	2.075	2.500	0.637	0.626	.	0.721
1973	2.398	1.611	0.487	0.475	.	0.507
1974	1.010	1.450	0.521	0.526	.	0.622
1975	1.210	1.293	0.536	0.580	.	0.526
1976	1.338	1.914	0.651	0.640	.	0.486
1977	2.655	2.187	0.699	0.527	.	0.468
1978	1.427	1.657	0.400	0.534	.	0.284
1979	1.494	1.439	0.504	0.516	.	0.286
1980	2.222	1.243	0.355	0.303	.	0.198
1981	1.630	1.656	0.390	0.386	.	0.256
1982	1.506	1.166	0.368	0.398	.	0.247
1983	1.560	1.348	0.391	0.400	0.307	0.305
1984	1.182	1.376	0.401	0.516	0.362	0.396
1985	1.330	1.194	0.360	0.416	0.363	0.395
1986	0.743	0.904	0.465	0.424	0.479	0.440
1987	0.462	0.446	0.357	0.374	0.352	0.386
1988	0.411	0.409	0.321	0.336	0.348	0.412
1989	0.386	0.432	0.402	0.376	0.460	0.466
1990	0.544	0.499	0.529	0.502	0.595	0.598

rate, temperature and chloride concentrations, from which the chemical parameters are calculated (using the equations in Table 1) are listed in Table 7. The method for the solution of eq.49, the cubic equation for dissolved alkalinity, is listed in Table 8. The model parameters are listed in Table 9.

Table 9
Model Parameters

w_s	=	0.10 (m/d)
K_{LOI}	=	0.25 (m/d)
K_p	=	10,000 (L/mol-d)

The computation of the TIC loading to use in the yearly average analysis is not straightforward. The tributaries supply organic carbon as well as inorganic carbon to the lake. Most of this organic carbon will be oxidized to inorganic carbon since the half life for oxidation is considerably shorter than the half life for water residence in the lake. Therefore, the labile fraction of the organic carbon input should be added to the inorganic carbon loading to form the total effective inorganic carbon input to the lake.

A parallel issue is the impact of the uptake of inorganic carbon by photoplankton. This is a sink of TIC. However, phytoplankton organic carbon will also be oxidized as well as being exported in the outflow or permenantly buried in the sediment. Therefore, phytoplankton primary production is a net sink of TIC which is smaller than the magnitude of the net primary production. As a consequence, there is some uncertainty about the actual TIC loading. For the calculations presented below, the tributary and point source TIC and labile TOC are added and the loss due to primary production is ignored. A check of these assumptions is presented below, where the loadings to the lake are estimated from in-lake concentrations and compared to these estimates.

The comparison of model calculations and observed yearly average data are shown in Fig.9. The solid lines are the model results. They connect the steady state concentrations computed for each year. The dotted lines represent the steady state concentrations of total calcium, alkalinity, and inorganic carbon, which would occur if these variables were not afffected by any loss mechanism besides dilution. They are presented so that the losses due to atmospheric exchange and sedimentation are illustrated. The concentrations due to dilution only are:

Onondaga Lake

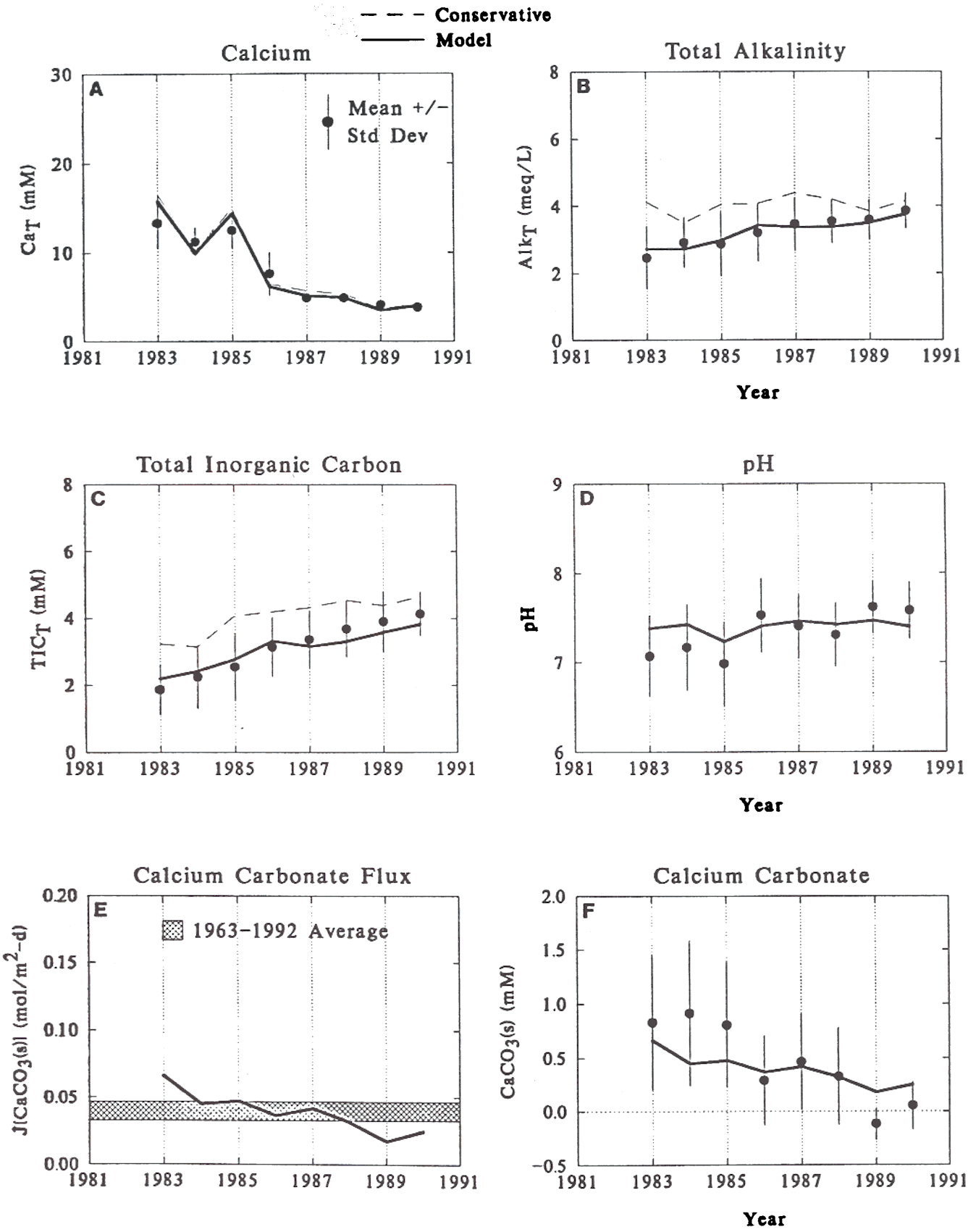

Figure 9

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Table 7

Onondaga Lake Annual Averages

Year	*q*	Temp	Chloride	Total Calcium	Total Alkalinity	Total Inorganic Carbon
	(m/d)	^{o}C	(mg/L)	(mM)	(meq/L)	(mM)
1970	0.190	11.9	1778	23.45	3.45	3.78[a]
1971	0.122	8.7	1489	21.52	3.88	3.78[a]
1972	0.171	8.8	1656	14.56	3.58	3.78
1973	0.133	12.0	1444	11.93	3.20	3.22
1974	0.141	12.2	1516	10.31	3.74	4.01
1975	0.132	10.7	1387	9.54	3.86	3.30[a]
1976	0.152	12.9	1375	12.12	3.27	2.58
1977	0.143	13.9	1653	14.97	3.01	2.66
1978	0.117	13.5	1414	13.16	2.57	1.42
1979	0.123	14.0	1730	10.83	2.47	1.44
1980	0.085	14.8	1989	13.99	2.17	1.61
1981	0.103	14.0	1737	15.42	2.37	1.74[a]
1982	0.089	10.6	1565	12.34	2.88	1.74[a]
1983	0.095	12.7	1602	13.32	2.46	1.87
1984	0.115	14.2	1435	11.19	2.90	2.25
1985	0.089	13.5	1648	12.49	2.86	2.55
1986	0.114	11.7	1010	7.66	3.21	3.14
1987	0.081	13.1	626	4.92	3.46	3.37
1988	0.077	12.8	602	4.92	3.54	3.68
1989	0.105	12.7	481	4.12	3.58	3.90
1990	0.128	13.1	424	3.87	3.85	4.13

[a]No measurement. Estimated by interpolation/extrapolation

Table 8
Solution of a Cubic Equation for Dissolved Alkalinity

$$x^3 + a_0 x^2 + a_1 x + a_2 = 0$$

where: $x = Alk_d$

$$q = \frac{a_0{}^2 - 3\,a_1}{9}$$

$$r = \frac{2\,a_0{}^3 - 9\,a_1\,a_0 + 27\,a_2}{54}$$

$$\text{disc} = q^3 - r^2$$

if(disc) ≥ 0 then :

$$\theta = \arccos\left(\frac{r}{q^{3/2}}\right)$$

$$x_{p,1} = -2\sqrt{q}\,\cos\left(\frac{\theta}{3}\right) - \frac{a_0}{3}$$

$$x_{p,2} = 2\sqrt{q}\,\sin\left(\frac{\theta}{3} + \frac{\pi}{6}\right) - \frac{a_0}{3}$$

$$= -2\sqrt{q}\,\sin\left(\frac{\theta}{3} - \frac{\pi}{6}\right) - \frac{a_0}{3}$$

if(disc) < 0 then :

$$= \frac{r}{|r|}\left(\sqrt[3]{|r| + \sqrt{r^2 - q^3}} + \frac{q}{\sqrt[3]{|r| + \sqrt{r^2 - q^3}}}\right) - \frac{a_0}{3}$$

Correct root satisfies: $0 \leq x_{\ell,j} \leq \frac{J_{Alk}}{q}$

$$TIC_T = \frac{J_{TIC}}{q}$$

$$Ca_T = \frac{J_{Ca}}{q}$$

$$Alk_T = \frac{J_{Alk}}{q}$$

The calcium concentration (Fig.9A) is large relative to the alkalinity and total inorganic carbon (Figs.9B and 9C). Hence, the relative amount of calcium that is lost via calcium carbonate sedimentation is small. By contrast, the relative amounts of alkalinity and total inorganic carbon that are removed is larger, with the loss of CO_2 to the atmosphere contributing a significant amount. The model reproduces the year to year variation in alkalinity and inorganic carbon reasonably well (Figs.9B and 9C). The computed variation in pH is not as large as the observations (Fig.9D) although the trend is correct. It should be pointed out that computing pH correctly is quite difficult because it is a sensitive function of the ratio of dissolved alkalinity and inorganic carbon, Fig.1. A 10% error in the ratio of Alk_d/TIC_d = 0.9 - 1.1 corresponds to a pH range of 7.3 - 9.4.

The model reproduces the trend of decreasing calcium carbonate concentrations from 1983 to 1990 reasonably well (Fig.9F) although the observations have a steeper decline. The predicted calcium carbonate flux is compared to the estimated long term average in Fig.9E. The flux is below the observed average, which is consistent with the larger calcium carbonate concentrations in the past, Fig.3. The 21 year record is analyzed in the next section.

2. Estimating the Historical Loadings.

Unfortunately, the TIC loading data for the years preceding 1983 are not available. However, it is possible to use the mass balance equations to estimate the loadings if the other terms in the equations are known. The in-lake concentrations are measured, and the calcium carbonate concentration have been estimated. Hence, the outflow and depositional losses can be quantified. The loss of CO_2 to the atmosphere can be estimated as well. The concentrations used for this estimation are listed in Table 7, and the estimated loadings are listed in Table 6.

3. Modeling the 21 Year Period

The comparison of the model results and data is presented in Fig.10. The dashed lines are the concentrations that correspond to conservative behavior (eqs.58-60). The model reproduces

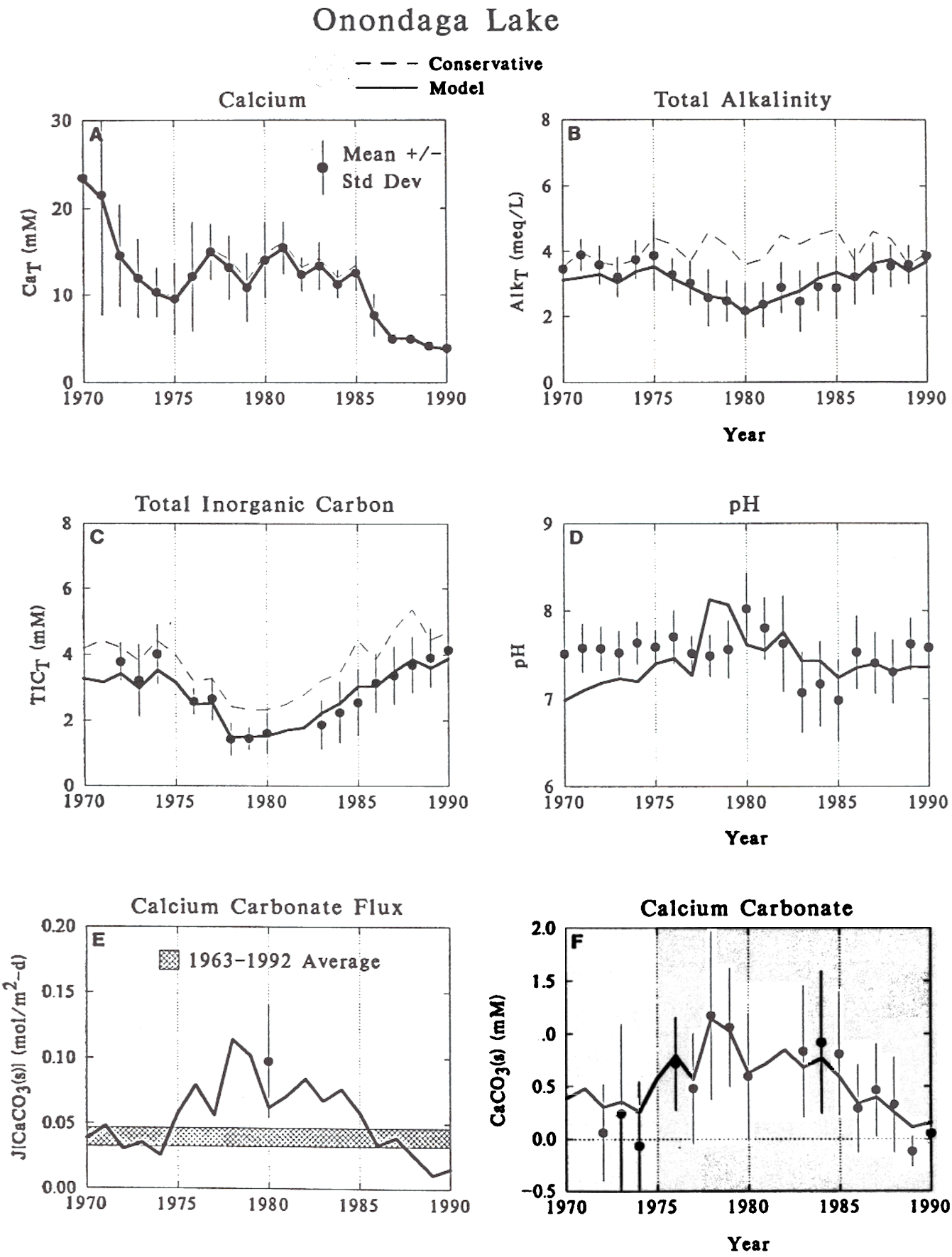


Figure 10

FINALP2

the data for total calcium, alkalinity, and inorganic carbon quite well. This finding is not surprising because the loading is computed from the observations. However, the calcium carbonate concentration and flux are also reasonably well reproduced. The measurement in 1980 is from Effler and Driscoll (24); the long term average is from an analysis of dated cores (25). They are not forced by the loading estimates. Therefore, the extent to which they are reproduced support the validity of the model. The computed pH (Fig.10D) is not reproduced very well. Certain trends are approximately captured: the rise near 1980 and the drop near 1985 and the subsequent rise thereafter. However there is a systematic deviation before 1975. The difficulty in computing pH has been discussed above.

The question of the degree to which the estimation technique can estimate the loading is examined in Fig.11, where the loading estimates are compared to observed loadings for the years in which they exist. The calcium loadings are in very good agreement with the exception of one very large value, which is inconsistent with the in-lake calcium concentrations for those years. The alkalinity loading is in reasonably good agreement with observations with one exception as are the inorganic carbon loading estimates. Therefore, the estimated loading for the 21 year period is likely to be reliable.

4. Causes of the Fluctuations in Calcium Carbonate

The model successfully reproduces the observed increase and then decrease of calcium carbonate over the 21 years (Fig.10F). However, it is not clear why this pattern occurs. The linear relationship (eq.54) between TIC_{xs} and Ca_x for a constant dissolved alkalinity concentration (Alk_d) can be used to understand the causes of the variations.

Fig.12A presents the excess calcium concentration (Ca_x) which is simply the excess calcium concentration that would be produced by the loading of excess calcium to the lake if there were no removal processes other than outflow (eq.56). This is superimposed on the *computed* calcium carbonate concentrations. The loading history of calcium to the lake can be divided into three periods, which are coded by different shading for the calcium carbonate concentrations: (1) from 1970 to 1974, when the excess calcium loading is declining by approximately one-half, (2) from 1975 to 1984, when the excess calcium loading was reasonably constant, (3) and from 1985 to 1990, when the excess calcium loading decreased even further, almost approaching zero. The total alkalinity (Alk_T) and excess total inorganic carbon (TIC_{xs}) are plotted in Fig.12B as a stacked bar plot where TIC_{xs} is added to the alkalinity concentration and the sum is plotted. The length of the filled bars is the concentration of TIC_{xs}. Note that the alkalinity loading to the lake has remained approximately constant throughout the 21 years, whereas the excess TIC loading has changed substantially.

Estimated vs Observed Loadings

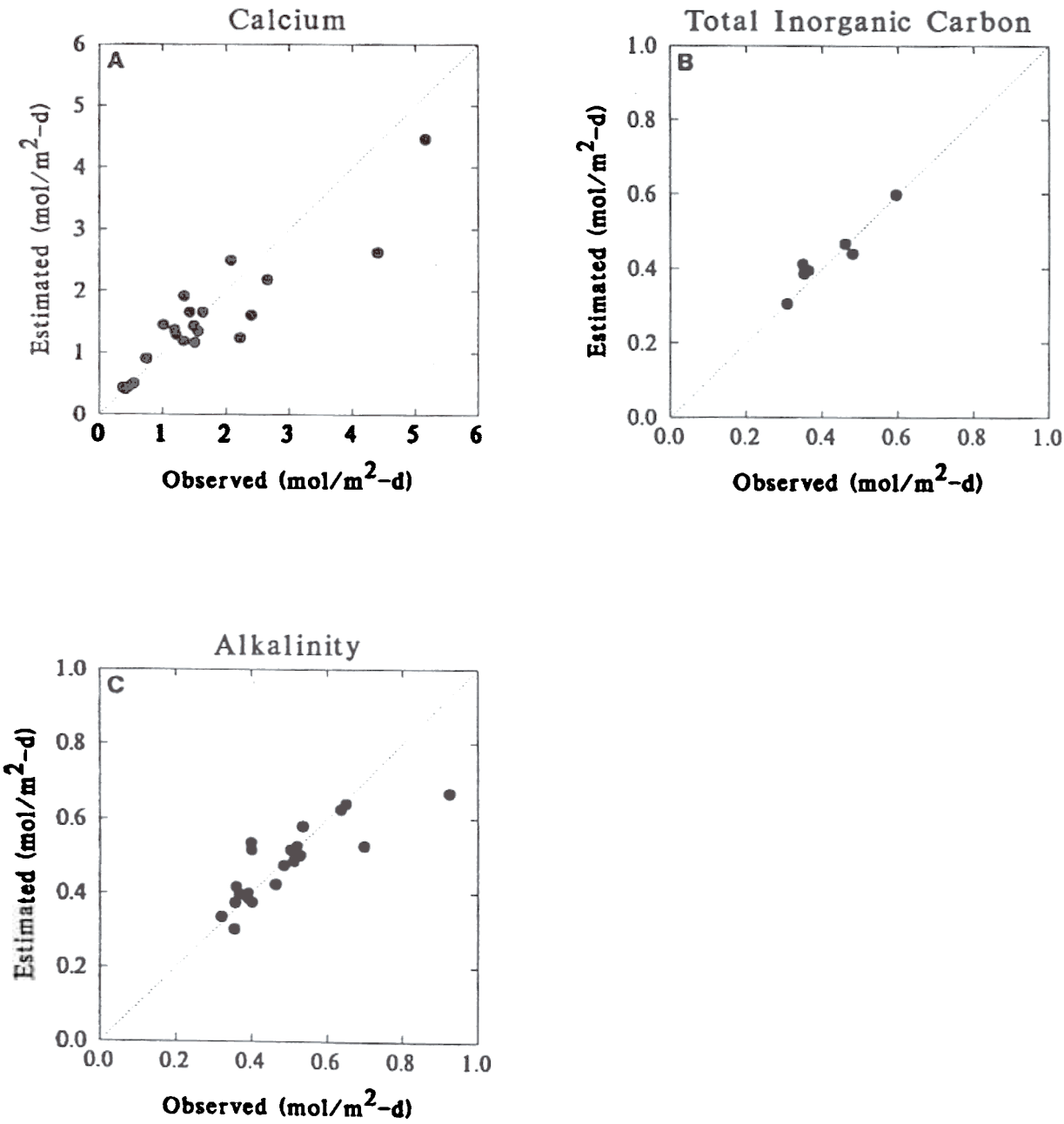
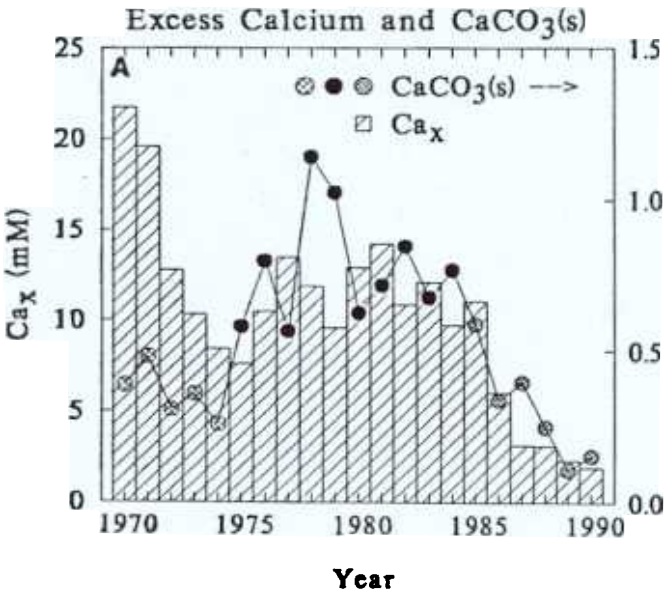
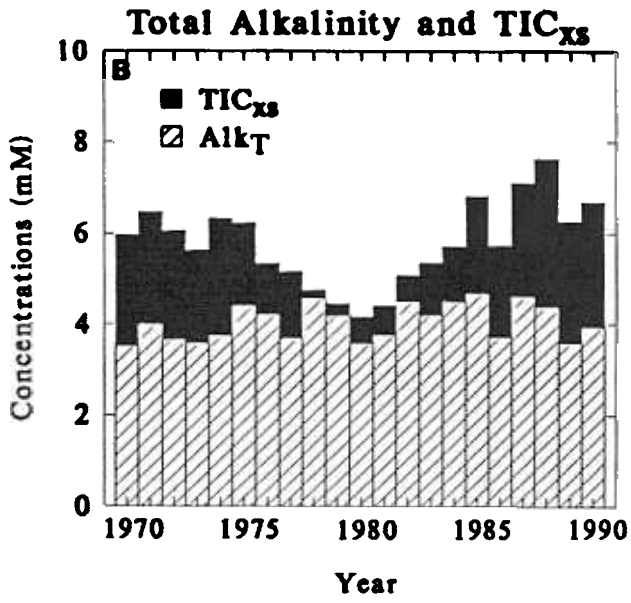


Figure 11

FINALP3

Analysis of Calcium Carbonate Formation





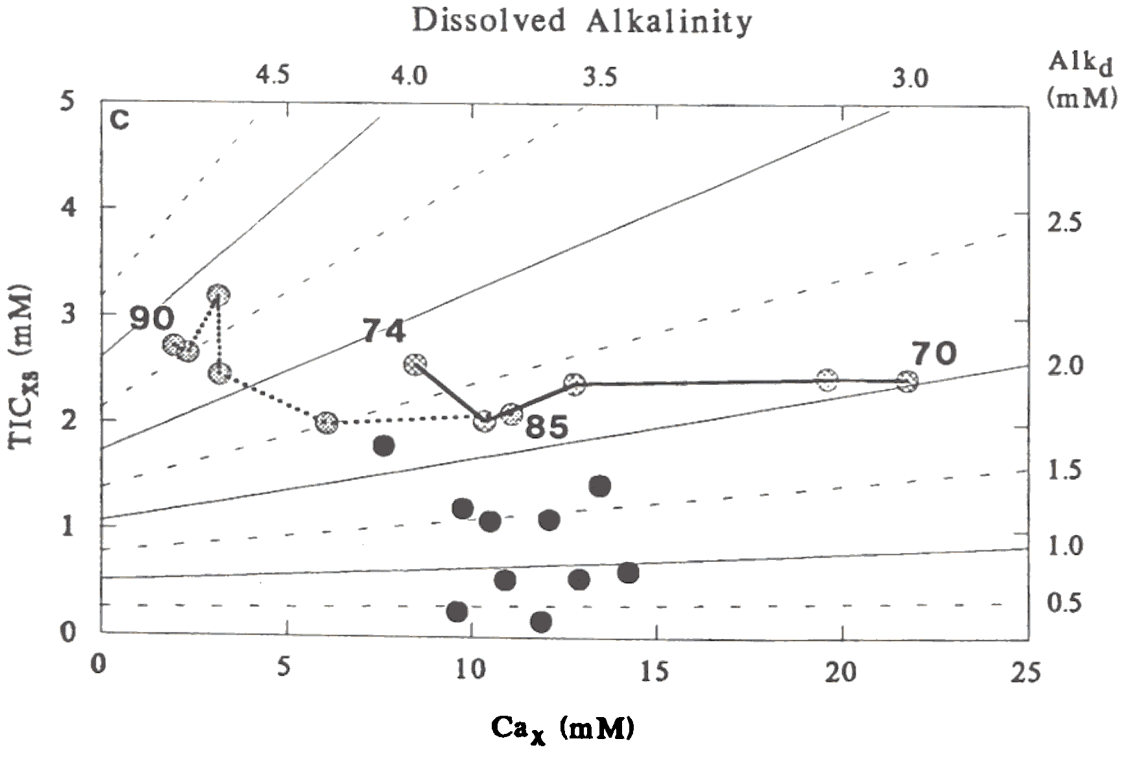


Figure 12

LOADP9B

The key to understanding how the loading variations have affected the calcium carbonate concentration in the lake is presented in Fig.12C. Lines of constant dissolved alkalinity are shown which are computed from the linear relationship (eq.54) between TIC_{xs} and Ca_x for each indicated dissolved alkalinity concentration (Alk_d). The other parameters in eq.54 are set at their twenty one year averages and are listed in Table 10. The plotted symbols represent each year's TIC_{xs} and Ca_x concentrations.

Table 10
Twenty One Year Average Parameters

β_0	=	160 (mM^2-m)
β_1	=	39.4 (mmol-d/L-m)
Alk_T	=	4.04 (mM)

Consider the first period: 1970 to 1974, for which the initial and final concentrations are labeled with the year and the symbols are connected with a solid line. Excess calcium decreased dramatically from 22 mM to 8.4 mM, while excess TIC remained approximately constant. The result is that the dissolved alkalinity changed slightly from 2.3 mM to 2.8 mM. Since the total alkalinity, which is the sum of the dissolved alkalinity and calcium carbonate concentrations, stayed approximately constant (Fig.12B), the calcium carbonate concentration decreased only slightly, as shown.

The next period, 1975-1984, denoted by the solid filled symbols in Fig. 12A and 12C, are characterized by approximately constant excess calcium loading (Fig. 12A) but changing excess TIC loading (Fig.12B). TIC_{xs} decreases from 1976 to a minimum in 1979-1980 and then increases. As TIC_{xs} decreases, dissolved alkalinity decreases from 2.8 mM to less than 0.5 mM (Fig.12C). Since total alkalinity is constant, the calcium carbonate concentration increases. It is the variation in TIC_{xs} that is causing the variation in calcium carbonate concentration during this period.

The beginning and ending years of the final period, 1985-1990, are also labeled in Fig.12C. The points are connected with a dotted line. Excess calcium loading is decreasing from 11 mM to 2 mM (Fig.12A) whereas TIC_{xs} is increasing from 2 mM to almost 3 mM (Fig.12B). The result is an increase in dissolved alkalinity from 2.2 mM to 3.4 mM (Fig.12C). The resulting calcium carbonate concentration drops in response to this change.

REFERENCES