The presence of carbonate minerals exerts a major influence on the chemistry of a soil. In areas with inputs of acid rain, both the soils and overall watershed chemistry are best classified according to whether or not carbonate minerals are present. Most soil silicate minerals are both thermodynamically unstable relative to carbonates and also more abundant under most soil conditions. Despite these factors of stability and abundance, dissolution of alkali earth cations is usually orders of magnitude greater when carbonates are present than when they are not present. Under conditions of high rainfall, noncalcareous soils often become acidified and pH is then controlled by Al chemistry. Calcareous soils maintain much higher pH values, alkalinity and alkali earth cation concentrations than do noncalcareous soils. If carbonate minerals are present, prediction of soil pH requires consideration of carbonate equilibrium reactions. Soil pH is required for evaluation of many processes in soils, including micronutrient availability, heavy metal transport and plant availability, and Al toxicity. Under arid conditions calcium carbonate precipitation is a dominant process affecting solution chemistry and pedogenesis. The solution composition in a carbonate system, depends on the partial pressure of CO$_2$ ($P_{CO_2}$). The system can be described using equations for dissociation of water ($K_w$),

\[ (H^+)(OH^-) = K_w \]

\[ \text{dissolution of CO}_2\text{ gas in water, and hydration of dissolved CO}_2\text{ to H}_2\text{CO}_3^\ast \text{, generally combined into the overall equation} \]

\[ \frac{(H_2CO_3^\ast)}{P_{CO_2}} = K_H \]

where $H_2CO_3^\ast$ denotes dissolved aqueous CO$_2$ + the undissociated carbonic acid, $H_2CO_3$ and parentheses denote activity. At 25°C,$H_2CO_3^\ast$ is almost completely
comprised of the unhydrated species (Stumm & Morgan, 1981). The first and second dissociation expressions for carbonic acid ($K_{1a}$ and $K_2$), are represented in the following equations:

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3^*)} = K_{1a}$$  \[3\]

$$\frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} = K_2$$  \[4\]

where $K_{1a}$ is the first apparent dissociation constant for carbonic acid. The solution of these four equations requires i) data for the equilibrium constants which vary significantly with temperature and ii) activities of two of the species in the system (e.g., $H^+$, $CO_3^{-}$).

The solution of a CO₂ equilibria problem with a computer program requires a routine to calculate ion activities from concentration, electroneutrality and mass balance equations and input for two of the following three components: Partial pressure of CO₂, pH, and dissolved inorganic carbon (DIC) or inorganic C alkalinity. The DIC is the sum of all inorganic C species in solution (CO₂, aq, $H_2CO_3^*$, HCOJ, CO$_3^{2-}$ and all ion pairs of HCO$_3^-$ and CO$_3^{2-}$) and inorganic C alkalinity is the alkalinity component of these species determined by titration. Addition of a solid phase constraint, for example calcite equilibria, results in an additional equation and calculation of Ca$^{2+}$ activity,

$$(Ca^{2+})(CO_3^{2-}) = K_{sp}$$  \[5\]

where $K_{sp}$ represents the solubility product of the calcium carbonate solid phase. If the problem is to determine if the solution is in equilibrium with calcium carbonate, then the Ca concentration must be specified in the input (and the ion activity product is to be determined).

**Open versus Closed Systems**

Two idealized equilibrium systems have been used to describe the interaction of CO₂ gas with solutions; these are generally described as “open” and “closed” systems (Stumm & Morgan, 1981). Closed systems do not allow for transfer of C into or out of the system. The term has also been used to include the restriction that there is no gas phase. Open systems are open to the atmosphere or to a gas phase of fixed $P_{CO_2}$.

The closed system model is often utilized for descriptions of the chemistry of groundwater systems and can also be used for some laboratory experiments and closed pipe water delivery systems. The model is generally unrealistic for soil systems, as will be detailed in subsequent sections.

The open system condition allows for transference of C into or out of the system. Typically, the term open system is used whenever the gas phase is of constant
CO₂ pressure, independent of precipitation or dissolution. In the open system case, the \( \text{H}_2\text{CO}_3^- \) is constant and fixed by the gas composition. The open system model is a more realistic model for earth surface conditions than that described by the closed system, and thus is more commonly used. This concept is suitable for controlled laboratory reactions where \( \text{CO}_2 \) gas is bubbled through soil water suspensions and is often valid for soil water reactions open to the atmosphere. It is not an entirely satisfactory description for soils under field conditions.

Soils in their field condition are characterized by variable \( \text{CO}_2 \) pressures that are greater than the \( \text{CO}_2 \) pressure in the atmosphere. They are still “open” in the sense that there is gas exchange between the atmosphere and the soil and that the chemical reactions in the soil solution do not appreciably affect the soil gas composition. An example of an annual soil \( \text{CO}_2 \) profile is shown in Fig. 4-1, which shows large changes in \( \text{CO}_2 \) pressure (expressed in kPa) with time. Biological

![Graph showing changes in water content and soil \( \text{CO}_2 \) concentration over time.](image)

Fig. 4-1. Mean percentage \( \text{CO}_2 \) and moisture in soil air at a depth of 20 cm at Columbia, Missouri, 1982 (from Buyanovsky & Wagner, 1983).
production is the primary source of CO₂ and varies with temperature, gas composition, water content and nutrient availability. The CO₂ pressure measured in a soil results from the interaction of CO₂ production and the diffusive and convective transport to the atmosphere. In soil systems, this interaction results in a lack of CO₂ equilibrium with the atmosphere. As a result of the dynamics of these processes, the CO₂ pressure of the soil gas may not always be in equilibrium with the soil solution.

For purposes of predicting solution composition in equilibrium with a solid phase carbonate, it is useful to make the following distinctions: (i) Open system—with fixed $P_{CO_2}$ or with $P_{CO_2}$ determined by factors not considered in the set of chemical equations (such as biological activity). For the open system, we must input $P_{CO_2}$ and one of the following variables—pH, alkalinity, or DIC. (ii) Closed system without a gas phase. This condition requires the input of pH and alkalinity or pH and DIC (used by the program GEOCHEM (Sposito & Mattigod, 1980)). (iii) Closed system with a gas phase. This condition requires the input of a gas/solution ratio, initial gas composition ($P_{CO_2}$), and one of the following: pH, alkalinity, or DIC, if the gas and solution are initially equilibrated. If the gas and solution are not initially equilibrated then the input requires two out of three of the following variables: pH, initial $P_{CO_2}$ and alkalinity or DIC.

Theoretically, if the other dissolved species are given, the pH can be calculated by use of the electroneutrality condition, thus pH or $P_{CO_2}$ need not be input. Although some of the programs described below can be used to calculate pH in this manner, it is not reasonable for most actual analyses, since the analytical errors in almost all instances produce errors much greater than the proton concentration.

Input of $P_{CO_2}$ and pH is recommended for open system problems in several programs. The major difficulty with this approach is that the $P_{CO_2}$ is rarely measured or known. For example, when analyzing saturation extracts using pH and alkalinity, the computed $P_{CO_2}$ is always greater than atmospheric. Elevated CO₂ in saturation extracts is likely the result of biological production during the saturation and extraction process. Similar elevated CO₂ levels have been determined for soil-water suspensions reacted in the laboratory. In addition to the biological effects causing disequilibrium between the liquid and gas phases, chemical reactions such as proton producing or consuming reactions also may cause disequilibrium. Furthermore, CO₂ concentrations inside most occupied buildings are elevated up to twofold with respect to the quoted atmospheric value of 35 Pa or $10^{-3.5}$ atmosphere. Data collected in our laboratories in Riverside, California, are typically between 45 to 60 Pa (450-600 ppm, D.L. Suarez, unpublished data). As a result of the above discussion, it seems undesirable to do carbonate chemistry calculations using pH and $P_{CO_2}$ unless the $P_{CO_2}$ is measured and there is assurance that the solution is in equilibrium with that CO₂ pressure. This condition will usually require that the solutions be bubbled with a gas of known composition and no net H⁺-consuming or H⁺-releasing reactions are occurring.

Input of DIC and pH allows for computation of HCO₃⁻ and CO₃²⁻ activities. This procedure is convenient if DIC is analyzed and avoids some problems associated with total alkalinity determinations. Analysis of DIC avoids problems
associated with noncarbonate acid species that have an acid neutralizing capacity, such as weak organic acid ligands and weak inorganic acids such as boric, phosphoric and silicic acids. Conceptually it can be considered the preferred input for a calculation scheme for soil waters and extracts, however, it is generally preferable to determine and utilize alkalinity values. The DIC is commonly not available from published analytical data. Alkalinity is more convenient to measure than DIC, and if properly determined, alkalinity measurements have the advantage of not changing if the sample degasses after collection (as long as precipitation does not occur). Determination of DIC is not convenient because it includes the unstable component of dissolved CO₂, and must be analyzed immediately. Analysis of DIC (by a C analyzer) also is not as rapid nor as reproducible as alkalinity determinations. The pH also must be measured immediately because degassing of CO₂ will increase the solution pH. Most currently available data include pH and alkalinity measurements and not DIC.

If DIC is not available but required, and if the P_CO₂ is known, it is suggested to use Henry’s law (Eq. [2]) and add the calculated H₂CO₃⁺ to the carbonate alkalinity value and input this value as DIC. This is accurate for solutions below pH=8.0. At higher pH values the contribution of CO₃²⁻ species to alkalinity becomes important. The DIC measures CO₂⁻ containing species as mol C but CO₃²⁻ species contribute 2 mol C per mol CO₃²⁻.

SOLUTION SPECIATION MODELS

The objectives and implicit assumptions of the commonly used equilibrium models are quite different, thus they will be categorized according to their function. All equilibria models assume equilibrium among dissolved species, but in some models, equilibria with solid phases is not assumed. These programs are often called equilibria or solution speciation programs. Some models make the additional assumption that the solution is in equilibrium with the thermodynamically predicted solid phases. These latter equilibrium models are predictive in that they modify the solution composition using the assumption that only the most stable phase or phases can occur and that the solution is always in equilibrium with them. These models are discussed below in the section on simulations and predictive models.

The different objectives in the use of the equilibria models is apparent in the earliest models developed by soil scientists. Adams (1971) developed a multicomponent speciation model to calculate ion activities. Tanji and Doneen (1966) developed a predictive model considering equilibria with respect to calcite.

The primary objective of some of the initial comprehensive multicomponent chemical equilibrium speciation models, such as WATEQ (Truesdell & Jones, 1974), were to characterize the status of the chemical composition of a water with respect to thermodynamically stable solid phases. These programs initially considered only major ions in solution but, versions of the programs have been developed to include numerous trace elements and organic constituents. The models incorporate corrections for activity coefficients and solution complexation, thereby allowing for an evaluation of the saturation status of the solution with respect to the thermodynamically stable solid phases. Examination of model
output can be useful in understanding the chemical processes which control solution composition and allows an investigator to consider the potential changes in the solution with time. Prediction of solution composition based on solid phase equilibria was explicitly not one of the goals of these initial programs. Subsequently, these and other similar programs have been modified to predict solution compositions based on mineral equilibrium assumptions.

**SOLUTION-SOLID EQUILIBRIA MODELS**

Instead of calculating saturation status, equilibrium solution-solid models calculate the solution composition in equilibrium with specified minerals. The saturation status is typically reported as the saturation index or SI defined as

\[
SI = \log \frac{\text{IAP}}{K_{sp}}
\]

where IAP represents the ion activity product and \( K_{sp} \) is the solubility product constant for the mineral of interest. Unfortunately these solution-mineral equilibria models are often used as predictive models for earth surface environments without either experimental data or explicit justification of the assumptions made. Most model descriptions do not discuss this point nor consider that the equilibrium assumption might not be valid for prediction in natural systems. Equilibrium models which include solid-solution equilibria are sometimes directly incorporated into predictive models for natural systems, where mineral-solution equilibria is almost never a reasonable assumption.

Many of the predictive models such as GEOCHEM (Sposito & Mattigod, 1980) and MINTEQ (Felmy et al., 1984) and MINTEQA2 (Allison et al., 1990) can be utilized as speciation programs by specifying the omission of solid phase reactions. These models are discussed in the following section as used in solution speciation problems rather than as predictive models.

**WATEQ**

WATEQ (Truesdell & Jones, 1974) WATEQF (Plummer et al., 1976) and updated versions such as WATEQ4F (Ball et al., 1987) are typical of what is now a large set of chemical equilibria programs which input total alkalinity as well as pH, and compute \( P_{CO_2} \) and saturation status but do not have the option to force the solution to solid phase equilibrium. The calculation scheme allows for apportioning the alkalinity between inorganic C alkalinity and phosphate, hydroxide, borate, sulfide, silicate and ligands.

WATEQ is designed for input of analyzed water compositions. There is no requirement of overall charge balance. This is convenient for analyzed water compositions which always have some analytical error. The program converges based on mass balance of the individual input species. The program iterates until the sum of all weak acids, complex ions, and free ions for all the anions agree within 0.5% of the input values. Input of temperature (field pH for field samples) is required as the temperature dependence of most equilibrium constants are cal-
calculated by the program. If sufficient information is available, temperature dependence is calculated using a power function of the form

\[ \log K = A + BT + C/T + D \log T, \]  

[7] where \( T \) is absolute temperature. Where experimental data is available at only a few temperatures, then the temperature dependence is calculated using the Van't Hoff relation

\[ \log K = \log K_{T_r} - \frac{\Delta H_r}{2.3R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \]  

[8] where \( T_r \) is the reference temperature of 25°C, \( \Delta H \) is the enthalpy of reaction, and \( R \) is the gas constant.

If evaluation is made of the saturation status with respect to a redox dependent species, then either dissolved \( \text{O}_2 \), or measured Eh must be input. Although the program can calculate Eh from dissolved \( \text{O}_2 \), this is not recommended, as often dissolved \( \text{O}_2 \) is not in equilibrium with redox couples of interest, such as \( \text{Fe}^{2+}/\text{Fe}^{3+} \). Calculation of \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) activities is based on input of total dissolved Fe and Eh. The program calculates saturation with respect to siderite \((\text{FeCO}_3)\), which can control Fe solubility under reduced conditions in neutral to alkaline environments. The program does not include organic species. Solution density is set equal to 1.0, unless specified by the user (very high salinity solutions).

Various models exist to correct solution concentrations to activities, and not all models give the same results. WATEQ utilizes an extended version of the Debye-Huckel equation to calculate single ion activity coefficients

\[ \log \gamma = \frac{-Az^2}{1 + Ba \sqrt{I}} + bi \]  

[9] where \( A \) and \( B \) are constants depending only on the dielectric constant, solution density, and temperature; \( z \) is the ionic charge; and \( I \) is the ionic strength. The a parameter is no longer the hydrated ion radius or Debye-Huckel constant as in the original formulation of the equation, but instead the \( a \) and \( b \) terms are fitted parameters specific to each ion. The values are based on experimental mean salt single-ion activity coefficients determined from mean molal activity coefficients using the MacInnes assumption \((\gamma \text{KCl} = \gamma K^+ = \gamma Cl^-)\) and fitted up to ionic strength of 4.0 (Truesdell & Jones, 1974). It is assumed that the activity coefficients depend only on the ionic strength and not on the specific ions present. This assumption is questionable above \( I = 0.5 \), where ion interactions become more important.

Similar to WATEQ, there are other speciation programs which consider carbonate equilibria with inputs of pH and alkalinity and output of \( P_{\text{CO}_2} \) and mineral saturation. Among these are relatively simple models which consider only major ion chemistry and calcium sulfate and calcium carbonate, such as those described by Tanji and Doneen (1966) Oster and Roahades (1975) and Suarez (1977). These inputs have represented the preferred approach for evaluating carbonate systems. However, input of alkalinity is not well suited for systems with large amounts of
noncarbonate weak acid ligands, such as organic rich waters or those with low alkalinity.

GEOCHEM

GEOCHEM (Sposito & Mattigod, 1980), and variations such as SOILCHEM (Sposito & Coves, 1988) and GEOCHEM PC, (Parker et al., 1995) are frequently used by soil scientists. GEOCHEM is a modified version of REDEQL2 (McDuff & Morel, 1973). The program MINEQL (Westall et al., 1976) and the derivative model MINTEQA2 (Allison et al., 1990) have a different computational scheme, but these programs treat carbonate problems in a manner similar to REDEQL2. GEOCHEM PC (Parker et al., 1995) is a modified version of GEOCHEM. All of these programs are comprehensive, multicomponent models which include solid phase equilibria as an option. The discussion of the carbonate equilibria and options available for GEOCHEM are generally applicable to GEOCHEM PC, MINEQL and REDEQL2.

GEOCHEM and similar models can be directly utilized for carbonate speciation when the solution pH and DIC are input. In this case GEOCHEM must be executed without consideration of a gas phase, and the output does not give the calculated $P_{CO_2}$. GEOCHEM PC has been modified to calculate the hypothetical $P_{CO_2}$ in equilibrium with this solution. Output of $P_{CO_2}$ is useful, as it serves as a check on the pH and C determinations (if $P_{CO_2}$ is independently known).

Use of GEOCHEM (also SOILCHEM and GEOCHEM PC, among others) for direct solution of open system problems requires the input of pH and $P_{CO_2}$ (Sposito & Mattigod, 1980). Under these conditions the programs allow transference of C into or out of the solution phase and calculates total inorganic C. In GEOCHEM, DIC is represented by the notation CO$_3^-$, and the concentration of CO$_3^{2-}$ as free $CO_3^{2-}$ concentration. When utilizing GEOCHEM and GEOCHEM PC a large arbitrary value of CO$_2$ (meaning a large quantity of DIC, such as 0.5 molal) must be entered for computational purposes. This additional entry is required to insure sufficient dissolved carbonate to allow for proper speciation. In this case proper speciation is indicated in the output by “precipitation” of the excess DIC. Carbon dioxide outgasses since these models consider CO$_2$ gas as if it were a solid phase. GEOCHEM apportions inorganic C into gas and solution phases to force the system to overall equilibrium. Input of pH and $P_{CO_2}$ is rarely utilized in solution of carbonate problems.

GEOCHEM can not directly solve problems where $P_{CO_2}$ is input, and alkalinity or DIC is known. Specification of the $P_{CO_2}$ defines an open system and allows for movement of C into or out of the solution. GEOCHEM and GEOCHEM PC require the additional input of total H (listed as totH) whenever DIC and $P_{CO_2}$ are input. The total H represents the net sum of all the H balance in the dissolved species, i.e., totH = $\Sigma n$ [acid] + $[H^+]$ - $\Sigma m$ [base] - [OH-] where [ ] denote concentration and n and m are, respectively, the number of dissociable protons and hydroxides in each acid or base (Sposito & Mattigod, 1980). In the case of input $P_{CO_2}$, the CO$_2$ gas is treated similarly to a solid phase and the Henry’s law constant for CO$_2$ is taken as the solubility relationship.

Neither GEOCHEM nor GEOCHEM PC can be used to directly solve problems where alkalinity rather than DIC is available, since alkalinity is not
recognized as an input component. If pH and alkalinity are known, it is necessary to estimate DIC (add an estimate of $\text{H}_2\text{CO}_3^-$ to the alkalinity). It is recommended that the input DIC be adjusted (using several trial and error iterations) until the value of the estimated input DIC minus the output $\text{H}_2\text{CO}_3^-$ equals the measured alkalinity. GEOCHEM PC provides alkalinity as an output value. This addition to GEOCHEM facilitates making the trial and error iterations, since DIC is adjusted until alkalinity output equals the known analytical value of alkalinity, without the need for the user to make additional computations.

If $P_{\text{CO}_2}$ and alkalinity are known, it is possible to run GEOCHEM as an open system problem by input of the $P_{\text{CO}_2}$, an excess estimated DIC and an estimated pH. Iterations are made by adjusting the pH until the calculated output alkalinity equals the known alkalinity. At this point the iteration is complete and the estimated pH is the correct equilibrium pH. Again, calculation of alkalinity from the GEOCHEM output requires that the user add the equivalent concentrations of the contributing species or subtract the $\text{H}_2\text{CO}_3^-$ from the output DIC (assuming that CO, species can be neglected). GEOCHEM PC is somewhat more convenient to use than GEOCHEM when performing these calculations since the user does not have to calculate the alkalinity after each iteration.

If $P_{\text{CO}_2}$ and DIC are known an estimate of pH is still required, however there are several iterative methods which can be used to solve this problem. As mentioned above, evaluation of an open system case requires a trial and error set of iterations. One possibility is to input the DIC and $P_{\text{CO}_2}$ and an estimated pH and iterate with different values of pH until there is neither dissolution nor precipitation of the input DIC. Alternatively, when using GEOCHEM PC, DIC can be input with an estimate of pH and no input of $P_{\text{CO}_2}$. Since a gas phase is not specified, this is considered a closed system problem and GEOCHEM does not distribute the DIC into a gas phase. Output of the hypothetical $P_{\text{CO}_2}$ value can be compared to the known $P_{\text{CO}_2}$ and the input pH estimate is adjusted until the known and output $P_{\text{CO}_2}$ values match. It is often useful to compare the calculated $P_{\text{CO}_2}$ with a known estimated $P_{\text{CO}_2}$ (when available) for problems with input of pH and alkalinity or DIC. This comparison provides the user with a check on alkalinity, pH, or evaluation of the assumption of equilibrium between the gas and solution phases. Similarly the saturation status with respect to a carbonate phase can be computed from a complete analysis in which $P_{\text{CO}_2}$ and pH, are specified, with the output, HCO, CO, and saturation status. Table 4-1 provides a summary of the input or iteration procedures to solve carbonate chemical problems.

The thermodynamic data bases used in GEOCHEM and GEOCHEM PC contain constants for 25°C. The programs do not contain provision for temperature dependence of the thermodynamic constants, thus the user must modify the data base if temperatures other than 25°C are required. Both GEOCHEM and GEOCHEM PC allow for specification of the maximum number of iterations and convergence criteria. Since the programs terminate whenever either criterium is met, it is necessary to check the output to insure that the desired convergence was achieved.

GEOCHEM utilizes an expression for calculation of activity coefficients which reduces to the Davies equation below $I = 0.5$ and which is similar in form to Eq. [9] above $I = 0.5$, but has a fixed $b$ value of 0.041 and an $a$ value that depends only on ion valence (in contrast to Eq. [9] which has ion specific
Table 4-1. GEOCHEM, GEOCHEM PC and IMINTEQA2 program options.

<table>
<thead>
<tr>
<th>VARIABLE</th>
<th>GEOCHEM</th>
<th>GEOCHEM PC</th>
<th>MINTEQA2</th>
<th>GEOCHEM</th>
<th>GEOCHEM PC</th>
<th>MINTEQA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. DIC pH</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>totH</td>
<td>totH alkalinity</td>
<td>Alkalinity totH ( P_{CO_2} )</td>
</tr>
<tr>
<td>2. Alkalinity pH</td>
<td>\‡</td>
<td>\‡</td>
<td>None</td>
<td>DIC (from input)</td>
<td>Alkalinity DIC (from input) ( P_{CO_2} )</td>
<td>DIC ( P_{CO_2} ) totH</td>
</tr>
<tr>
<td>a. Estimate DIC pH</td>
<td>Iterate DIC until sum of alkalinity species = known value</td>
<td>Iterate DIC until alkalinity output = known value</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. ( P_{CO_2} ) pH</td>
<td>Input excess DIC</td>
<td>Input excess DIC</td>
<td>None</td>
<td>Equilibrium DIC</td>
<td>Alkalinity equilibrium DIC</td>
<td>DIC, totH alkalinity</td>
</tr>
<tr>
<td>4. DIC ( P_{CO_2} )</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>Incorrect due to totH assumption</td>
<td>Incorrect due to totH assumption</td>
<td>Incorrect due to totH assumption</td>
</tr>
<tr>
<td>a. Estimate pH</td>
<td>Iterate pH until ( H_2CO_3 ) (s) is sufficiently small</td>
<td>Iterate pH until ( H_2CO_3 ) (s) is sufficiently small</td>
<td></td>
<td>pH (from input)</td>
<td>pH (from input) alkalinity</td>
<td>pH (from input) alkalinity</td>
</tr>
<tr>
<td>b. Estimate pH DIC</td>
<td>Iterate pH until ( P_{CO_2} ) output = ( P_{CO_2} ) known</td>
<td></td>
<td></td>
<td></td>
<td>pH (from input)</td>
<td>pH (from input)</td>
</tr>
<tr>
<td>5. Alkalinity ( P_{CO_2} )</td>
<td>\‡</td>
<td>\‡</td>
<td>totH = 0</td>
<td></td>
<td></td>
<td>pH, totH DIC</td>
</tr>
<tr>
<td>a. Estimate DIC ( P_{CO_2} )</td>
<td>Iterate DIC until sum of Alkalinity species = known alkalinity</td>
<td>Iterate DIC until output alkalinity = known alkalinity</td>
<td></td>
<td>totH, DIC (from input)</td>
<td>totH, DIC (from input) pH</td>
<td></td>
</tr>
<tr>
<td>6. Alkalinity DIC</td>
<td>\‡</td>
<td>\‡</td>
<td>\‡</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Estimate pH DIC</td>
<td>Iterate pH until sum of alkalinity species comprising alkalinity = known alkalinity</td>
<td>Iterate pH until output alkalinity = known value</td>
<td></td>
<td>pH (from input)</td>
<td>pH (from input)</td>
<td></td>
</tr>
</tbody>
</table>

\(^\dagger\) Alkalinity computed from DIC – \( H_2CO_3 \) (aq).
\(^\ddagger\) Cannot solve directly.
parameters). This modified equation used in GEOCHEM assumes that all ions of the same valence have the same activity coefficient, i.e., $\gamma_{\text{Ca}^{2+}} = \gamma_{\text{Mg}^{2+}}$. Differences between this equation and the extended Debye-Huckel are substantial even for moderately saline solutions. For example, at $I = 0.1$ the extended Debye-Huckel activity coefficients are 9% greater for $\text{Mg}^{2+}$ and 4.6% greater for $\text{Ca}^{2+}$ than those calculated using the Davies equation. Since similar data bases are utilized in most programs for the major species, these differences in calculated activity coefficients will result in comparable discrepancies in calculated activities.

Values for HCO$_3$ concentration in the output for GEOCHEM are found under the listing of complexed species. Determination of the activity of an individual species in GEOCHEM requires calculation of the activity coefficient from the output ionic strength and multiplication of the concentration of the individual species of interest. GEOCHEM PC provides output of the activities of the individual species.

**MINTEQA2 MODEL**

The model MINTEQA2 (Allison et al., 1990) can be used as either a speciation or predictive model. Use of MINTEQA2 for speciation problems in a carbonate system can be performed by specifying no precipitation of solids. Under these conditions the model gives results similar to WATEQ, which is to be expected, as MINTEQA2 uses the same thermodynamic data base as WATEQ. MINTEQA2 also can calculate equilibrium constants at other than 25°C using the same temperature correction Eq. [7,8] as WATEQ. If the AH, data for a thermodynamic constant is not available, MINTEQA2 uses the 25°C data.

MINTEQA2 allows for input of either alkalinity or DIC, although DIC is required if solid phases are considered. Without consideration of mineral reactions, the model can directly solve the following problems: (i) input of alkalinity and pH with output of $P_{\text{CO}_2}$ [listed in the MINTEQA2 output under Type 6 species as CO, (g) expressed in mol], DIC, ion activities and mineral saturation status; (ii) input of DIC and pH with output of $P_{\text{CO}_2}$, alkalinity, ion activities and mineral saturation status; (iii) input of $P_{\text{CO}_2}$ and pH with output of DIC (listed as id no. 140, CO$_3^{2-}$ in mass distribution section) ion activities and mineral saturation status; (iv) input of $P_{\text{CO}_2}$ and alkalinity. Execution of Problem 4 also requires that totH be specified and set equal to zero in the input (the requirement is not described in the user manual). In this case, the output provides calculation of solution pH, DIC, ion activities and mineral saturation status. Input of DIC and alkalinity is to be avoided as the model will give an incorrect solution due to omission of the totH. Solution of this and other problems, summarized in Table 4-1, requires input of an estimate of an additional component and iteration until the equilibrium conditions are achieved. Closed system cases are solved by input of DIC and total H$^+$ without consideration of a solid or gas phase.

If equilibria with respect to solid phases is desired, it is necessary to input DIC. If DIC is not available it must first be determined by making preliminary runs without consideration of solid phases (by input of either pH-alkalinity, pH-CO$_2$, or alkalinity-CO$_3$). This value of DIC is then input in the subsequent runs for equilibration with a solid phase, instead of specification of the alkalinity.
Activity calculations in MINTEQ are the same as those used in WATEQ, and includes the use of the extended Debye-Huckel equation. If the constants for Eq. [9] are not available, the program computes activity coefficients using the Davies equation

$$\log \gamma_1 = A z^2 \left[ \frac{I^{1/2}}{1 + I^{1/2}} - 0.24I \right]$$

where the terms $\gamma, A, z,$ and $I$ are as defined with Eq. [9].

A few programs exist which input $P_{CO_2}$ and pH and output carbonate species (e.g., GEOCHEM and MINTEQA2) but input of $P_{CO_2}$ and alkalinity with direct output of pH is less utilized in speciation programs since most researchers consider measurement of pH preferable to the additional assumption that the gas phase is indeed in equilibrium with the solution. Under field conditions, however, it is usually not possible to directly measure the soil solution pH. Typically, vacuum extractors are utilized to extract water from unsaturated soils, sampled at depth at a field site. Use of a vacuum extractor causes degassing of CO$_2$ and an increase in the solution pH (Suarez, 1987). Although there are ways of minimizing the degassing and keeping the pH error within acceptable limits (Suarez, 1986) it requires a modified extractor which has not been generally utilized. Use of the pH values measured in solutions obtained from conventional extractors is not recommended for calculations of mineral saturation status. In this situation it appears preferable to either use the modified extractors or to measure the CO$_2$ concentration in the soil gas and input that value and the measured alkalinity into the chemical speciation models.

The computational structure of MINEQL is such that it can be modified to treat HCO$_3$ or total alkalinity as a fixed component thereby avoiding the need for iterations, in most cases.

**SIMULATION AND PREDICTIVE MODELS**

These groups of models predict solution composition based on assumed mineral-solution equilibria. Some of the models include water flow and solute transport for predicting the solution composition in natural environments. Chemical equilibria models have been directly incorporated into models for predicting solution composition in natural systems. Predictions from such models, must be interpreted with extreme caution since mineral-solution equilibria is almost never a reasonable assumption.

GEOCHEM can operate with imposition of a solid phase control (such as calcite) by adding the solid as an additional component. This calculation is done in the closed system mode. The computational result in this instance is based only on the transference of inorganic C between the solid and solution phases. Since these computations are based on the assumption of no gas phase, the results are of limited applicability for soil-water systems. For example, precipitation of calcite produces an increase in $H_2CO_3$ since the pH is shifted downward. Such a reaction may be reasonable for a confined aquifer or a closed laboratory reaction with no gas phase but does not provide satisfactory results for either unconfined
laboratory experiments or in situ soil processes. In these cases the open system model is appropriate, which would result in a constant gas composition and a constant $\text{H}_2\text{CO}_3$ during precipitation of calcite. In these instances it is suggested that the problem first be solved by calculating the $P_{\text{CO}_2}$ without solid reactions and then using the input of $P_{\text{CO}_2}$ when allowing reaction with solid phases. Differences between these two model assumptions is often substantial as indicated in Fig. 4-2. In this example, dissolution of calcite in the closed system results in rapid depletion of $\text{H}_2\text{CO}_3$, a much higher pH and a lower HCO, and Ca than occurs for open systems.

In addition to forcing the solution to equilibrium with specified solid phases, these programs have the option to force equilibrium only for solids when the initial speciation calculations indicate that the solution is supersaturated. This option does not require that the solid be already present. In contrast, imposition of the solid as a component forces equilibrium of the solution with the solid phase in all cases.

**Open Systems**

Fixed pH. Predictive models which simulate open systems with fixed pH implicitly assume that carbonate chemistry does not control the pH. The water flow chemistry model of Robbins et al. (1980) and versions by Tillotson et al. (1980) and Russo (1986) among others, are among the most utilized models for predicting carbonate chemistry of soils under field conditions. These models follow the assumptions of Bower et al. (1968) among others who considered that calcareous soils were buffered at pH 8.4. However, as mentioned earlier, it is generally accepted that in carbonate systems the pH is dependent on the carbonate reactions and typically varies from pH 6.5 to 9, depending on $P_{\text{CO}_2}$ and alkalinity.

The extent to which a soil system behaves as a simple carbonate-solution system depends on the system examined. Inskeep and Bloom (1986b) observed that with varying $P_{\text{CO}_2}$ the pH of their soils remained relatively constant.

![Fig. 4-2: Open and closed system calcite dissolution path and equilibria for initial $P_{\text{CO}_2}$ of 0.035 kPa.](image)
contrast in arid regions at relatively high pH, $H^+$ buffering by exchange or sorption is relatively minor and increasing $P_{CO_2}$ decreases the pH.

The LEACHM model (Wagenet & Hutson, 1987) also contains a modified version of the chemical model of Robbins et al. (1980) and requires the input of both pH and $P_{CO_2}$ with depth. Since input of these two variables fixes HCO$_3$ activity and thus in turn Ca$^{2+}$ activity, the soil carbonate system is fixed independently of the input solution composition. Proper use of this model can be made only for simulations where the pH and $P_{CO_2}$ have been measured, and not for predictive cases where carbonate chemistry is of interest.

Other open system models with fixed pH require input of pH and solution composition and predict Ca and alkalinity at calcite equilibrium. In this case $P_{CO_2}$ is not output but is a dependent variable calculated from pH and equilibrium HCO$_3$ activity. These types of programs are well suited for simulations of laboratory and field experiment data where pH has already been measured. As mentioned earlier, data sets with measured pH and alkalinity are the most common; however, these conditions are of limited use for predictive carbonate models either in the laboratory or for field conditions. For example, use of a fixed pH will not enable prediction of acidification or alkalinization of waters due to acid or high bicarbonate inputs in combination with evapotranspiration, nor will it allow predictions in cases where CO$_2$ changes occur. The Tillotson et al. (1980) model allows for calcite supersaturation to the IAP value of 1.13 $\times 10^{-8}$ observed in groundwaters by Suarez (1977), thus is not strictly speaking an equilibrium model. Equilibration with an “apparent K” will improve the predictive ability, as shown by Suarez (1977, 1985). The discrepancies between observed ion activity products and thermodynamic K values are most likely due to kinetic constraints rather than uncertainties in the thermodynamic constants, or formation of unstable phases. From these considerations, it is considered suitable to use such apparent values in predictive models but not in thermodynamic equilibria models.

Predictive programs with fixed $P_{CO_2}$ are probably among the most realistic presently available for simulation of soil-water systems. Jury et al. (1978) described a soil-water transport model based on steady state water flow and the chemical model of Oster and Rhoades (1975). The model considers CO$_2$ as the independent variable which is fixed at various soil depths and includes ion exchange reactions. Input requirements are CO$_2$, irrigation water composition including alkalinity, and leaching fraction (and initial cation exchange composition and CEC if exchange is considered). The model predicts Ca, alkalinity and pH at calcite saturation. Although the assumption of time invariant CO$_2$ is not realistic in most instances (see Fig. 4-1), these models have the potential advantage of being able to describe gradual chemical processes such as acidification or alkalinization of a soil with time, based on irrigation water or amendment inputs.

**REACTION PATH PROGRAMS**

The program MIX2 (Plummer et al., 1975) was developed to compute the equilibrium species distribution and pH for a closed system as a function of reaction progress. The program allows for following the progress of a solution under-
going dissolution of one or more phases and has provision for precipitating a solid phase and maintain a fixed level of supersaturation if desired. An expanded version of this program, PHREEQE (Parkhurst et al., 1980) also allows for mixing of waters or following of a reaction path to equilibrium. These models are very useful for examining possible reaction pathways but provide no time dependent information.

Operation of PHREEQE without consideration of CO₂ as an equilibrating phase results in closed system reaction paths without allowance for degassing or CO₂ input to the solution. The program PHREEQE can be used to follow the reaction path of a carbonate phase in an open system by specifying CO₂ as an equilibrating phase. Although these models give reaction progress they are not kinetic models as they do not consider reaction rates nor do they provide time dependent information. Some programs, such as PATH I (Helgeson et al., 1970) consider partial equilibrium reaction paths, which allows for forced equilibrium with some phases while gradually approaching overall equilibrium.

**Open Systems with Prediction of Carbon Dioxide as an Independent Variable**

The chemistry routine in the soil-water transport model of Dutt et al. (1972) is also the basis for several predictive field and basin scale water quality models, among which are the Bureau of Reclamation Engineering and Research Center model (1975) and the NTRM model (Shaffer & Gutpa, 1987). These models consider that \( P_{CO_2} \) varies inversely with water content (i.e., the higher the moisture content the lower the \( P_{CO_2} \). The calculated \( P_{CO_2} \) is then incorporated into the \( K^' \) value in the expression \( K^' = (CA)(HCO_3^-)^2 \gamma_{CO_2} \gamma_{HCO_3} \), and the solution is forced to saturation by dissolving or precipitating calcite. Simplifications include the lack of consideration of CO₂ species—thus they are not suitable for high pH environments where an appreciable amount of the alkalinity is in the \( CO_3^{2-} \) species and associated ion pairs. These models can be classified as open system in the sense that they consider CO₂ to be fixed independent of the solution reactions (dependent only on moisture content). The moisture content-\( P_{CO_2} \) relation, however, was based on experiments in closed vessels with injection of increasing amounts of water. In this system, calcite dissolves as water is added and the \( P_{CO_2} \) decreases. Under natural conditions \( P_{CO_2} \) is directly, not inversely related to moisture content, i.e.; increasing soil water content results in increased \( P_{CO_2} \). This positive relationship can be seen from the data of Buyanovsky and Wagner (1983) Kiefer (1990) and Inskeep and Bloom (1985) among others.

**NONEQUILIBRIUM APPROACHES**

In as much as nonequilibrium conditions have been observed under field conditions (Suarez, 1977) it seems promising to consider the use of kinetic expressions for calcite dissolution and precipitation rather than the equilibrium approach. The kinetic approach can be utilized regardless of the other assumptions of the model (open vs. closed, fixed pH or fixed CO₂, etc.). There has been surprisingly little application of kinetics to carbonate modeling,
especially in soil science. This is at least partly the result of emphasis on labora-
tory reactions with simplified systems and the relatively few studies of carbonate 
systems under field conditions. Equilibrium is more likely to result with sufficient 
time under controlled conditions in which reactions are performed in the absence 
of both competing reactions and reaction inhibitors. Various expressions have 
been developed to describe either calcite dissolution or calcite precipitation, but 
most have been specific to the experimental conditions used. Plummer et al. 
(1978) developed a kinetic expression for calcite which considers both forward 
and back reactions and thus is suitable for both dissolution and precipitation. The 
reaction rate is given as

\[ R = k_1a_{H^+} + k_2a_{H_2CO_3} + k_3a_{H_2O} - k_4a_{Ca^{2+}} \cdot a_{HCO_3^-} \]  \[ \text{[11]} \]

where \( a_x \) is the activity of the species in the bulk solution and the forward rate 
constants \( k_1, k_2 \) and \( k_3 \) are temperature dependent. The term \( k_4 \) represents the back 
reaction constant given by

\[ k_4 = \frac{K_2}{K_c} \left[ k_1 \left( 1 + a_{H^+}^{\text{surface}} \right) \right] \]  \[ \text{[12]} \]

\( K_2 \) and \( K_c \) are the second dissociation constant and solubility product for calcite 
respectively, and \( k_1 \approx 10k_4 \) (Plummer et al., 1978). The kinetic expression for the 
back reaction requires the \( H^+ \) activity at the calcite surface, which is assumed to 
equal the \( H^+ \) activity of the solution at calcite equilibrium. The \( H^+ \) assumption 
requires that a predictive model determine the solution composition when equili-
brated with calcite.

Inskeep and Bloom (1985) modified the Nancollas and Reddy (1971) model 
to account for changes in ionic strength and found an improved fit to experi-
tmental laboratory data for \( pH > 8.5 \) and \( CO_2 < 1.0 \) kPa using the rate equation

\[ R = \gamma^2 k_f S \left[ Ca^{2+} \cdot CO_3^{2-} \right] - K_{sp} \gamma^{-2} \]  \[ \text{[13]} \]

where \( k_f = 118 \text{ L}^2 \text{ mol}^{-1} \text{ m}^{-2} \text{ s}^{-1} \) and \( S \) is the surface area in square meters. Under 
field conditions the reaction rates are reduced due to the presence of inhibitors. 

Suarez (1985) described computer simulations of soil solution composition 
using a model based on the Plummer et al. (1978) expressions. The model con-
tains a carbonate speciation model with fixed \( P_{CO_2} \) (open system) including a 
computer scheme to solve for the equilibrium solution composition. The model 
was combined with a simple piston flow model where hydraulic conductivity was 
related to volumetric water content using a relation determined by Bresler (1983, 
personal communication). The output provides a satisfactory fit to laboratory 
reactions but requires input of the calcite surface area, as well as irrigation water 
composition, leaching fraction, and \( P_{CO_2} \) distribution with depth. The model pro-
vided a reasonable simulation of the degree of calcite supersaturation in a soil and 
properly simulated changes in pIAP with depth (Fig. 4-3). Calcium and alkalini-
ity predictions with depth were generally improved over those based on an equi-
librium model, as shown in Fig. 4-4. However, overall model assessment using field data was difficult due to other factors not considered such as ion exchange, preferential flow, and nonuniform plant water uptake.

In the presence of soil, organic inhibitors likely reduce crystal growth such that precipitation may predominantly occur by heterogeneous nucleation rather than by crystal growth. Suarez (unpublished data) found differences in supersaturation to be 1.5

Fig. 4-3. Comparison of measured pIAP of $CaCO_3$ with depth (+) to predicted pIAP values from kinetic model (A). Calcite equilibria is at pIAP = 8.47 (from Suarez, 1985).

Fig. 4-4. Comparison of measured alkalinity, expressed as mmol L$^{-1}$ (+) with that predicted from the equilibrium model (X), kinetic model (A) and assuming no precipitation (Cl) (after Suarez, 1985).
unrelated to calcite content or surface area. Crystal growth kinetic models such as described above may provide realistic concentration vs. time or IAP vs. time relationships but are likely not mechanistically correct, i.e., the reaction rate likely does not depend on the calcite surface area in the soil system.

Dynamic Carbon Dioxide Models

All of the above models either regard CO₂ as a fixed input variable (open system) or as a dependent variable in a closed system. Natural environments are usually open systems but with variable CO₂. No presently available models incorporate this concept, but several CO₂ models have been proposed. Buyanovsky and Wagner (1983) reported on CO₂ cycles in soil air in a cultivated field. They did not model the data but determined that a multiple linear regression equation with the variables soil moisture and temperature explained 50% of the variance in their data set. Solomon and Cerling (1987) determined CO₂ concentrations in a montane soil and developed a simulation model based on variable diffusion and production terms fit to the experimental data.

Simunek and Suarez (1992, 1993) developed a generalized predictive model, from more fundamental variables. This model, SOILCO₂, contains the following: a predictive submodel for CO₂ production, a water flow submodel which considers convection and dispersion and predicts hydraulic properties based on the pressure head vs. moisture curve, a plant water uptake routine based on moisture and crop growth, a root development routine and a gas phase diffusion flow submodel. Water inputs of rain or irrigation and potential evapotranspiration are considered. The model considers mass flow as well as gas diffusion through the air-filled pores and dissolution of the gas into the water phase. The model predicts moisture content, CO₂ production as a function of time and depth, drainage volume, and CO₂ concentration as a function of time and depth. The output of CO₂ concentrations with depth and time can be stored in an array and used as input to a carbonate model requiring \( P_{CO₂} \). Although parameters can be fit to provide simulation of existing data, the model is intended for predictive use. A typical seasonal simulation is provided in Fig. 4-5 using the water input data shown in Fig. 4-1 (Suarez & Simunek, 1993). It is seen that the model predicts increases in CO₂ with depth and CO₂ maxima during the late spring. Increases in CO₂ after irrigations are also evident, similar to that seen in Fig. 4-1.

Combined Dynamic Carbon Dioxide and Kinetic Model

The model UNSATCHEM (Suarez & Simunek, 1992) incorporates the SOILCO₂ model described above with a speciation and kinetic carbonate model which also includes ion exchange and the use of Pitzer equations for calculation of activity coefficients at high ionic strength. The model includes the option of using either the Plummer et al. (1978) kinetic model or that of Inskeep and Bloom (1985) modified to consider the inhibition of reaction rates due to the presence of DIC (based on the data of Inskeep & Bloom, 1986a). Dolomite dissolution is specified by the reaction model of Busenberg and Plummer (1982).
CONCLUSION

The major focus of carbonate modeling of soil systems has been on the equilibrium chemistry of calcite. Improved prediction of soil solution composition using carbonate chemical modeling will require application of kinetic expressions. Existing kinetic models provide an incomplete description of calcite and dolomite dissolution-precipitation and dolomite dissolution but are an improvement over the equilibrium models. Increasing concerns about trace element species will generate increased interest in the modeling of the carbonate chemistry of trace elements. In these systems there is also a need to utilize kinetic models, as the kinetic constraints are more severe than with calcite. These kinetic models are not currently available. Modeling trace elements also requires information on the thermodynamic stability of solid phases and the elemental distribution in mixed solid phases. This is a relatively new research area with promising application to complex natural systems.
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