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Equilibrium Soil Chemistry Submodels

Abstract

The inorganic composition of soil water impacts biological, chemical, and physical processes in the soil. Plant growth (biomass) is impacted by the availability of essential nutrients as well as the toxicity of specific elements, ion imbalances, and overall salinity. The soil solution composition also impacts water transport, runoff, and erosion as well as transport of individual ions via interaction with the soil mineral phase. Complex models attempting simulation of soil and plant processes including solute transport, nutrient and solution chemistry impacts on plant growth, and water transport must in turn be able to simulate major chemical processes that impact solution chemistry. Important chemical processes include dissolution–precipitation of minerals, ion exchange, ion adsorption, and oxidation–reduction. In this chapter we review chemical process models used in equilibrium soil chemistry submodels.

Introduction

The inorganic composition of soil water impacts biological, chemical, and physical processes in the soil. Plant growth (biomass) is impacted by the availability of essential nutrients as well as the toxicity of specific elements, ion imbalances, and the overall salinity. The soil solution composition also impacts water transport, runoff, and erosion as well as transport of individual ions via interaction with the soil mineral phase. Chemical and biological processes impact the soil solution composition and are in turn impacted by the solution composition. Models simulating mineral–water interactions and soil chemical processes have existed for about six decades. Among the earliest aqueous computer models are EQBRAT (Detar, 1969), WATCHEM (Barnes & Clarke,

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1969), WATEQ Truesdell & Jones, 1974), and SOLMNEQ (Kharaka & Barnes, 1973). Early soil water models include those developed by Dutt (1961) for CaCO_3 and water and Dutt et al. (1972) adding cation exchange, the U.S. Bureau of Reclamation Irrigation Return Flow Model (Shaffer et al., 1977), and WATSUIT (Oster & Rhoades, 1975). More advanced models that coupled chemical processes with one-dimensional solute transport include LEACHM (Wagenet & Hutson, 1987), hydrosalinity models presented by Shaffer and Gupta (1981), the Nitrogen–Tillage–Residue Management (NTRM) model (Shaffer & Larson, 1987), UNSATCHEM (Suarez & Šimůnek, 1993, 1997), the Root Zone Water Quality Model (RZWQM) (Ahuja et al., 2000; Shaffer et al., 2000), and models coupled with two-dimensional transport (UNSATCHEM 2-D [Šimůnek & Suarez, 1994] and Hydrus 2D/3D [Šimůnek et al., 2018]).

Complex models attempting simulation of soil, plant processes including water and solute transport, plant growth including nutrient effects, and the impact of solution chemistry on plant growth and water transport must in turn be able to simulate major chemical processes that impact solution chemistry. The important processes include dissolution–precipitation of minerals, ion exchange, ion adsorption, and oxidation–reduction. With modern and continuing advances in computational speed, it is now possible to calculate equilibrium reactions for a huge database of mineral solubilities and couple them to solute transport models. Unfortunately, this is of limited value because classical thermodynamics evaluates only what is possible and not what can occur in relevant time frames. The authors of one of the earliest solution chemical equilibria programs, WATEQ (Truesdell & Jones, 1974), cautioned against using such thermodynamic equilibrium models to predict solution composition. Relevant time frames for soil-water modeling is on the order of hours to tens of years, thus we should consider equilibrium only for mineral phases that equilibrate in those time frames. Most soil minerals are thermodynamically unstable yet persist for thousands to hundreds of thousands of years. In addition, the chemical environment including pH, soil water content, and thus ion concentrations are constantly changing due to wetting and drying events, creating a dynamic environment that makes equilibrium even more problematic.

In arid regions, modeling of mineral precipitation–dissolution reactions are generally restricted to equilibrium with calcite and gypsum. Other chemical process often considered are ion exchange and, very rarely, oxidation–reduction. Prediction of redox equilibrium currently requires input of the redox status of couples (i.e., Fe^{3+} – Fe^{2+}) considered to be controlling other species, often via Eh measurements. Such predictions do not consider changes due to biological processes or production and transport of reactive gases (such as O_2 , CO_2 , and H_2S), and there is an understanding that redox couples are not generally in equilibrium with one another due to kinetic considerations.

For major ions, the ability to predict ion composition also requires the ability to calculate the soil pH as well as the concentrations of the major cations and anions, such as Ca^{2+} , Mg^{2+} , Na^+ , NO_3^- , HCO_3^- , CO_3^{2-} , Cl^- , and SO_4^{2-} and minor elements such as NH_4^+ , B, P, Fe, and Mn. Some models can predict B (UNSATCHEM 2.1) or crop NO_3^- and NH_4^+ uptake (the SOLCHEM module of RZWQM), but no model accurately predicts a suite of minor species with strong adsorption.

An important consideration in arid land soils is the maintenance of good soil physical properties for sustained agricultural production. Reclamation of saline and

sodic soils and improving or maintaining adequate hydraulic conductivity require information about solution salinity, cation composition, and pH. A useful and unique feature of UNSATCHEM is the prediction of changes in relative hydraulic conductivity as related to these variables.

A chemical equilibrium approach is preferred to a chemical kinetic method primarily due to its simplicity. Highly soluble salts are assumed not present in the soil and also assumed to not form due to high solubility, with consideration of only the reaction or formation of calcite and gypsum. This simplification is generally valid except for highly salinized soils where the solubility of other sulfate salts ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) must be considered, especially in the surface crust under dry conditions. In some cases, limited chemical kinetics have been included, such as silicate weathering (UNSATCHEM), but these processes are generally not relevant to short-term predictions. Nonetheless, kinetic approaches are essential to predicting long-term processes related to mineral dissolution and formation.

Chemical Equilibrium Relationships

The basic reactions used in most models are presented below. Application of thermodynamics to natural systems was first popularized by Garrels and Christ (1965) in the geochemical literature and by Lindsay (1979) in soil chemistry. More modern texts that consider solution chemistry, such as Stumm and Morgan (1996) and Appelo and Postma (2005), place more emphasis on kinetic processes. Evaluation of solution status with regard to mineral solubility requires comparison of the solubility to ion activities in solution. The use of an equilibrium constant considers forward and back reactions.

A simple soil chemical reaction is



In this reaction, a moles of reactant A combine with b moles of reactant B to form c moles of product C and d moles of product D . In the case where both the forward reaction

$$\text{RATE}_1 = K_{1R} A^a B^b \quad (6.2)$$

and the backward reaction

$$\text{RATE}_2 = K_{2R} C^c D^d \quad (6.3)$$

are at equilibrium, then

$$K_{1R} A^a B^b = K_{2R} C^c D^d \quad (6.4)$$

and

$$K_{\text{eq}} = \frac{K_{1R}}{K_{2R}} = \frac{C^c D^d}{A^a B^b} \quad (6.5)$$

where K_{eq} is the equilibrium constant.

The equilibrium constant K_{eq} can be determined experimentally or calculated from the Gibbs free energies of formation for the reactants and products. The Gibbs free

energy for many ions, solid phases, and elements as well as equilibrium constants are readily available in various references including Wagman et al. (1982), Woods and Garrels (1987), Nordstrom et al. (1990), and Stumm and Morgan (1996), often with data only at 25 °C and 1 atm pressure but often with thermodynamic data that permit calculation of temperature dependence.

The standard change in free energy for a chemical reaction is, by convention, equal to the sum of the free energies of the products, $\Delta G_{\text{pr}}^{\circ}$, minus the sum of the free energies of the reactants, $\Delta G_{\text{re}}^{\circ}$. This can be written as

$$\Delta G_{\text{r}}^{\circ} = \sum \Delta G_{\text{pr}}^{\circ} - \sum \Delta G_{\text{re}}^{\circ} \quad (6.6)$$

where $\Delta G_{\text{f}}^{\circ}$ refers to the Gibbs free energies of formation in the standard states. The Gibbs free energy of the reaction, $\Delta G_{\text{r}}^{\circ}$, is related to the equilibrium constant K_{eq} by the relationship

$$\Delta G_{\text{r}}^{\circ} = -RT \ln K_{\text{eq}} \quad (6.7)$$

where R is the universal gas constant and T is temperature (K).

Because the equilibrium constant is temperature dependent and temperatures in natural systems can deviate by more than 25° from 25 °C, the K_{eq} values often need to be corrected for temperature. This can be determined either experimentally or, in the absence of experimental data, using an integrated form of the van't Hoff equation assuming ΔH° is independent of temperature (Stumm & Morgan, 1996):

$$\ln \frac{K_{\text{eq}}(T_2)}{K_{\text{eq}}(T_1)} = \frac{-\Delta H^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (6.8)$$

where T_1 is the reference temperature (298.15 K), T_2 is the temperature of interest (K), and ΔH° is the change in heat content. Some models include temperature correction (UNSATCHEM), but most do not (LEACHM, RZWQM). Alternatively, the following temperature-dependent equation for the correction of equilibrium constants is preferred because it is accurate across a wider temperature range, with constants available for a number of mineral solubility and carbonic acid dissociation constants (Truesdell & Jones, 1974):

$$\log K_{\text{eq}} = a_1 + \frac{a_2}{T} + a_3 T + a_4 \log T + \frac{a_5}{T^2} \quad (6.9)$$

Ionic interactions in solution cause a departure from “ideal” behavior, with increasing departure as the solution concentration increases. Activity values rather than species concentrations are utilized to account for non-ideal behavior. Individual ion activities are obtained by multiplying the species concentration by an experimentally determined activity coefficient γ_i that varies with ionic strength. Ionic mobility is impacted by interaction with other species, primarily electrostatic effects. For very dilute solutions, the Debye–Huckel equation is used to compute appropriate activity coefficients for the species (Lewis et al., 1961):

$$-\log \gamma_i = 0.509 z_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}} \quad (6.10)$$

where z_i is the charge of the i th constituent and I is the ionic strength computed by the relationship

$$I = 0.5 \sum_{i=1}^M z_i^2 c_i \quad (6.11)$$

where M is the number of species and c_i is the concentration (mol kg^{-1}) of the i th constituent. Equation 6.10 is used in RZWQM but is accurate only at very low ionic strengths.

An extended form of Equation 6.10, sometimes named the Debye–Huckel equation (Garrels & Christ, 1965) and sometimes the extended Debye–Huckel equation (Stumm & Morgan, 1996), is

$$-\log \gamma_i = 0.509 z_i^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}} \quad (6.12)$$

where B is a characteristic of water and a is an adjustable parameter related to ion size. Equation 6.12 is considered applicable up to 0.1 M (Stumm & Morgan, 1996).

Many soil chemical models have used the Davies equation, modified from the Debye–Huckel limiting law:

$$-\log \gamma_i = 0.509 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad (6.13)$$

Stumm and Morgan (1996) and others have indicated that the Davies equation is applicable up to 0.5 M.

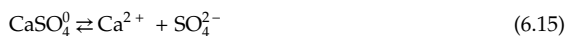
Note that the Debye–Huckel limiting law equation (Equation 6.10) and the Davies equation (Equation 6.13) consider only charge. It is well known that individual ions of the same charge have differing activity coefficients thus the use of these equations will lead to substantial errors at moderate ionic strength (Suarez, 1999). If using the ion association model with individual activity coefficients, it is much preferable to use the extended form of the Debye–Huckel equation proposed by Truesdell and Jones (1974):

$$\ln \gamma_i = \frac{Az_i^2 \sqrt{I}}{1 + Ba_i \sqrt{I}} + b_i I \quad (6.14)$$

where A and B are constants depending on the dielectric constant of water, density, and temperature, and a_i and b_i are adjustable parameters provided for each species. The a_i and b_i parameters are available for a large set of individual ions (Truesdell & Jones, 1974). These parameters were developed from mean molal salt activity coefficients based on experimental data (where molal concentration is moles per kilogram of water). Their single ion activity coefficients were obtained from the assumption that $\gamma_{\text{K}^+} = \gamma_{\text{Cl}^-}$ and utilize mean salt data for KCl up to 4.0 M to obtain these two calculated γ_i values as a function of ionic strength. Next, the ion activity coefficients for other ions as a function of ionic strength were calculated from other mean salt data (e.g., CaCl_2), with excellent fits up to 4.0 M. However, as there are no specific ion–ion interactions considered other than of the individual pairs examined, the fit to mixed salt solutions is less accurate, probably up to 0.3–0.5 m (molal) depending on the solution composition. Equation 6.14 is utilized in UNSATCHEM. Some chemical speciation models

make Equation 6.14 available as an option but utilize the Davies equation for ions where the a_i and b_i parameters are not available (MINTEQA2; Allison et al., 1991).

Utilizing a single ion association model such as Equation 6.14 requires consideration of complexes and ion pairs. Complexes are ion associations where the ligand is sufficiently close to partially or completely displacing the hydration shell surrounding the cation and forming bonds observable via spectroscopic analysis, with corresponding reactions such as



The corresponding equilibrium expression is

$$K_{\text{eq}} = \frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{\text{CaSO}_4^0} \quad (6.16)$$

where square brackets indicate activity. Note that this is a standard convention in the chemical and geochemical literature, but in the soil chemistry literature brackets often denote concentration.

Ion pairs can be viewed as weak ion associations in which the individual hydration shells are maintained, thus there is no chemical evidence of their existence as individual entities. An example is the species CaHCO_3^+ . Thus they are numerical constructs necessary to predict the activity of individual species in mixed electrolytes when using the ion association model. At higher ionic strength (>0.3 M) the solution is sufficiently concentrated so that all ion-ion interactions must be considered for calculation of activity coefficients, thus ion pairs as separate chemical entities are not utilized. In this instance, the Pitzer expressions (Pitzer, 1979) are utilized. The activity coefficients are expressed in a virial-type expansion having the form

$$\ln \gamma_i = \ln \gamma_i^{\text{DH}} + \sum_j B_{ij}(I)m_j + \sum_j \sum_k C_{ijk}m_j m_k + \dots \quad (6.17)$$

where γ_i^{DH} is a modified Debye-Huckel activity coefficient, B_{ij} and C_{ij} are coefficients specific to each ion interaction, and m is the molal concentration of each species. The Pitzer approach considers ion-ion interactions for every species in solution and thus it does not consider the individual ion pairs and complexes such as NaSO_4^- described above as species. The model is considered suitable for prediction of species activity in solutions up to 20 mol kg⁻¹, a concentration well above the intended use of the models relevant to agriculture. In UNSATCHEM the user can select activities calculated from the Pitzer equations or by the extended Debye-Huckel expressions.

For most solutions of low-salinity neutral molecules can be assumed to have activity coefficients equal to 1, as used in RZWQM. At higher ionic strength, neutral species activity coefficients can be calculated using Equation 6.14, available for a number of species (Truesdell & Jones, 1974) and used in UNSATCHEM. The actual use of activity coefficients is illustrated in

$$K_{\text{eq}} = \frac{C^c \gamma^c D^d \gamma^d}{A^a \gamma^a B^b \gamma^b} \quad (6.18)$$

Soil Chemistry Equations

The full soil water system can be represented as a system of simultaneous nonlinear equations (in the form of Equation 6.18) together with mass and charge balance equations for the system. The system is generally solved numerically using Newton's method. Processes typically included are chemical dissolution-precipitation involving calcium carbonate (calcite), calcium sulfate dihydrate (gypsum), and gibbsite (aluminum hydroxide) or the more soluble amorphous aluminum oxyhydroxide $[\text{Al}(\text{OH})_3]$; the bicarbonate buffer system including interactions with CO_2 gas, ion pairing, and ion exchange involving Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , and Al^{3+} . Most models consider pH as a fixed model input; this is suitable for the examination of saturation status of an analyzed solution but is not suitable for coupling with water and solute transport, as discussed below.

Ion Pairs and Complexes

Consideration of the complexes of calcium sulfate and magnesium sulfate, and the ion pairs CaCl^+ , CaHCO_3^+ , CaCO_3^0 , MgCl^+ , MgHCO_3^+ , MgCO_3^0 , NaSO_4^- , and KSO_4^- are important in all but very dilute systems. In acid systems, Al ion species such as AlOH_2^+ and AlSO_4^+ are important components. Significant amounts of Ca^{2+} , Mg^{2+} , Al^{3+} , and SO_4^{2-} can be in ion pairs and complexes thereby either decreasing the activities of the uncomplexed ions if there is no solid phase interaction or, in the presence of a solid phase, the complexes and ion pairs result in increased total element concentrations.

Calcium sulfate ion pair (CaSO_4^0):

$$\frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{[\text{CaSO}_4^0]} = K_{\text{CaSO}_4} \quad (6.19)$$

Magnesium sulfate ion pair (MgSO_4^0):

$$\frac{[\text{Mg}^{2+}][\text{SO}_4^{2-}]}{[\text{MgSO}_4^0]} = K_{\text{MgSO}_4} \quad (6.20)$$

Sodium sulfate ion pair (NaSO_4^-):

$$\frac{[\text{Na}^+][\text{SO}_4^{2-}]}{[\text{NaSO}_4^-]} = K_{\text{NaSO}_4} \quad (6.21)$$

Aluminum hydroxide ion pair (AlOH^{2+}):

$$\frac{[\text{Al}^{3+}]}{[\text{H}^+][\text{AlOH}^{2+}]} = K_{\text{AlOH}} \quad (6.22)$$

Aluminum sulfate ion pair (AlSO_4^+):

$$\frac{[\text{Al}^{3+}][\text{SO}_4^{2-}]}{[\text{AlSO}_4^+]} = K_{\text{AlSO}_4} \quad (6.23)$$

Bicarbonate Buffer System

The pH in soil–water systems under acidic conditions is buffered by Al species and H as well as organic species and soil organic matter; under neutral to alkaline conditions, it is buffered by carbonate species and to a lesser extent organic species and organic matter. In the carbonate system, the pH is part of the combined pH– P_{CO_2} – HCO_3^- –alkalinity system—specifying any two entities fixes the third (where P_{CO_2} is the partial pressure of CO_2).

Carbon dioxide in the soil air reacts with water to form carbonic acid (H_2CO_3). The reaction,



is generally written as a form of Henry's law.

The total aqueous-phase CO_2 concentration, c_w , is defined as the sum of $\text{CO}_2(\text{aq})$ and H_2CO_3 , and is related to the gas-phase CO_2 concentration, c_a , by (Stumm & Morgan, 1996)

$$c_w = K_H RT c_a \quad (6.25)$$

where K_H is the Henry's law constant, R is the universal gas constant, and T is the absolute temperature. An expression for the value of K_H as a function of temperature was given by Harned and Davis Jr. (1943). Equation 6.25 is commonly expressed as

$$K_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3^*]}{P_{\text{CO}_2} [\text{H}_2\text{O}]} \quad (6.26)$$

where P_{CO_2} is the partial pressure of CO_2 (atm), the activity of water is 1.0, and $\text{H}_2\text{CO}_3^* \equiv c_w$ is the preferred notation for the total aqueous-phase CO_2 concentration. The weak acid H_2CO_3 dissociates to form bicarbonate, HCO_3^- , and a hydrogen ion:



with the equilibrium expression

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]} \quad (6.28)$$

Bicarbonate dissociates to form a carbonate ion, CO_3^{2-} , and another hydrogen ion



with the corresponding equilibrium constant

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \quad (6.30)$$

These three equations (6.26, 6.28, and 6.30) define the carbonate species. Often chemical speciation models coupled with a transport model consider pH as a fixed input that, along with the measured alkalinity, defines the system. This approach is valid for speciation of an analyzed solution where P_{CO_2} is determined from total inorganic C

along with the other carbonate species (closed system) but is not valid for predicting solution composition in the soil. In the soil system, the P_{CO_2} is best regarded as an independent variable, determined from production and transport of the gas, independent of the inorganic chemical reactions (open system) (Šimůnek & Suarez, 1993). This approach is utilized by UNSATCHEM and is justified because the production and consumption of CO_2 from inorganic mineral reactions is generally orders of magnitude smaller than the production from biological processes in soil. The pH is then calculated from the alkalinity and P_{CO_2} .

The UNSATCHEM model considers CO_2 production from plant and microbial respiration. Because these processes are very dependent on temperature and water and to a lesser extent salt stress, these relations are included as well. The model also assumes that the nutritional status is ideal. This assumption will, in many instances, overestimate CO_2 production and thus the concentration, especially in non-agricultural soils. The complexity of the numerous CO_2 production processes and their dependence on temperature and nutrient status means that the prediction is difficult and the model parameters may need to be optimized differently for different environments. In some cases it may be preferable to input a fixed soil CO_2 concentration, which can also be varied for the environment and season to be predicted. This assumption is much preferable to that of a fixed pH as used in most models because it allows prediction of the impacts of water composition and additions of gypsum, calcite, and acid on soil pH, plus subsequent changes in solution composition and soil hydraulic conductivity. The closed system approach is exclusively used in subsurface transport modeling (e.g., NETPATH; Plummer et al., 1991) and is justified by the consideration that there is no change in total C in or out of the system (neglecting gas diffusion or biological production), a generally reasonable assumption for groundwater but not for soil.

The chemical speciation model in UNSATCHEM includes consideration of nine major aqueous components: Ca, Mg, Na, K, SO_4 , Cl, alkalinity, NO_3 , and B. Alkalinity is defined as

$$\begin{aligned} \text{alkalinity} = & (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + 2(\text{CaCO}_3^0) + (\text{CaHCO}_3^+) + 2(\text{MgCO}_3^0) \\ & + (\text{MgHCO}_3^+) + 2(\text{NaCO}_3^-) + (\text{NaHCO}_3^0) + (\text{B}(\text{OH})_4^-) - (\text{H}^+) + (\text{OH}^-) \end{aligned} \quad (6.31)$$

where parentheses represent concentrations (mol kg^{-1}). From these components we obtain 11 species: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Cl^- , HCO_3^- , CO_3^{2-} , NO_3^- , $\text{B}(\text{OH})_4^-$, and H_3BO_3 . It is reasonable to assume that all aqueous species are in equilibrium as defined by the ion association expressions and constants, as these reactions are essentially instantaneous. Alkalinity as defined in Equation 6.31 is a conservative species with respect to changes in CO_2 , in this instance affected only by dissolution or precipitation of a carbonate phase (such as calcite). However, the combined species H_2CO_3^* does have a slower reaction process as it consists of both dissolved CO_2 and the H_2CO_3 aqueous species. Nonetheless, for soil systems where changes in CO_2 are relatively slow (minutes to days), it is enough to also consider H_2CO_3^* to be in equilibrium with soil CO_2 gas.

Solid Phases

Soil–water systems are not in equilibrium with the numerous solid phases in the soil, and the use of a thermodynamic equilibrium approach to predict solution composition will lead to very large errors, specifically underestimating the solubility of almost all elements. Thus geochemical models such as PHREEQE (Parkhurst et al., 1980),

PHREEQE C (Parkhurst & Appelo, 2013), and MINTEQA2 (Allison et al., 1991; USEPA, 1999) contain a large list of solid phases for a large number of elements. The model developers indicate that these are assessment tools rather than predictive tools. The models are of more value to subsurface hydrochemical systems than for predicting soil solution compositions. They are useful to evaluate the extent of nonequilibrium and the possible occurrence of particular reactions in soil. However, even that approach is limited as there is nonequilibrium not just with respect to solid phases but also with respect to solution-redox sensitive species, probably due to the effects of microbial processes. Thus reactions that should not occur within an overall thermodynamic equilibrium system can occur, such as the presence of unstable reduced species within an aerobic system.

The predominant silicate minerals in soils are very slow to both dissolve and precipitate. In almost all instances, primary minerals are thermodynamically unstable (feldspars, micas, hornblendes, etc.) in soil environments yet persist for more than tens of thousands of years. Most soil oxides are also thermodynamically unstable. Slow dissolution of primary minerals results in the formation of unstable silicate and oxide phases (such as illite, smectites, and poorly crystalline amorphous phases) rather than the less soluble phases predicted by thermodynamics. The soil solid phase is thus a combination of mostly unstable primary minerals and unstable secondary minerals slowly transforming to more stable forms.

It is generally considered that soil is in chemical equilibrium with certain relatively soluble minerals such as calcite, gypsum, and gibbsite. These mineral phases form the basis for the soil chemical submodels used in agronomic applications such as coupled water solute transport and plant models. If these minerals are present, we assume that the solution phase is in equilibrium; if the solution is at or above saturation, we assume that the mineral will precipitate and the solution will be in equilibrium. Solubility equations are thus coupled to the speciation equations to allow for dissolution and precipitation of these minerals:



The equilibrium expression is

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{SP}} \quad (6.33)$$

where brackets denote activities and $K_{\text{SP}} = 10^{-8.47}$ at 25 °C. Because CO_3^{2-} is a generally minor carbonate species in solution, it is greatly preferable to solve for equilibrium using an expression considering bicarbonate rather than carbonate. Thus the equilibrium condition of a solution with calcite in the presence of CO_2 can be described by

$$[\text{Ca}^{2+}][\text{HCO}_3^-]^2 = \frac{K_{\text{SP}}K_{\text{CO}_2}K_{\text{a1}}}{K_{\text{a2}}}P_{\text{CO}_2}[\text{H}_2\text{O}] = K_{\text{SP}}K_{\text{T}} \quad (6.34)$$

where K_{CO_2} is the Henry's law constant for the solubility of CO_2 in water, K_{a1} and K_{a2} are the first and second dissociation constants of carbonic acid in water, and K_{SP} is the solubility product for calcite. The saturation status of a solution is determined by calculation of the ion activity product (IAP):

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = \text{IAP} \quad (6.35)$$

where in this case the solution ion activities are calculated from the concentration and the IAP calculated. To attain equilibrium, that is, when the IAP is equal to the solubility product K_{SP} , a quantity x of Ca^{2+} and HCO_3^- must be added or removed from the solution to satisfy the equilibrium condition. The quantity x is obtained by solving the following third-order equation:

$$(\text{Ca}^{2+} + x)(\text{HCO}_3^- + 2x)^2 = \frac{K_{SP}K_T}{\gamma_{\text{Ca}^{2+}} + \gamma_{\text{HCO}_3^-}^2} \quad (6.36)$$

It has been shown that waters below irrigated lands in arid zone regions are supersaturated with respect to calcite (Suarez, 1977a; Suarez et al., 1992), thus the equilibrium condition underestimates the Ca solubility in soil water. The cause of supersaturation has been shown to be due to poisoning of crystal surfaces by dissolved organic matter (Inskeep & Bloom, 1986; Lebron & Suarez, 1996), thus effectively preventing crystal growth. This is consistent with the observation that we do not see calcite crystals in the soil. Nonetheless, the solid phase of calcium carbonate found in soils is almost always calcite and not less thermodynamically stable calcium carbonates such as aragonite and vaterite. There is thus no solid phase that can accurately represent solution Ca and alkalinity.

Calcite crystal growth models are not applicable to soil systems because the concentrations of dissolved organic C in near-surface natural environments (Lebron & Suarez, 1996) are usually comparable to the levels found by Inskeep and Bloom (1986) to completely inhibit calcite crystal growth. Lebron and Suarez (1996) developed a precipitation rate model that considers the effects of dissolved organic C on both crystal growth and heterogeneous nucleation. The combined rate expression is

$$R_T = R_{CG} + R_{HN} \quad (6.37)$$

where R_T is the total precipitation rate ($\text{mmol L}^{-1} \text{s}^{-1}$), R_{CG} is the precipitation rate related to crystal growth, and R_{HN} is the precipitation rate due to heterogeneous nucleation. Because for soil systems the crystal growth rate can be neglected, only nucleation is an important process. The R_{HN} term is given by

$$R_{HN} = K_{HN}f(\text{SA})[\log(\Omega - 2.5)](3.37 \times 10^4 \text{DOC}^{-1.14}) \quad (6.38)$$

where K_{HN} is the precipitation rate constant due to heterogeneous nucleation, $f(\text{SA})$ is a function of the surface area of the particles (e.g., clay) upon which heterogeneous nucleation occurs ($=1.0$ if no solid phase is present), Ω is the calcite saturation value, and 2.5 is the Ω value above which heterogeneous nucleation can occur. This equation leads to calcite precipitation rates that are independent of the calcite surface area, consistent with the experimental data of Lebron and Suarez (1996).

The precipitation model predicts that calcite nucleation is not initiated until the solution phase is approximately 2.5-fold supersaturated with respect to calcite. This value corresponds reasonably well to the observed average of threefold calcite supersaturation found in waters beneath irrigated lands (Suarez, 1977a; Suarez et al., 1992). Thus in this instance an empirical constant or apparent K_{sp} of $10^{-8.0}$ gives a similar result to the more complex kinetic approach. This constant is best utilized instead of the calcite equilibrium constant ($10^{-8.47}$) for prediction purposes, although thermodynamically meaningless. Numerically one could also assume that the solid phase is not equal to 1 and adjust by this approximate factor of 3; however, this is chemically not justified because

there is no evidence that the calcite formed in the soil is more soluble than well-formed crystalline calcite (Suarez & Rhoades, 1982).

In contrast to the calcite case, solid-phase activity coefficients could be used to predict Al solubility, using a solid-phase coefficient <1 for Al predictions based on gibbsite solubility, because the formed solid is less stable (more soluble than gibbsite). Alternatively, the solution could be equilibrated with amorphous Al(OH)₃, which has a larger equilibrium constant. Pedogenic calcites in the arid, irrigated, southwestern United States often contain 1–7% Mg substituted for Ca in the structure (Suarez & Rhoades, 1982), which may if anything result in more stable (less soluble) calcite according to the data of Busenberg and Plummer (1989), thus not explaining calcite supersaturation in soils.

When gypsum is present in the soil, it can generally be assumed that the soil solution will be in equilibrium with the solid. Crystal growth is possible despite the presence of organic matter, as evidenced by the formation of relatively large assicular (needle like) formed gypsum crystals in arid zone soils. Although the assumption of gypsum equilibrium is generally reasonable, it is known that supersaturation when precipitating and undersaturation when dissolving does occur in soil. The biggest error will probably occur when applying gypsum to a sodic soil for reclamation. In this instance a kinetic approach may be preferred if the objective is to predict the dynamics of the system during infiltration of water during reclamation; however, the equilibrium assumption has been found suitable for predicting the final exchangeable ion composition after reclamation (Suarez, 2001).

As with calcite, predictive models require input as to the presence or absence of the mineral phase. If the mineral is present, the models force equilibrium of the solution with the solid phase; if the solution is supersaturated, the model forces precipitation and equilibrium regardless of whether or not the mineral was initially present.

Sometimes only the presence or absence of the mineral is specified. However, many models (including UNSATCHEM) can track the concentrations of the solid phase, enabling prediction of the extent of dissolution—important during leaching for sodic soil reclamation. The reaction for dissolution and precipitation of gypsum is



with the equilibrium expression given by

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = \frac{K_{\text{SP}}}{[\text{H}_2\text{O}]^2} \quad (6.40)$$

where K_{SP} is the solubility product in solution, taken as $10^{-4.61}$. To obtain equilibrium, that is, when the IAP is equal to the solubility product K_{SP} , a quantity of gypsum, x , must be added or removed from the Ca^{2+} and SO_4^{2-} concentrations in solution, obtained by solving the quadratic equation

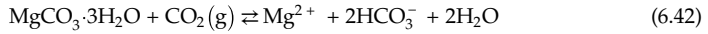
$$(\text{Ca}^{2+} - x)(\text{SO}_4^{2-} - x) = \frac{K_{\text{SP}}}{\gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}} [\text{H}_2\text{O}]^2} \quad (6.41)$$

In addition to calcite and gypsum, other phases are sometimes considered. Under high-pH conditions, magnesium carbonate precipitation should be considered. The UNSATCHEM model includes provision for the precipitation–dissolution of a Mg phase.

The Mg carbonate regarded as most thermodynamically stable under Earth surface conditions is magnesite (MgCO_3), with a solubility of about three times that of calcite. The phase is thus considered in some (MINTEQA2) but not all thermodynamic geochemical assessment models (PHREEQE, PHREEQE C). However, it is not suitable for predictive models such as coupled water and solute transport and plant models. The soil predictive models should consider only phases that either precipitate under Earth surface conditions or occur frequently and are reactive under Earth surface conditions; these need not be the thermodynamically the most stable. With this consideration, magnesite, the thermodynamically more stable Mg carbonate, should be neglected because it apparently does not form under Earth surface temperatures, is extremely rare, and its dissolution rate is exceedingly slow, such that its solubility has not been satisfactorily determined from dissolution studies at or near 25 °C. Including magnesite in predictive models will result in large underestimation of Mg concentrations in arid environments.

Magnesium precipitation can occur as a carbonate (either nesquehonite or hydromagnesite) or as a silicate (sepiolite) under very saline and high-pH conditions. All three phases readily dissolve and precipitate in time frames suitable for soil water transport and are considered in the UNSATCHEM model.

At 25 °C and at CO_2 partial pressures above $10^{-3.27}$ kPa, nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) is stable relative to hydromagnesite, thus this is the Mg carbonate phase of potential relevance to soils in hypersaline environments. The precipitation (if saturation is achieved) or dissolution of nesquehonite (if specified as a solid phase) in the presence of CO_2 can be described by



with the solubility product K_{SP} defined by

$$K_{\text{SP}} = [\text{Mg}^{2+}] [\text{CO}_3^{2-}] [\text{H}_2\text{O}]^3 \quad (6.43)$$

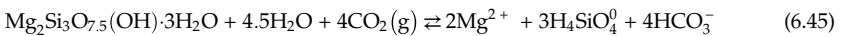
where $K_{\text{SP}} = 10^{-5.62}$. Substituting the equation for Henry's law for the solubility of CO_2 in water and the equations for the dissociation of carbonic acid in water into the solubility product, we obtain

$$[\text{Mg}^{2+}] [\text{HCO}_3^-]^2 = \frac{K_{\text{SP}} K_{\text{CO}_2} K_{\text{a1}}}{K_{\text{a2}}} \frac{P_{\text{CO}_2}}{[\text{H}_2\text{O}]^2} = \frac{K_{\text{SP}} K_{\text{T}}}{[\text{H}_2\text{O}]^3} \quad (6.44)$$

This relation is solved for equilibrium in a manner similar to that used for calcite, with a third order equation and substitution of Mg^{2+} concentration and $\gamma_{\text{Mg}^{2+}}$ for activity of Mg^{2+} and substitution of HCO_3^- concentration and $\gamma_{\text{HCO}_3^-}$ for activity of HCO_3^- in Equation 6.44.

Sepiolite will readily precipitate into a solid but with a K_{SP} greater than that of well crystallized sepiolite. Formation of this mineral requires high pH, high Mg concentrations, and low CO_2 partial pressure.

The precipitation or dissolution of sepiolite in the presence of CO_2 can be described by the reaction



with the solubility product K_{SP} defined by

$$K_{SP} = \frac{[Mg^{2+}]^2 [H_4SiO_4^0]^3 [OH^-]^4}{[H_2O]^{4.5}} \quad (6.46)$$

In this instance, UNSATCHEM utilizes the precipitated sepiolite solubility value given by Wollast et al. (1968) rather than the well crystallized equilibrium value. Freshly precipitated sepiolite has been prepared in the laboratory at IAP values of 10^{-35} comparable to the K_{SP}^S listed by Wollast et al. (1968), but the K_{SP} for a precipitated phase has been more recently listed as $10^{-37.2}$ (USEPA, 1999). These differences are probably related to the extent of reaction or aging of the solid. A kinetic expression for precipitation would be preferred but is not available for the prediction of unsaturated zone solution composition. The equilibrium condition is expressed as

$$[Mg^{2+}]^2 [HCO_3^-]^4 = \frac{K_{SP} K_{CO_2}^4 K_{a1}^4}{K_w^4} \frac{P_{CO_2}^4 (H_2O)^{4.5}}{(H_4SiO_4^0)^3} = K_{SP} K_T^+ \quad (6.47)$$

Solution of Equation 6.47 requires knowledge of Si concentrations. Relatively little information exists on the controls on Si concentrations in soil waters, especially in arid zones. In soil systems, Si concentrations are not fixed by quartz solubility but rather by the dissolution and precipitation of aluminosilicates and Si adsorption onto oxides and aluminosilicates. As a result of these reactions, Si concentrations in soil solution follow a U-shaped curve with pH, similar to Al oxide solubility, with a Si minimum around pH 8.5 (Suarez, 1977b) rather than following the solubility curve of quartz or amorphous Si, which give a constant total Si in solution until higher pH when total Si increases as the weak acid H_4SiO_4 dissociates to H^+ and $H_4SiO_4^-$. Data from eight arid land soils reacted at various pH values for two weeks by Suarez (1977b) were fitted to a second-order relationship as

$$\sum SiO_2 = 0.001 (6.34 - 1.34pH + 0.0819pH^2) \quad (6.48)$$

where SiO_2 is the sum of all silica species ($mol L^{-1}$). This U-shaped relationship with pH probably provides only a rough estimate of Si concentrations, but we consider it acceptable because it is used only to restrain Mg concentrations at high levels of evapotranspiration, when Mg concentrations become very high at low CO_2 and elevated pH. Formation of sepiolite in soils has been documented by numerous researchers (Diaz-Hernandez et al., 2018).

In the presence of calcite or whenever Ca in solution equals or exceeds the values in equilibrium with calcite, the most thermodynamically stable phase containing Mg is dolomite, not a pure Mg carbonate. Dolomite $[CaMg(CO_3)_2]$ has an equilibrium expression of

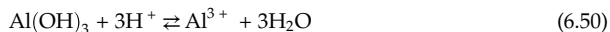
$$K_{SP} = [Ca^{2+}] [Mg^{2+}] [CO_3]^{-2} \quad (6.49)$$

with a K_{SP} of $10^{-17.09}$. Thus if calcite and gypsum were in equilibrium, the ion activity product of $[Mg][CO_3]$ would be $10^{-17.09}/10^{-8.48}$ or $10^{-8.61}$ and Mg would be below Ca and thus always be undersaturated with respect to magnesite, hydromagnesite, and nesquehonite. However, true dolomite, a well-ordered mineral with layers of Mg, Ca, and CO_3 , appears to rarely form in soil environments. As a result, dolomite

precipitation and equilibrium from a supersaturated solution is not considered in UNSATCHEM. When dolomite is present in the soil (from parent geological material), predictions of solution composition could use the kinetic model of Busenberg and Plummer (1982) to represent the dissolution process. The dissolution rate of dolomite is slow, especially as the solution IAP values approach within two to three orders of magnitude of the solubility product. In arid zone soils, when dolomite is present calcite is also present. In this instance in the presence of calcite and evapotranspiration, Ca concentrations in solution typically exceed Ca solubility and, given typical Mg concentrations, solutions are generally supersaturated with respect to well-ordered dolomite. Thus dolomite dissolution needs to be considered, primarily in the case where calcite is not present (such as liming an acid soil with dolomitic material). In this case a kinetic expression for dolomite dissolution is necessary.

Under elevated Mg concentrations, Mg is incorporated into calcite, forming high-Mg calcites, which may over time transform into Ca-enriched poorly ordered dolomite, with solutions remaining very supersaturated with respect to dolomite. The Mg carbonate precipitated (nesquehonite), combined with precipitation of calcite, will probably represent the mixed Ca–Mg precipitate that is observed in hypersaline environments, sometimes called protodolomite. However, the resulting solution composition is much different than that produced by simply forcing equilibrium with respect to dolomite, as the model forms this mixed precipitate (calcite + magnesium carbonate) under conditions of approximately 200–500 times supersaturation with respect to dolomite. This result is consistent with the high levels of dolomite supersaturation maintained in high-Mg waters (Suarez, 1977a; Suarez et al., 1992). Recently Diaz-Hernandez et al. (2018) reported on the presence and pedogenic formation of calcian (nonstoichiometric) dolomite, calcite, sepiolite, and palygorskite (Mg-rich, poorly ordered clay) in soil formed in an arid region from weathering of volcanic tephra. Solution compositions were not provided, so supersaturation indices cannot be calculated. However, based on the precipitation of calcite and sepiolite, it is evident that solutions would be many orders of magnitude supersaturated with respect to dolomite. The representation of this system by threefold supersaturation with calcite and equilibrium with a poorly crystallized sepiolite might be adequate to predict the solution composition.

Acid soils are often in equilibrium with the mineral gibbsite, $\text{Al}(\text{OH})_3$, or an amorphous form (non-crystalline) called an amorphous aluminum oxyhydroxide phase, and its solubility can be the chemical reaction expressed as



with the equilibrium equation

$$\frac{[\text{Al}^{3+}]}{[\text{H}^+]^3} = K_{\text{SP}} \quad (6.51)$$

Ion Exchange

Soil clays have negative surface charge that is neutralized by solution cations that are loosely bound to the surface (exchangeable cations). Cation exchange reactions are extremely important in soil–water systems. Exchange ions can be readily exchanged for other ions but are not available for leaching, thus maintaining electrical neutrality. They also are not directly available to participate in reactions occurring in the solution

phase. Ion exchange equations generally included are Ca^{2+} , Mg^{2+} , Na^+ , and, to a lesser extent, K^+ , Al^{3+} , and NH_4^+ . These represent the major cations found in many soil systems. Anion exchange is generally less important and often omitted. Three forms of the ion exchange relationships are commonly utilized: the Gapon (1933), the Vanselow (Vanselow, 1932), and the Gaines–Thomas (1953) equations. All three forms have been successfully used to fit exchange data. Assuming ideal exchange phase behavior (concentration = activity), they all result in deviations from measured exchange data across exchanger phase composition.

The exchanger selectivity coefficients change with exchanger phase composition for a number of reasons, including non-ideal behavior of individual minerals as well as the consideration that in soils there is usually a number of exchange sites related to different minerals, exchange associated with organic matter, and even different affinities on different sites within a specific mineral.

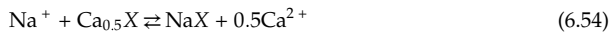
The Vanselow convention has been considered preferable based on theoretical considerations, but it is not clear if this results in any less variability in the coefficient across exchanger composition. For homoivalent exchange, for example, the reaction can be written as



All conventions are similar with the following equilibrium expression:

$$\frac{[\text{K}^+]}{[\text{Na}^+]} \frac{[\text{NaX}]}{[\text{KX}]} = k_{\text{Na/K}} \quad (6.53)$$

where X is either the mole fraction of the exchange ion or the charge fraction of the exchange ion. In the case of heterovalent exchange, the approaches differ. For Na–Ca exchange, using the Gapon convention, the reaction is written as (where $\text{Ca}_{0.5}$ represents $\frac{1}{2}$ mol of Ca):

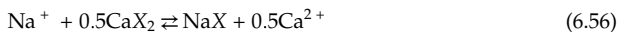


with the following equilibrium expression:

$$\frac{\sqrt{[\text{Ca}^{2+}]}}{[\text{Na}^+]} \frac{[\text{NaX}]}{[\text{Ca}_{0.5}\text{X}]} = k_{\text{Na/Ca}} \quad (6.55)$$

where X is the fraction of charged sites occupied by the ion (moles of charge).

With the Vanselow convention, the Na–Ca exchange reaction is written as



and the corresponding equilibrium expression is

$$\frac{\sqrt{[\text{Ca}^{2+}]}}{[\text{Na}^+]} \frac{[\text{NaX}]}{\sqrt{[\text{CaX}_2]}} = k_{\text{Na/Ca}} \quad (6.57)$$

where X represents the mole fraction of the ion on the exchange complex, X_2 is two times the exchange mole fraction, and k is the selectivity constant. In cation exchange application, the term *selectivity* rather than *equilibrium* constant is used because these relationships do not meet the criteria for thermodynamic relations, as discussed below.

Because the selectivity coefficients are dependent on the convention chosen, users must be careful when selecting values to insert into the various chemical models. UNSATCHEM uses the Gapon expressions, shown to provide good prediction of exchangeable Na across a wide range of arid zone soils and exchanger composition (U.S. Salinity Laboratory Staff, 1954). These constants should ideally consider activities of the solution species as well as exchanger phase activity. The use of activity coefficients for only the solute species will lead to overestimation of exchangeable Na in saline soils (Appelo & Postma, 2005). Hence, either the same activity coefficients are used for the exchanger phase as the solute species, as in PHREEQC, or only concentrations are used, as in UNSATCHEM.

The RZWQM models Ca–Mg ion exchange using the expression

$$\frac{[\text{Ca}^{2+}]}{[\text{Mg}^{2+}]} \frac{[X_{\text{Mg}^{2+}}]}{[X_{\text{Ca}^{2+}}]} = k \quad (6.58)$$

where X is the mole fraction of the ion on the exchanger phase, with a selectivity coefficient $k = 0.67$.

UNSATCHEM uses the expression

$$\frac{(\text{Ca}^{2+})}{(\text{Mg}^{2+})} \frac{\sqrt{X_{\text{Mg}^{2+}}}}{\sqrt{X_{\text{Ca}^{2+}}}} = k \quad (6.59)$$

where X is the charge fraction on the exchanger and $k = 0.9$.

The RZWQM models Na–NH₄ ion exchange using

$$\frac{[\text{Na}^+]}{[\text{NH}_4^+]} \frac{[X_{\text{NH}_4^+}]}{[X_{\text{Na}^+}]} = k \quad (6.60)$$

where $k = 0.22$. UNSATCHEM does not consider NH₄⁺.

The RZWQM simulates Ca–Al ion exchange using

$$\frac{[\text{Ca}^{2+}]^3}{[\text{Al}^{3+}]^2} \frac{[X_{\text{Al}^{3+}}]^2}{[X_{\text{Ca}^{2+}}]^3} = k \quad (6.61)$$

where $k = 0.67$.

The newer versions of UNSATCHEM and SWS version (Suarez, 2012) use a multi-site mixing model containing separate consideration of Ca–Na selectivity on organic matter versus clays, accounting for the much greater preference of organic matter for Ca and enabling improved prediction of Ca²⁺–Na⁺ cation exchange for soils of varying organic matter. UNSATCHEM also considers K exchange, which RZWQM does not. Predictions of cation exchange are adequate with all the approaches; the limiting factor is that generalized cation selectivity coefficients, even with consideration of organic matter content, may not be adequate in many instances.

Aluminum and Sodium Complexes with Soil Organic Matter

Aluminum and Na are known to form complexes with charged particles of soil organic matter (SOM). In acid systems, the Al–organic matter complex in RZWQM is given as

$$\frac{[\text{Al}^{3+}][\text{SOM}^-]}{[\text{AlSOM}^{2+}]} = 1 \times 10^6 \quad (6.62)$$

where SOM^- is soil organic matter and AlSOM^{2+} is the divalent Al-organic matter complex.

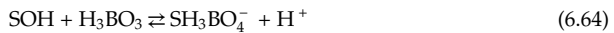
In alkaline systems in the RZWQM, the Na-organic matter complex is written as

$$\frac{[\text{Na}^+][\text{SOM}^-]}{[\text{NaSOM}^0]} = 1.06 \quad (6.63)$$

Adsorption-Desorption

Adsorption, or what is often deemed *specific adsorption*, refers to the attachment of solution species that are not exchanged. They may be either charged or noncharged species and thus may impact the surface charge of the mineral. The Langmuir isotherm is the most utilized adsorption equation in soil science and has been used in several models to describe non-competitive adsorption. The difficulty in using the Langmuir isotherm is that it is specific to the soil and chemical conditions being evaluated while many adsorption reactions are pH dependent; hence changing the pH will adversely affect the prediction, for example, of B transport during reclamation of a sodic alkaline soil. The oxyanions of B, As, and Mo, with potential plant and animal toxicity, are of interest in arid land soils. In this instance, a surface speciation model is preferred rather than the more utilized Langmuir isotherm. A relatively simple adsorption model, the constant capacitance model (CCM) has been successfully applied in soils (Goldberg, 1992). This model considers the pH dependence of the adsorption using pH-dependent apparent equilibrium constants obtained from experimental data. The practical application of the CCM to modeling was limited by the need to obtain adsorption envelopes for each soil of interest, requiring extensive adsorption experiments, each with a large range of solutions with different pH values. However, it has been established that for B (Goldberg et al., 2000) and Mo (Goldberg et al., 2002) the apparent equilibrium constants for the CCM can be predicted from several known soil properties: clay surface area, organic matter content, and Fe and Al oxide content. This application is incorporated into the more recent versions of UNSATCHEM and SWS (Suarez, 2012). Alternatively, the Langmuir isotherm approach could be used with the addition of pH-dependent relationships or the more detailed CD-MUSIC adsorption model (Hiemstra & van Riemsdijk, 1996), but in both instances detailed soil-specific data would need to be obtained.

The B adsorption reaction is



The intrinsic equilibrium constants are given as

$$K_+ = \frac{(\text{SOH}_2^+)}{(\text{SOH})(\text{H}^+)} \exp\left(\frac{F\psi}{RT}\right) \quad (6.65)$$

$$K_- = \frac{(\text{SO}^-)(\text{H}^+)}{(\text{SOH})} \exp\left(-\frac{F\psi}{RT}\right) \quad (6.66)$$

$$K_{B^-} = \frac{(\text{SH}_3\text{BO}_4^-)(\text{H}^+)}{(\text{SOH})(\text{H}_3\text{BO}_3)} \exp\left(\frac{F\psi}{RT}\right) \quad (6.67)$$

(Goldberg et al., 2000) where F is the Faraday constant ($C \text{ mol}_e \text{ L}^{-1}$), ψ is the surface potential (V), R is the molar gas constant, T is the absolute temperature (K), S denotes the surface site, and parentheses indicate concentrations (mol L^{-1}). Goldberg et al. (2000) developed regression equations for the prediction of the three CCM surface complexation constants based on generally available soil properties. They developed the following equations based on batch equilibrium adsorption experiments conducted with 32 arid land soils:

$$\log K_{B^-} = -9.14 - 0.375 \ln(\text{SA}) + 0.167 \ln(\text{OC}) + 0.11 \ln(\text{IOC}) + 0.466 \ln(\text{Al}) \quad (6.68)$$

$$\log K_+ = 7.85 - 0.102 \ln(\text{OC}) - 0.198 \ln(\text{IOC}) - 0.622 \ln(\text{Al}) \quad (6.69)$$

$$\log K_- = -11.97 + 0.302 \ln(\text{OC}) + 0.0584 \ln(\text{IOC}) + 0.302 \ln(\text{Al}) \quad (6.70)$$

where SA is the surface area measured by ethylene glycol monoethylether (EGME), OC is the organic C, IOC is the inorganic C, and Al is the extractable Al (adsorbed, hydroxides, and oxides). Using these relationships, Goldberg et al. (2000) satisfactorily predicted the adsorption envelopes (adsorption as a function of pH) for a series of arid land soils. They concluded that the fits using the CCM with the constants determined from the above predictive equations were acceptable for use in modeling adsorption. Of these properties, only the surface area term is not readily available with descriptions of soil properties. Surface area can be directly determined or estimated from the clay content and mineralogy of a soil. UNSATCHEM application of these equations provided good predictions for both B adsorption and desorption in soil columns packed for three different soils and with a range of solution pH values without the need to conduct B adsorption experiments (Suarez et al., 2012).

Other adsorption models have been included in solution transport models including CD MUSIC (in PREEQEC), a comprehensive model requiring extensive input information incorporating the triple-layer model in addition to a diffuse layer mode. These models are well suited to specific critical applications, such as U transport from a proposed containment facility, but in the absence of generalized input parameters are less practical for general application in models that consider variably saturated water transport, plant water uptake, etc., applicable to soil–water systems.

Model Testing and Validation

Models need to be tested for internal consistency and to ensure that the equations utilized are accurately solved. Models also need to be evaluated by comparison with sets of observed data, often called *validation*. Surprisingly, some models do not converge on the equations provided, most commonly due to expressing solubility with minor species (i.e., solving for calcite solubility from the primary expression using Ca and CO_3 species) and insufficient iteration. Most models have the necessary mass balance tests to be certain that the model conserves both mass and charge. True validation is probably impossible for a number of reasons, such as insufficient change in the variables examined, range of concentrations evaluated, and scale of measurement (in both time and space). A distinction also needs to be made between prediction and simulation. In many models, a number of “calibration” parameters serve, in essence, as curve fitting. Using the same or similar data sets to calibrate the model (inverse modeling) provides evidence of good *simulation* without indicating predictive capability in a general sense.

There are a very large number of publications where models have provided good representation (simulation) of experimental data but far fewer where actual predictions

were successfully made. Successful UNSATCHEM predictions include soil CO₂ and water content predictions (Suarez & Šimůnek, 1993), prediction of electrical conductivity and changes in the sodium adsorption ratio (SAR, where $SAR = Na^+ / (Ca^{2+} + Mg^{2+})$, in units of mmol L⁻¹) with reclamation (Suarez, 2001), and prediction of B transport for various soils and pH conditions (Suarez et al., 2012). The HYDRUS model includes a module with the earlier version of UNSATCHEM and has been successfully utilized in a number of studies including gypsum reclamation of sodic soil (Reading et al., 2012; Shaygan et al., 2018; Wang et al., 2016) and prediction of the effects of solution composition on hydraulic conductivity (Reading et al., 2012; Wang et al., 2016). Successful applications of RZWQM include water content and Br predictions (Ahuja et al., 1996) and water content and NO₃ (Cameira et al., 1998).

Questions relevant to model application that need to be addressed in future research:

1. Under what circumstances might equilibrium models not be suitable to predict soil solution Ca concentrations?
2. If using a kinetic model for mineral dissolution, what soil information would be required that is not generally available?
3. In addition to the carbonate system, what other pH buffer systems are present in arid zone soils? In acid soils?

Notation

R	universal gas constant
T	temperature (K)
T_1	reference temperature for van't Hoff equation (K)
T_2	temperature of interest for van't Hoff equation (K)
γ_i	Single ion activity coefficient (unitless)
ΔH°	change in heat content
ΔG_f°	Gibbs free energies of formation in the standard states
I	ionic strength (mol per kg of solvent)
z_i	charge of i th ion in solution
c_i	solution concentration of the i th constituent
K_{eq}	equilibrium constant
k	selectivity constant for exchange
P_{CO_2}	partial pressure of carbon dioxide in soil air (atm)
m_i	molal concentration of ion in solution (moles per kg water). For dilute solutions this is equal to M (moles per liter of water)
X	Exchange phase, mole fraction of an exchangeable ion in Vanselow convention (unitless)
X	Exchange phase, charge fraction of exchangeable ion in Gapon convention (unitless)
X_2	Exchange phase, two times mole fraction of exchangeable ions in Vanselow convention (unitless)
SOM^-	concentration of charged soil organic matter in solution (mol L ⁻¹),
$AlSOM^{2+}$	concentration of aluminum-organic matter complex in solution (mol L ⁻¹)
$NaSOM^0$	concentration of sodium-organic matter complex in solution (mol L ⁻¹)
S	concentration of surface sites in the constant capacitance adsorption model
[.]	species activity (dimensionless, =1 for solid phases by convention)

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