

Using the Soil Model YASE
Alone or in Combination with TREGRO

Model Description and User's Guide

Version 3.0.2

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ABSTRACT

YASE is a model that simulates the chemical composition of soil solutions as determined by chemical equilibria, organic matter transformations, and mineral weathering. Different properties can be assigned to different soil layers in the model. Uptake of solutes from the soil by plants, addition of organic matter, movement of soil solution between soil layers, and influx of solution from above or below the soil can be provided as inputs to YASE, either by the TREGRO model or by the user. YASE can be run alone at any time step; when called by TREGRO it is called on a daily time step.

Chemical equilibria in YASE are based on the Chemical Equilibria in Soils and Solutions model, CHESS (Santore 1991). CHESS uses a matrix representation of solution chemistry (Morel, 1983). Equilibrium problems of any composition and complexity (or simplicity) can be simulated using this model, because the chemical components and the rules for combining them into species are supplied by the user.

Decomposition in YASE follows the algorithm of GEM (Rastetter et al., 1991): transformations among extractives, cellulose, lignin, and humus are affected by temperature, soil moisture, N availability, and a ligno-cellulose index. Weathering in YASE is defined by the user using mineral compositions, weathering rates, and reaction orders with respect to pH and the amount of mineral present. Cation exchange is treated as an equilibrium between adsorbed and dissolved species interrelated by selectivity coefficients.

YASE was developed to be compatible with TREGRO. To be used in combination with TREGRO, YASE must be parameterized to include the nutrients of possible importance to the plant. A Hypercard interface aids in the parameterization and running of the model, whether alone or in combination with TREGRO.

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1 INTRODUCTION

Need for such a model

The soil model YASE was developed to be used in conjunction with TREGRO, which is a detailed physiological model of an individual plant (Weinstein et al. 1992). TREGRO has been used to simulate the response of red spruce seedlings (Laurence et al. 1993) and white fir trees (Arthur et al. in review) to ozone, the response of red spruce saplings to ozone and acid rain (Weinstein et al. 1991a) and temperature (Weinstein et al. 1991b), the response of ponderosa pine and red spruce to ozone stress and nutrient deficiency (Weinstein and Yanai 1994), and the effect of winter damage on mature red spruce (Laurence et al. 1995). The soil in these TREGRO simulations is static; soil concentrations of nutrients are held constant for the duration of a simulation. Nutrient deficiency was simulated by setting low concentrations. Nutrient uptake (Yanai 1994) was limited by these soil concentrations, but there was no feedback from the plant to the soil, such as litter addition or reduction of nutrient stores by uptake.

Previous models of plants and soil have not been so detailed both above and below ground as the combination TREGRO-YASE allows. Detailed plant and forest models such as FORTNITE (Aber et al., 1978, 1982), FORCYTE (Kimmins and Scoullar, 1984), and FOREST-BGC (Running and Coughlan, 1988) have not included soil simulators. Detailed soil models, such as ILWAS (Gherini et al., 1985; Davis et al., 1987), MAGIC (Cosby et al., 1986), and STEADYQL (Furrer et al., 1989, 1990) have had no plants or very simple simulations of plant growth.

The design or selection of a simulation model should be made in accordance with the problem to be addressed. Separate models of plants and soil can be usefully applied to problems in which feedbacks are not important to simulate. Combinations of soil models with plant models simpler than TREGRO will also have their uses. The combination TREGRO-YASE will be most useful for studying plant-soil interactions at the scale of the individual plant, where feedbacks in growth partitioning and carbon storage are of interest. For example, the amount and quality of leaf litter, the rate of root growth and root turnover, and water uptake by the plant all affect soil processes such as weathering and organic matter decomposition. These soil processes in turn affect the availability of resources and limitations to growth of the plant.

The purpose of this document is to describe the soil model YASE. The version of TREGRO compatible with YASE will be described in a separate document.

Model Overview

YASE is a model that simulates the chemical composition of soil solutions as determined by chemical equilibria, organic matter transformations, and mineral weathering (Figure 1-1). Different properties can be assigned to different soil layers in the model. Uptake of solutes from the soil by plants, addition of organic matter, movement of soil solution between soil layers, and influx of solution from above or below the soil can be provided as inputs to YASE, either by the TREGRO model or by the user. YASE can be run alone at any time step; when called by TREGRO it is called on a daily time step.

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YASE was developed to be compatible with TREGRO. To be used in combination with TREGRO, YASE must be parameterized to include the nutrients of possible importance to the plant. A Hypercard interface (described in Section 4, Using the model) aids in the parameterization and running of the model, whether alone or in combination with TREGRO.

2 MODEL DESCRIPTION

Equilibria (CHESS)

Many reactions in the soil solution can be assumed to be at equilibrium. For example, the formation of complexes of inorganic ions, such as aluminum hydroxides, complexation of metals with organic acids, and the dissolution of carbon dioxide can all be described in terms of equilibrium constants. Anion adsorption and cation exchange can also be treated as cases of equilibrium reactions.

Tableau notation, definition of components and species. Chemical equilibria in YASE are based on the Chemical Equilibria in Soils and Solutions model, CHESS (Santore 1991). CHESS uses a notation convention established by Morel (1983), in which reactions are specified in a form called a tableau. The principal advantage of the tableau notation is that a matrix algebra approach for finding the solution to the equilibrium problem can be easily developed. The result is that the same numerical algorithm can be used to solve virtually any equilibrium system, and the addition or removal of reactions in the tableau can be made without any rewriting of computer code.

To construct a tableau, it is necessary to list all of the reactions desired in the simulation. Next a list of all the chemical species that participate in these reactions is made. From this list of species, a set of components is selected such that (1) all of the remaining species can be formed as the product of reactions involving only components, and (2) no component can be formed as the product of a reaction involving only other components. Examples of chemical problems described in this form are given in Section 5.

The tableau is composed of a matrix of coefficients ($a_{i,j}$) that specify the molar combinations of components (X_j) required to form species (S_i).

	X_1	X_2	. . .	X_{Nc}	
S_1	$a_{1,1}$	$a_{1,2}$. . .	$a_{1,Nc}$	K_1
S_2	$a_{2,1}$	$a_{2,2}$. . .	$a_{2,Nc}$	K_2
.
S_{Ns}	$a_{Ns,1}$	$a_{Ns,2}$. . .	$a_{Ns,Nc}$	K_{Ns}
	T_1	T_2	. . .	T_{Nc}	

Virtually all of the information that defines the equilibrium system can be incorporated into the tableau. The only exceptions are the extra thermodynamic assumptions used to incorporate real-world deviations from ideal systems, such as corrections for ion activities.

Basic Problem Description. The basic problem consists of a set of reactions defining the formation of all relevant species from components. No solid or gaseous phases are present and so the total amount of every component is specified and cannot change.

A set of mass action equations can be defined specifying the concentration of species at equilibrium. Variables are defined in Table 2-1.

$$S_i = K_j \prod_{j=1}^{N_c} X_j^{a_{i,j}} \quad i = 1, N_j \quad (\text{eq. 1})$$

A set of mole balance equations can be defined based on the distribution of components within the system.

$$T_j = \sum_{i=1}^{N_s} S_i * a_{i,j} * Q_i \quad j = 1, N_c \quad (\text{eq. 2})$$

Eqs. 1 and 2 can be rearranged into a set of residual equations

$$R_j = \sum_{i=1}^{N_s} (K_i \prod_{j=1}^{N_c} X_j^{a_{i,j}}) * a_{i,j} * Q_i \quad j = 1, N_c \quad (\text{eq. 3})$$

In eq. 3 there are N_c independent equations (R_j) and N_c independent unknowns (X_j). The values for X_j corresponding to the simultaneous roots of R_j are the solution to the basic problem. The remaining species concentrations can be obtained by substitution into eq. 1.

Basic Problem Numerical Solution. Eq. 3 represents a set of simultaneous non-linear equations. The roots to these equations can be found by a Newton-Raphson iterative technique (Press et al. 1986). The iteration is seeded with an initial guess for the values X_j . These values are improved until the simultaneous roots have been found. For a given X_j^t an improved set of values X_j^{t+1} is given by

$$X_j^{t+1} = X_j^t - W_j \quad (\text{eq. 4})$$

The correction factor W_j is found by solving the linear system

$$\sum_{k=1}^{N_c} Z_{j,k} * W_k = R_j \quad j = 1, N_c \quad (\text{eq. 5})$$

The matrix $Z_{j,k}$ is the Jacobian matrix and has dimensions $N_c \times N_c$. Each element of Z can be found by

$$Z_{j,k} = \frac{2R_j}{2X_k} = \sum_{i=1}^{N_s} \frac{S_i * a_{i,j} * a_{i,k} * Q_i}{X_j} \quad (\text{eq. 6})$$

Iteration over eqs. 6, 5, and 4 are repeated until the values of the residual equations are near zero within a specified error tolerance.

Activity Corrections and Cation Exchange. *Aqueous species.* At some ionic strengths typical of soil solutions there is a departure of ion activity values from ion concentrations. Since the use of concentrations is required in the mole balance equations (eq. 2) and chemical activity is required by mass action equations (eq. 1), some provision must be made for converting from one to the other. This is generally accomplished by the use of an estimate for ion activity corrections. The Davies equation can be used for this purpose and has an advantage over other equations in that it does not require ion-size parameters (Stumm and Morgan 1981).

$$\log_{10} \gamma_i = -A * z_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right] \quad (\text{eq. 7})$$

where γ_i is the activity coefficient and z_i is the charge for species i . I is the ionic strength calculated as

$$I = 0.5 \sum_{i=1}^{N_s} (Z_i^2 * S_i) \quad (\text{eq. 8})$$

The activity coefficient for all species can be combined into a conditional equilibrium constant

$${}^cK_i = K_i * \gamma_i^{-1} \prod_{j=1}^{N_c} \gamma_j^{a_{i,j}} \quad (\text{eq. 9})$$

The substitution of cK into eq. 1 corrects for the effect of ionic strength on ion activities.

Cation Exchange Species. The activity correction of chemical species associated with soil surfaces cannot be estimated with the Davies equation. Several theories have been proposed for correcting chemical activity in cation exchange reactions. The model allows the use of mole fraction for Vanselow exchange (also called Gapon) or charge fraction for Gaines-Thomas exchange reactions.

For either type of activity correction the model must keep track of all the species that participate in exchange reactions. The model determines the appropriate species by examining the list of reactions and the activity correction type specified by the user in the input file. To illustrate the possible activity corrections, we use a specific example. An exchange reaction between calcium and aluminum can be written:

$$\text{Ca} + 2/3 X_3\text{Al} = 2/3 \text{Al} + X_2\text{Ca} \quad (\text{eq. 10})$$

$$K = \{\text{Al}\}^{2/3} \{X_2\text{Ca}\} \{\text{Al}\}^{-2/3} \{\text{Ca}\}^{-1} \quad (\text{eq. 11})$$

The activities of the exchange species are estimated as either the mole fraction (N_i) or charge fraction (E_i), calculated as

$$N_{\text{Ca}} = \frac{X_2\text{Ca}}{(X_2\text{Ca} + X_3\text{Al})} \quad (\text{eq. 12})$$

$$E_{\text{Ca}} = \frac{2X_2\text{Ca}}{(2X_2\text{Ca} + 3X_3\text{Al})} \quad (\text{eq. 13})$$

It is convenient to rearrange these expressions to calculate activity coefficients in a manner similar to that for aqueous species.

For mole fraction activity corrections (Vanselow Exchange)

$$N_{\text{Ca}} = \gamma_{X_2\text{Ca}} * X_2\text{Ca} \quad (\text{eq. 14})$$

therefore

$$\gamma_{X_2\text{Ca}} = \frac{1}{(X_2\text{Ca} + X_3\text{Al})} \quad (\text{eq. 15})$$

For charge fraction activity corrections (Gaines Thomas Exchange)

$$E_{\text{Ca}} = \gamma_{X_2\text{Ca}} * X_2\text{Ca} \quad (\text{eq. 16})$$

therefore

$$\gamma_{X_2\text{Ca}} = \frac{2}{(2X_2\text{Ca} + 3X_3\text{Al})} \quad (\text{eq. 17})$$

The calculated γ coefficients are used to calculate conditional stability constants as before (eq. 9).

Species used to represent cation exchange are designated as surface species (species type SPMassBal) so that they will not be affected by movement of the soil solution.

Modification for Solid and Gaseous Phases. The basic problem can be modified to include the effects of solid or gaseous phases on the aqueous system. Each phase included in a simulation has a corresponding solubility equation. A solubility condition can be expressed as

$$Ks_p = \prod_{j=1}^{Nc} X_j^{c_{p,j}} = X_q^{c_{p,q}} \prod_{j=1, j \neq q}^{Nc} X_j^{c_{p,j}} \quad (\text{eq. 18})$$

According to Gibb's Phase Rule, each phase present reduces the degrees of freedom of the problem by one. In the CHESS model, each solubility equation is used to eliminate the mole balance equation for a single component X_q . The X_q selected for a phase p can be any of the components present in the solubility equation that has not already been selected for a different phase. The equation is solved for the selected component X_q

$$X_q = Ks_p \frac{1}{\prod_{j=1, j \neq q}^{Nc} X_j^{c_{p,q}}} \quad (\text{eq. 19})$$

and this selected component is eliminated from the mass action equations

$$S_i = K_i X_q^{a_{i,q}} \prod_{j=1, j \neq q}^{Nc} X_j^{a_{i,j}} = K_i Ks_p^{1/c_{p,q}} \prod_{j=1, j \neq q}^{Nc} X_j^{a_{i,j} - \frac{a_{i,q}}{c_{p,q}}} \quad (\text{eq.20})$$

The residual for component X_q , which reflects mole balance, can now be eliminated from the Newton-Raphson procedure.

$$R_j = \sum_{i=1}^{Ns} (K_i \prod_{j=1}^{Nc} X_j^{a_{i,j}}) * a_{i,j} * Q_i + M_p * c_{p,j} - T_j = 0 \quad j = 1, Nc \quad (\text{eq. 21})$$

where M_p is the change in mass of the phase p.

By setting the residual equation equal to zero, and solving for the M_p , we can calculate the amount of mass transfer from dissolution or precipitation of phase p.

$$M_p = \left[T_q - \sum S_i * a_{i,q} * Q_i \right] \frac{1}{C_{p,q}} \quad (\text{eq. 22})$$

Weathering

Weathering is a non-equilibrium process. The model calculates the amount of each component contributed by non-equilibrium processes during a time step before equilibrating. The amount of each component released from soil minerals depends on the composition of the mineral and on the weathering rate. The composition of minerals is defined by the user using a matrix of minerals and components in the same form as for dependent species. For example, see Table 5-18.

The rate of weathering is calculated from a rate constant and from the amount of mineral present and the hydrogen ion concentration. The effect of the amount of mineral present and the hydrogen ion concentration can be of any order, including zero (no effect). The orders chosen affect the dimensionality of the rate constant. The mass of each mineral weathered is calculated as a fraction of the mass of soil in the layer in question:

$$WFrac = WRate * MinFrac^M * HConc^H * dt \quad (\text{eq. 23})$$

where WFrac is the fraction weathered (g mineral weathered/g soil/time step), WRate is a rate constant supplied by the user (units depend on the values of M and H), MinFrac is the current amount of this mineral as a fraction of soil weight (g mineral/g soil), HConc is the concentration of H⁺ in solution (mol/L), dt is the time step (sec), and M and H are reaction orders supplied by the user. The amount of mineral remaining is reduced by WFrac. The amount of each component released by weathering is calculated from the stoichiometry of the mineral:

$$WthrC = MinSC * WFrac * Mass / MinMW \quad (\text{eq. 24})$$

where WthrC is the amount of the component weathered (mol/time step), MinSC is the stoichiometric coefficient of this component in this mineral, Mass is the mass of the soil layer (g soil), and MinMW is the formula weight of the mineral (g mineral/mol mineral).

Soil Organic Matter Dynamics

Decomposition, like mineral weathering, is a non-equilibrium process. Mineralization and immobilization of nutrients are calculated each time step and used to update the total amounts of components in solution before equilibration. These calculations are accomplished in two different ways, depending on the nutrient.

Calcium, Mg, and K are mineralized at a constant rate, dependent only on the amount of the element present in organic matter. The release of these elements is simply

$$dA/dt = k * A \quad (\text{eq. 25})$$

where A is the amount of the nutrient in the organic pool and k is a nutrient-specific rate constant supplied by the user.

The equations governing the transformations of N, P and S are more complex. Nitrogen mineralization and immobilization are calculated by following the dynamics of C and N as represented by Ryan (unpublished manuscript) and included in the generalized ecosystem model GEM (Rastetter et al. 1991). In YASE, P and S are mineralized in proportion to N, because, like N, they are usually covalently bonded to organic molecules, and their mineralization depends on C transformations.

Compartments in this submodel are C and N in four pools: cellulose, extractives, lignin, and humus (Figure 2-1). Fluxes in the model are the transfer of N and C between these compartments, the loss of C in respiration, and the exchange of N with the soil solution (Figure 2-1). The rate of these fluxes depends on temperature, moisture, soil inorganic nitrogen, and the proportion of lignin to cellulose. The equations in this

model are given by Ryan (unpublished manuscript) and by Rastetter et al. (1991) and will not be repeated here, but the parameters required give an indication of the processes represented. The temperature response function is described by an optimal temperature, a maximum temperature, and a curvature parameter q (Figure 4-33). The effect of soil moisture is described by an optimal moisture and by breadth and skewness parameters. The effect of soil inorganic N is modeled as a Michaelis-Menten process, with parameters for the concentrations of N in solution at which transformation rates are half and fully saturated (Figure 4-34). The effect of lignin on the transformation of cellulose and extractives is to "shield" the substrate; this effect is implemented as a multiplier on the transformation rate (Figure 4-31). The efficiency of C transfer between compartments is analogous to microbial efficiency and determines the respiration associated with each transfer. The other parameters required to simulate decomposition are the initial amounts of C in the four compartments, the C to N ratio of the compartments, and the rate of addition of C and N to the various compartments by leaf and root litter, if TREGRO is not running to provide these inputs.

Solution Flux

The movement of solute between soil layers occurs with the movement of soil solution. Only those components and species that have been designated as aqueous (using species types) are allowed to move. They are moved in proportion to the amount of solution flow. That is, if 10% of the water content of one layer moves into the next layer, 10% of all dissolved constituents move with it. The model assumes that this movement takes place without mixing; that is, the fluxes from any layer can be calculated each time step without considering how the solute concentrations are simultaneously being altered by incoming solution from another layer. In order for this method to produce reasonable results, the model time step must be short relative to the rate of solution flux, such that small fractions of solution are moved each time step. The model will not allow more of a solute to move than was contained in the solution at the start of the time step, in the case where the rate of solution flux moves more than the amount of solution contained in the layer in a time step.

Fluxes of soil solution between layers are not calculated in YASE but are provided by TREGRO (on a daily time step) or by the user (as constant rates) if TREGRO is not running. The units of solution movement per time step are liters. Positive values denote downward fluxes; negative values denote upward fluxes.

Evaporation from the soil surface can drive soil water upward between rainfall events as simulated in TREGRO.

Input of solution at the top of the soil in precipitation or throughfall is also simulated by TREGRO. The concentrations of the nutrients (N, P, S, Ca, Mg, K) are simulated by TREGRO, taking into account interactions with the tree canopy (see TREGRO Documentation). Concentrations of additional solution components can be specified in YASE. When YASE is running alone, the concentrations of all components entering the top soil layer are defined by the user and are held constant along with the amount of water input per time step.

Water contents of soil layers are simulated by TREGRO and are used to calculate the concentrations of dissolved components and species. If TREGRO is not running, water contents are specified by the user and are constant.

Plant uptake

Plant uptake of solutes in each soil layer, like the movement of soil solution, is provided to YASE by TREGRO on a daily time step, or in the absence of TREGRO, by the user as a constant rate for each nutrient element and soil layer. The nutrients simulated by TREGRO are N, P, K, Ca, Mg, and S. These nutrient elements must be the first six components defined in YASE when the two models run together. There is a routine in YASE that maps the components, which may be specified in any order, to the nutrients required by the tree.

Nutrient uptake in TREGRO is calculated by a steady-state model of uptake at the root surface that includes diffusion and solution movement (Baldwin et al. 1973, Nye and Tinker 1977), modified to account for saturation uptake kinetics and new root growth (Yanai 1994). If the rate of nutrient uptake, as calculated by TREGRO or provided by the user, is higher than can be supplied from the soil layer, uptake is limited by the amount of the component present in the layer. Nutrient uptake can also be limited by the capacity of the simulated tree to store nutrients (see TREGRO documentation). Uptake will be zero if the tree's storage capacity for that nutrient is full and the tree is not growing.

3 PROGRAM DESCRIPTION

The computer program for YASE consists of 47 routines written in standard Fortran. Table 3-1 lists these routines. Figure 3-1 shows the relationship of the routines to one another. There is a flowchart for each subroutine (Appendix A) showing the structure and the operations performed by each routine. The code for each routine is in a separate text file; the code is fully commented, including definitions and units of all variable names.

The top level routine is **YASEDriver** if the model is called from TREGRO; the top level routine is **YASEQL_SE** if the model is run alone (Figure 3-1). These routines call **SoilChem** each model time step; they also take care of writing output and, in the case of **YASEQL_SE**, reading parameters that would otherwise be set by TREGRO. If it is the first iteration of the run, **SoilChem** calls **StartUp**, which calls routines required for model initialization. Also, if it is the first iteration of the model, the non-equilibrium processes are skipped and equilibrium is found (**FGuess** provides a first guess at component concentrations; **Solve** carries out the equilibrium calculations). This order is required because the rates of the non-equilibrium processes may be dependent on the species concentrations. In later time steps, the effects of non-equilibrium processes are calculated first. These processes include nutrient uptake (**NuTree**), soil organic matter transformations (**DeCntrl**), weathering (**WthrKT**), and soil water movement (**FluxKT**). These processes each add or remove components to or from solution, which changes the component totals available for equilibration. Given the total in solution for mass-balance constrained components and the fixed concentrations of the other components, **Solve** finds the equilibrium concentrations of all components (including equilibrium reactions involving soil surfaces).

Satisfying these simultaneous equilibria involves solving multiple non-linear equations. The solution is found by iteratively improving approximations until a specified convergence criterion is met. The steps in the iteration are as follows. The first estimates of component concentrations are those of the previous time step. **CalcSpeciesConc** calculates the concentration of the remaining (dependent) species from the component concentrations. **CalcResidual** sums the amount of each component contained in all species and compares this calculated total to the target total. If the difference (the residual) is greater than the defined convergence criterion, then the

estimates need to be improved. **Jake** evaluates the coefficients in the Jacobian matrix describing the effect of a change in the component concentrations on the residual concentrations. **Gauss** solves for the change in the set of component concentrations that would make the residual zero if the equations were linear (this is the Newton-Raphson procedure). **Update** alters the component concentrations by this change, and the process is reiterated until convergence is achieved.

4 USING THE MODEL

Overview

This section describes the interface between the program and the user. Instructions for running the program using this interface differ somewhat depending on whether YASE is being used alone or in conjunction with TREGRO. Most of the interface is the same for both configurations, and the files required and generated by the model are similar (Table 4-1). Using YASE alone and using YASE through TREGRO are described in the sections that follow. Examples of simulations are given in Section 5; following these examples provides experience in using the model and is recommended for new users.

Table 4-1. Files used in running YASE with and without TREGRO.

	File name	File Type	Description
Used in all cases	YASE.Stk	Hypercard stack	Interface
	<soilParamFile>	TEXT	input parameter file, ASCII
Used only when YASE runs alone	YASEQL_SE	Application	Program
	InParam.dat	TEXT	contains tree file name, ASCII
	<soilParamFile>.tree	TEXT	tree parameter file
Used only when YASE runs with TREGRO	TREGRO.Stk	Hypercard stack	Interface
	TREGRO	Application	Program (includes soil model)
	tregro.defaults	TEXT	contains TREGRO parameter filename
	<TreeParamFile>	TEXT	TREGRO parameter file, ASCII

<SoilParamFile> and <TreeParamFile> are names supplied by the user.

Using YASE alone

Installing the model. YASE runs on Power Macintosh and 68K Macintosh computers and requires System version 7.0 or later. You will need 3 MB of RAM (2500K for the interface and 400K for the model). The interface is black and white and sized for the smallest Apple monitor. To use the model interface, you need HyperCard® or HyperCard Player® version 2.1 or later; this software is available from Apple Computer, Inc, if it is not already on your computer. Make sure you allocate 2500K of memory to HyperCard, or the interface will operate very slowly (the suggested size is only 1050K). You will also need software for viewing and manipulating model output (a spreadsheet environment is recommended).

The model and related files are provided in two self-expanding archives on two high-density 3.5 inch floppy disks. You will need 6.3 MB of space for the expanded files, which include the model, the interface, the examples, and the code. Insert each disk, and double-click on the files YASE1.sea and YASE2.sea. You will be prompted to select a place to expand each archive. You may wish to combine the files into a single folder after you have expanded them.

Files required and generated by YASE. The interface to YASE provides a user-friendly environment for altering input files, viewing input parameters, and running the model. A number of files are required in using the model (Table 4-1). The user does not manipulate these files directly in running the model; the Hypercard interface keeps track of the names and location of files. The user need only to be able to recognize file names for organizing and storing them.

The interface is called "YASE.stk." The file containing the soil parameters is named by the user, generally through the Hypercard interface. The file of the same name with extension ".Tree" contains values for parameters and variables that would be supplied by TREGRO if YASE were called by TREGRO. A file called "InParam.dat" contains the path and filename of the YASE input file.

Note that the stack and the model must be in the same folder for the model to run.

Using the interface. To view or change model parameters or run the model requires running the interface, "YASE.stk." (Users unfamiliar with Macintosh computers will need to first become familiar with Macintosh conventions; refer to your User's Guide).

When you first open the stack you will see the title screen (Figure 4-1). You can return to this screen by clicking on the "Credits" button on the **YASE Main Menu** screen (Figure 4-2) which is the first screen on which you can click buttons.

The first screen, the **YASE Main Menu** screen (Figure 4-2) has three functions, with corresponding buttons. You can (1) Select an input file or files to view or change parameters or to choose input files to be used when the model is run, (2) run the model one or several times, depending on how many parameter files were chosen, or (3) print out all the user input cards in the stack. Most of the stack is devoted to viewing or changing parameter values; this part of (1) will be treated last.

Selecting the "Print out all user input cards" button will print out all the screens that a user visits in the stack. The cards can be printed one or two to a page. For those cards where the same information is input for each layer only layer one is printed. Note that the cards are not printed out in the same order as the figures of the cards in this documentation.

The first step in using the interface is selecting an input file that will be run or that will be viewed or changed and then run. Click on the "Select Input Parameter File(s)" button on the **YASE Main Menu** screen (Figure 4-2) to get to the screen where you can select the input parameter file. Before the stack sends you to this screen it will check and see if the currently selected file exists. If it does, you will arrive at the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3). If it doesn't, you will be told that the file could not be found and then asked if you want to select an existing file, create a new file, or cancel. If you choose to select an existing file you will be given the standard Macintosh file select box where you can navigate to the directory and filename of the input file that you want. If you choose to create a new file, you will be asked for a file name for the new file (you can navigate to any directory and locate the file there) and then asked to choose an existing file to be copied into the new file. Error messages will alert you if the file you have chosen is not a proper input parameter file.

Whether you choose an existing file or create a new file, if a tree file is not associated with the input parameter file, you have the option of copying a tree file that is associated with another parameter file or using a default tree file.

On the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3) you will notice a button near the top of the screen that says "Single run" and another that says "Multiple, unattended run". With the first button chosen, you can load, look at and run only one file at a time. With the second button chosen, you can select several files to run sequentially, although you can only look at the data for one file at a time. The arrow at the left of the file name and the shadow around the filename's box indicates

which file is loaded into the stack. It doesn't matter which file is loaded into the stack when you decide to return to the **YASE Main Menu** screen (Figure 4-2) and run the model. The model will start at the top of the list and run the files sequentially.

To select a file on the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3) just click where the file name is written or the empty box where the file name would be written. You will be asked whether you want a new or existing file as described above. When you are finished selecting the file or files to be run (information on changing parameters will be discussed later) click on the "Main Menu" button to return to the **YASE Main Menu** screen (Figure 4-2). Click on the "Start a YASE Model Run" button to begin the run or runs. No further input is required.

When you want to change parameters in an input parameter file click on the "Select Input Parameter File(s)" button on the **YASE Main Menu** screen (Figure 4-2) and select or create an input file. On the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3), click on the "Modify Parameter(s)" button to get to the **YASE Input Parameter Menu** screen (Figure 4-4). The only item that you can input on this card is a note. This note is generally used to describe the input file. You can type up to 256 characters here. A series of buttons lead to cards where parameter values can be viewed and changed. The "System Definition" button leads to the **System Definition** screen (Figure 4-5) where you can input the number of layers, components, species, minerals, solid or gaseous phases, indicate the type of output you want, and indicate whether decomposition is to be run. When you are finished click on the "Model Inputs" button to return to the **YASE Input Parameter Menu** screen (Figure 4-4).

When you view screens where data are displayed in a matrix, you will notice that the screen takes several seconds to set up the first time, but appears quickly on subsequent visits. However, if you return to the **System Definition** screen (Figure 4-5) and change one of the parameters describing the system, the matrix-type screens will again take several seconds to set up. This is because any addition or deletion of layers, components, species, minerals, or phases requires the cards to be reconfigured. Visiting the **System Definition** screen first can save you time later on.

Once the system is defined you can look at or change the parameters in any order you choose. The buttons and the screens they lead to will be described in the order that they appear on **YASE Input Parameter Menu** screen (Figure 4-4). Selecting the "General Parameters" button leads you to the **General Parameters** screen (Figure 4-6). Here you can set up the following general soil data: area, thickness, bulk density (used only to calculate the amount of minerals to be weathered), soil moisture (used to calculate both the amount of solution and the effect of soil moisture on decomposition)

and temperature, per layer, and the time step and number of time steps the model will run. For runs with multiple time steps, the model equilibrates in the first time step; time-dependent processes such as mineralization, weathering, and leaching are not expressed until the second time step. For example, to follow decomposition for one hundred years, set the time step to one year in seconds and the number of time steps to 101. The soil parameters can be input differently for each layer or you can make values the same for all layers by using the buttons at the bottom of the screen.

Some of the state variables have units that reflect the size of the soil system or the length of the model time step. For example, if you were to change the size of the soil system, you would also want to change the mass of soil, if bulk density were to remain constant. Likewise, the rates of organic matter transformations are in units of the fraction to be transformed per time step. To keep the rates constant, the values need to be changed if the time step is changed. By selecting the button "**List of variables that are dependent on the size of the system or the time step**" you will see a screen which lists these variables (Figure 4-7). There is a button on this screen that enables you to print the list for ready reference. Click on "**Back**" to go back. Click on the "Model Inputs" to return to the **YASE Input Parameter Menu** screen (Figure 4-4).

Selecting the button "Components " on the **YASE Input Parameter Menu** screen (Figure 4-4) leads to the **Define Components Layer 1** screen (Figure 4-8). On this screen you will find a line for each component. In the first column, you can name the components. When YASE is running alone, there are no limitations on the names of the components. When YASE runs with TREGRO, the nutrients required by TREGRO must be the first six components and hydrogen must be the seventh. There are buttons to help you with the exact names when YASE is running with TREGRO. The charge, species type, and analytical total of each component are entered in the next three columns. There is one such card for each soil layer. Note, however, that only the analytical total can change in each layer. The species type and the charge are constant over all layers. To facilitate the parameterization of multiple soil layers, there is a column of boxes at the right that allows the values entered on this card to be copied to the other cards for all other soil layers. If the layers are to have different parameter values, the arrows "Next layer" and "Prev. layer" permit visitation of all the cards. Definitions of species types (components are also species) are provided. Click on the "SType Def'n" button to lead to the **SType Definition** screen (Figure 4-11).

To define the dependent species names, stoichiometry, species types, and equilibrium constants, begin by clicking on the "Dependent Species" button on the **YASE Input Parameter Menu** screen (Figure 4-4). This will lead to the **Dependent**

Species screen (Figure 4-10). Selecting the "Dependent Species Stoichiometry" button will lead to Figure 4-11 where the dependent species names and stoichiometry can be input. There is a line for each species (the number of species was defined on the **System Definition** screen (Figure 4-5)) and a column for each component. The names of the species are defined on this screen. There are no limitations on the names of the species. The names of the components are taken from the **Define Components Layer 1** screen (Figure 4-8). The stoichiometry of each dependent species is defined as a series of coefficients (called $a_{i,j}$ in Section 2) describing the contribution of each component in the formation of the species. This array is the "tableau" described in the Model Description section. Examples of chemical systems defined using this tableau notation are given in Section 5. The display allows a tableau of ten dependent species and all the components to fit on one screen, although only the first few digits of stoichiometric coefficients are shown. To view or change any coefficient, click in the tableau and the value will appear on the input line at the bottom of the screen. The values of coefficients cannot be changed by typing directly in the tableau.

Selecting the button "Dependent Species Species Type" on the **Dependent Species** screen (Figure 4-10) leads to the **Species Types for Dependent Species** screen (Figure 4-12) on which the Species Types are defined for each species (component types were defined on the **Define Components Layer 1** screen (Figure 4-8)). Definitions of species types are provided. Click on the "SType Def'n" button to lead to the **SType Definition** screen (Figure 4-11). The names of the species can also be changed here.

Selecting the button "Dependent Species Equilibrium Constants, per layer" on the **Dependent Species** screen (Figure 4-10) leads to the **Equilibrium Constants for Dependent Species, Layer 1** screen (Figure 4-13) on which the equilibrium constants are defined for each species. Equilibrium constants may be defined differently in each soil layer, as in the case of empirically derived selectivity coefficients for cation exchange. If the equilibrium constants are the same in all layers, a button allows the values on the current card to be copied to all layers. The names of the dependent species can also be changed here.

Selecting the button "Minerals" on the **YASE Input Parameter Menu** screen (Figure 4-4) leads to the **Minerals** screen (Figure 4-14) where you can input the names of the minerals, their molecular weights, the initial amount of the mineral as a fraction of soil mass, and three weathering constants. Note that if there are no minerals in the system, this button will appear italicized; if you click on it a dialog box will appear telling you to set the number of minerals on the **System Definition** screen (Figure 4-5).

Selecting the "Mineral Stoichiometry" button on the **Minerals** screen (Figure 4-14) leads to the screen where you can define the composition of each mineral (Figure 4-15). As in the case of dissolved species, the names of the components come from the **Define Components Layer 1** screen (Figure 4-8). The stoichiometry of minerals is constant across soil layers; variations in composition can be accommodated by defining different minerals.

Selecting the "Mineral Fraction, per layer" button on the **Minerals** screen (Figure 4-14) leads to the **Mineral Fractions Layer 1** screen (Figure 4-16). Here you can define the initial amount of each mineral as a fraction of the soil mass. To facilitate the parameterization of multiple soil layers, there is a column of boxes at the right that allows the values entered on this card to be copied to the other cards for all other soil layers. If the layers are to have different parameter values, the arrows "Next layer" and "Prev. layer" permit visitation of all the cards.

Selecting the "Molec. Wt, Weathering Rate, HOrder & MOrder" button on the **Minerals** screen (Figure 4-14) leads to the **Mineral Miscellaneous** screen (Figure 4-17). The equation showing the use of the weathering constants in calculating the amount of mineral weathered is shown at the bottom of the screen. These parameter values are constant over all soil layers.

Selecting the "Quickly Dissolving Phases" button on the **YASE Input Parameter Menu** screen (Figure 4-4) leads to the **Phases** screen (Figure 4-18). Note that if there are no phases in the system this button will be italicized; if you click on it a dialog box will appear telling you to set the number of phases on the **System Definition** screen (Figure 4-5).

Selecting the "Phase Stoichiometry" button on **Phases** screen (Figure 4-18) leads to a screen (Figure 4-19) where the names and stoichiometry for the phases are defined in the same way as the stoichiometry for dependent species and minerals. Selecting "Phase Equilibrium Constants, per layer" on the **Phases** screen (Figure 4-18) leads to the **Phase Equilibrium Constants Layer 1** screen (Figure 4-20) where names and equilibrium constants per layer are defined in the same way as those for dependent species and minerals.

Selecting the "Activity Coefficients" button on the **YASE Input Parameter Menu** screen (Figure 4-4) leads to the **Activity Coefficients** screen (Figure 4-21). Corrections for ionic strength can be made by one of three methods. The Davies correction is described in Section 2, eq. 7; Vanselow uses eq. 14 and Gaines-Thomas uses eq. 16. Using no correction means that the activity will equal the concentration.

Selecting the "Decomposition" button on the **YASE Input Parameter Menu** screen (Figure 4-4) leads to the **Decomposition** screen (Figure 4-22). Note that if decomposition has not been turned on in the system, this button will appear italicized; if you click on it a dialog box will appear telling you to turn decomposition on the **System Definition** screen (Figure 4-5). The **Decomposition** screen (Figure 4-22) has two buttons which allow you to set parameters for nitrogen mineralization and for the mineralization of other nutrients.

Selecting the "Nitrogen Mineralization" button on the **Decomposition** screen (Figure 4-22) leads to the **Nitrogen Mineralization** screen (Figure 4-23). There are seven buttons on this screen.

The first button, "Initial Amounts, per Layer" leads to the **Initial Amounts of Cellulose, Extractives, Lignin and Humus, Per Layer** screen (Figure 4-24). The initial amounts can be different in each layer or they can be made equal for all layers by using the buttons at the bottom of the screen.

The second button, "C:N Ratios" leads to the **C:N Ratios** screen (Figure 4-25). On this screen the C:N ratios for cellulose, extractives, lignin and humus can be input. They are constant across soil layers. Default values can be shown or hidden by clicking on the button on the lower left of the screen. The values themselves are written into the input positions by clicking on them. The default C:N ratios are based on values for a temperate deciduous forest (Ryan, personal communication; Rastetter et al. 1991).

The third button, "Transformation Rates and Efficiencies" leads to the **Transformation Rates and Efficiencies** screen (Figure 4-26). There are five transformations included in the model between the four nitrogen pools (see *Soil Organic Matter Dynamics* under Section 2, Model Description). Each transformation has both a rate and an efficiency. These values are applied equally across all soil layers. Default values can be shown or hidden and are written into the input positions by clicking on them. The default values are from Ryan (unpublished data), converted to units of day⁻¹ to be consistent with the TREGRO time step. When YASE is running alone, any model time step can be used (specified on the **General Parameters** screen (Figure 4-6) described above).

The fourth button, "Leaf Fractionation" leads to the **Leaf Fractionation** screen (Figure 4-27). The fraction of carbon in leaf cellulose and leaf extractives are input; the fraction of carbon in leaf lignin is calculated by difference because these three fractions must sum to unity. Leaf litter is always added to the uppermost soil layer. Default values can be shown or hidden and are written into the input positions by clicking on them.

The fifth button, "Root Fractionation, per layer" leads to the **Root Fractionation Per Layer** screen (Figure 4-28). Again, the fraction of carbon in root cellulose and root extractives are input; the fraction of carbon in leaf lignin is calculated by difference because these three fractions must sum to unity. Root litter may be added to any soil layer and the parameters may be given different values or one set of values may be applied to all layers. Buttons at the bottom of the screen facilitate the setting of one value over all layers.

The mass and nutrient content of leaf and root litter are also inputs to the decomposition routine. The amounts of litter are simulated by TREGRO or fixed by the user by clicking on the "Water and Nutrient Fluxes" button on the **YASE Input Parameters** screen (Figure 4-4) and further clicking on the "Leaf Senescence and Nutrient in Senescing Leaves" button and the "Root Senescence and Nutrients in Senescing Roots" button on the **Water and Nutrient Fluxes** screen (Figure 4-39). These screens are defined below.

The sixth button, "Soil Moisture Parameters" leads to the **Soil Moisture Parameters** screen (Figure 4-29). The soil moisture is defined in units of available water (mm). The equation for the effect of soil moisture on decomposition is given in Section 2, Model Description (*Soil Organic Matter Dynamics*). Note that the optimal soil moisture defined in these units will depend on the depth of each soil layer, but that these values are applied to all layers. The effect of soil moisture on decomposition has not been well exercised in YASE. The soil moisture breadth and skewness parameters are also input. Default values can be shown or hidden and are written into the input positions by clicking on them.

The seventh and final button, "Miscellaneous Parameters," leads to the **Miscellaneous Parameters** screen (Figure 4-30). These parameters control the effects on decomposition of lignin shielding (defined by a lignin-cellulose index, ILC), temperature, and dissolved nitrogen. Default values can be shown or hidden and are written into the input positions by clicking on them.

The ILC shielding parameters control the effect of lignin (as a fraction of lignin + cellulose) on the decomposition of cellulose and extractives. You can input the parameter directly (Figure 4-30) or look at the relationship graphically for both cellulose (Figure 4-31) and extractives (Figure 4-32). The effect of soil temperature is defined by maximal and optimal soil temperatures for decomposition and a curvature parameter. These parameters can be input directly and are also illustrated graphically (Figure 4-33). The parameter defining the half-saturation constant for the effect of N availability on decomposition is likewise input directly and illustrated graphically (Figure 4-34).

The mineralization of nutrients other than nitrogen is parameterized by selecting the button "Mineralization of Other Nutrients" (Figure 4-22), which leads to the **Mineralization of Other Nutrients** screen (Figure 4-35). There are five such elements in TREGRO: P, S, K, Ca, and Mg. Parameter values must be defined for all of them if decomposition is invoked, even if TREGRO is not running. The amounts of mineralizable nutrients can be set to zero to turn off the effects.

Selecting the "Initial Amounts, per layer" button on the **Mineralization of Other Nutrients** screen (Figure 4-35) leads to the **Initial Amounts of Calcium, Magnesium, Potassium, Phosphorus, Sulfur** screen (Figure 4-36). The initial amounts of nutrient elements contained in organic matter are given in grams of nutrient and are set for each soil layer. Buttons located at the bottom of the screen facilitate the assigning of the same initial amount of nutrient to all soil layers.

If TREGRO is running, additions to the pools of mineralizable nutrients are made daily through leaf and root litter. If TREGRO is not running, the amount and composition of leaf and root litter are simulated by constants for each time step, as described below under the "Water and Nutrient Fluxes" button which is found on the **YASE Input Parameter Menu** (Figure 4-4).

Selecting the "Mineralization Rates" button on the **Mineralization of Other Nutrients** screen (Figure 4-35) leads to the **Mineralization Rates** screen (Figure 4-37). Mineralization of Ca, Mg, and K is assumed to follow first-order kinetics; rate constants are set on this screen and apply to all layers. Mineralization of P and S is assumed to be proportional to N mineralization (see *Soil Organic Matter Dynamics* under Section 2, Model Description) and therefore no additional rate parameters need to be set.

Selecting the "Rainfall Concentrations" button on the **YASE Input Parameter Menu** screen (Figure 4-4) leads to the **Rainfall Concentration of Components** screen (Figure 4-38). These inputs are the concentrations of components in the solution entering the top of the soil column. When TREGRO is running it will simulate the concentrations of the nutrient elements (i.e. the first six elements in the soil model) on a daily time step, so only the other components need be specified. The "Water and Nutrient Fluxes" button on the **YASE Input Parameter Menu** (Figure 4-4) leads to the **Water and Nutrient Fluxes** screen (Figure 4-39). These parameters, along with those on the **General Parameters** screen (Figure 4-6) are only set in YASE when TREGRO is not running. When TREGRO is running these values are passed to YASE by TREGRO.

Selecting the "Water Fluxes" button on the **Water and Nutrient Fluxes** screen (Figure 4-39) leads to the **Water Fluxes** screen (Figure 4-40), which defines the rate of solution movement between each of the soil layers at each time step. The rate of rainfall

or water flux is constant for the duration of a model run when not simulated by TREGRO.

Selecting the "Nutrient Uptake" button on the **Water and Nutrient Fluxes** screen (Figure 4-39) leads to the **Nutrient Uptake, Per Layer, For All Nutrients** screen (Figure 4-41), which shows the amounts of each nutrient element removed from the soil solution each time step. These values are be defined for each soil layer. Buttons at the bottom of the screen facilitate assigning the same value over all layers. Like water fluxes, these uptake rates are constant for the duration of a model run when they are not simulated by TREGRO.

Selecting the "Leaf Senescence and Nutrients in Senescing Leaves" button on the **Water and Nutrient Fluxes** screen (Figure 4-39) leads to the **Leaf Senescence and Nutrient in Senescing Leaves per Timestep** screen (Figure 4-42). Again, the amount of leaf senescence per time step and the concentration of nutrient elements are constant during a model run when TREGRO is not running. The amount of nutrient contained in senescing tissue is calculated from the mass and concentration parameters; these amounts are displayed on the card. Leaf senescence is always added to the top layer.

Selecting the "Root Senescence and Nutrients in Senescing Roots" button on the **Water and Nutrient Fluxes** screen (Figure 4-39) leads to the **Root Senescence and Nutrient in Senescing Roots per Timestep, Layer 1** screen (Figure 4-43). The parameters are similar to those for leaves except that they must be input for each soil layer.

After all the parameters have been checked or entered, selecting the "Input Parameter File(s)" button from the **YASE Input Parameters Menu** screen (Figure 4-4) will allow you to (a) save all the parameters you've changed and return to the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3), (b) discard all the changes you've made and return to the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3), or cancel and remain on the **YASE Input Parameters Menu** screen (Figure 4-4). If you choose to discard changes, the data from the last version saved will be read into the stack the next time you return to look at the file; the cards will take as much time to set up as if this were a new file.

Running the model. There are several circumstances under which you will run the model. Here's the safest way to handle them:

(1) You have input files from some other source, such as the examples provided with this documentation. Make sure you save copies for later comparison and for protection against corruption. Open the stack and select the input file that you want to

run. Run the model. If you have ".Out" files generated by the input files, compare them with the newly generated one; they should be the same. See Section 4 *Using the model->Using YASE alone->Using the interface* for a description of how to do this. If you are given an input file without an associated ".Tree" file you will have the option of using a default tree file or copying a tree file associated with another input file. Note that your results may differ from the previous ".Out" file if the previous tree file was different.

(2) You want to create a new input parameter file. You need an old input parameter file to start with. When selecting an input parameter file (Figure 4-3), choose "New" when prompted and copy the old parameter file into the new file that you have created. Move throughout the stack setting up the new parameter file, save the parameter changes and run the model.

When you run the model, a screen will appear that tells you the name of the input parameter file being read, the name of the decomposition output file (if decomposition is being run), an indication that the "First Guess" routine is being used to set up the model, the user input note in the input file, and some indication that the model is running.

If you see a box at the bottom of the screen that lists the routine name and the line number currently being executed, you should unlock the Caps Lock key. This information is made available for debugging, but it slows the simulation.

Files created during a model run

When you run the model from the **YASE Main Menu**, the interface creates a file called InParam.dat. When the model runs, it looks to this file to find the path and name of the input parameter files. InParam.dat actually contains only the path and name of the tree file; the name of the input parameter file is obtained from the tree file name (they were given the same base name when they were created in the interface). The input parameter file and the associated tree file must be together, since they share the path designated in InParam.dat. The model and the interface should also be together, because InParam.dat is created in the location of the interface and the model looks for InParam.dat in the location of the model. Input files can be stored anywhere as long as the path is not too long to be specified in the "Name(s) of YASE Input Parameter File(s)." The InParam.dat file need not be saved because it is created every time the model is run.

Using the model in TREGRO

When YASE is called by TREGRO the name of the YASE input parameter file is passed to YASE from TREGRO. There is no need for an InParam.dat file nor a .Tree file. The cards seen in setting parameter values in the interface are for the most part the same as when YASE runs alone; the differences are listed as follows.

The **YASE Input Parameter Menu** screen (Figure 4-4) will instead appear as Figure 4-44: the "General Parameters" and the "Water and Nutrient Fluxes" buttons have been removed because all the data input on these cards is now calculated or input in TREGRO and passed to YASE. This means that the cards shown in Figures 4-6, 4-39, 4-40, 4-41, 4-42, and 4-43 are no longer accessible in the interface.

The first six components must be the TREGRO nutrients, N, P, S, K, Ca, and Mg. They can be in any order. The seventh component must be H. Therefore, the system must have at least seven components. There are several notes in the stack to this effect.

On the rainfall concentrations screen (Figure 4-38), the concentrations for the first six nutrients are concealed and a note indicates that these are passed to YASE from TREGRO so they are not input here. You can input concentrations for the other components.

Output files

YASE creates two output files. The first one has the same name as the input file with a ".Out" added at the end and the second one (created only if decomposition is simulated) has a ".Dec" added at the end. The first portion of the <anyfile>.Out lists all the input data in tabular form. The second portion gives the concentrations (mol/L) and the KTs (mol) for each component and species, with one line for each soil layer. The user has the option of choosing whether or not additional information (the number of iterations, the layer number, the maximum error, the maximum component, the residuals at convergence) is printed each time step by selecting "Yes" or "No" on the **System Definition** screen (Figure 4-5) as described in the *Using the model->Using YASE alone->Using the interface* section above. If this information is not included then this second portion of the <anyfile>.Out is easily copied into a spreadsheet for analysis.

The <anyfile>.Dec file, created only if the decomposition routine is run, contains the following information for each layer: Total respiration (gC/time step), net mineralization (gN/time step), extractives carbon (gC), cellulose carbon (gC), lignin carbon (gC), humus carbon (gC), extractives nitrogen (gN), and nitrogen (gN). This file is tab delimited, so it is viewed most easily as a spreadsheet.

Input file description

It would be possible to run YASE without the Hypercard interface. Output as well as input files are ASCII text (this is not the case for TREGRO output files), and input files are intended to be legible. There should be no reason to look at the input files as text files or to run them without the interface; this description of the input files is provided only in case difficulties arise in running the model in the normal way, and debugging the input file is necessary.

When YASE runs alone it requires three files (Table 4-1). The first file that it reads is called InParam.dat. This file contains the name, including the path name, of the tree file. The tree file, the second file that YASE needs, contains the all the information that would be provided to YASE by TREGRO if TREGRO were running. The names of the input and output files for YASE are found using the same root as the tree file. The tree file is an ASCII file with a file type of TEXT and can be read by any standard text editor.

The format for representing data in a file consists of two lines, in which the first line is a label and the second line is a value. For example:

Number of Layers

4

The label is read in and ignored by YASE. The input data file size is constant even though the number of layers and components for different models changes. Full arrays are read in and data not used in a particular model run are ignored. For example, for the parameters that are per layer there are 10 values no matter how many layers there are.

The third file required by YASE is the input parameter file that describes the soil system. The name of this file is found from the tree file name. This file is also an ASCII file. This file is organized like the tree file in that the data is in the format of alternating labels and values, one per line, and full arrays are read in, including values for layers, components, etc. beyond the size of the model.

Although these values beyond the size of the model are ignored in running the model and are not visible in the interface, they are retained in the parameter file; they are not zeroed. The advantage of saving these values is that the model size can be contracted and expanded without losing them. It is useful when working with a large and complex system to be able to experiment with reduced versions, containing fewer dependent species and processes. When the system is expanded, the values for the hidden parameters and processes again become visible in the stack.

When the model is running with TREGRO, the only data file needed is the input parameter file. YASE does not read InParam.dat and does not need a tree file. The name of the soil input data file, as chosen by the user, is provided by TREGRO.

Variables dependent on system size and time step

Table 4-2 gives a brief description of the variables in the model that depend on the size of the system. Remember to change these variables if you change the size of the system.

Table 4-2: Variables dependent on the size of the system.

Variable (units)	How/When Used	Extent of Input
Analytical Total (mol)	Used in all models.	Every component, every layer
Initial amounts of cellulose, extractives, lignin and humus (gC)	Used when decomposition turned on.	Four inputs per layer when decomposition is turned on.
Initial amounts of Ca, Mg, K, P, S per layer (g nutr)	Used when decomposition turned on.	Five inputs per layer when decomposition turned on.
Optimal soil moisture (mm available water)	Used when decomposition turned on.	One input per layer when decomposition turned on.

Table 4-3 gives a brief description of the variables in the model that depend on the time step of the system. Remember to change these variables if you change the time step of the system.

Table 4-3: Variables dependent on the time step of the system.

Variable (units)	How/When Used	Extent of Input
Nutrient uptake (mol/time step)	Used for all model runs.	Six (one for each nutrient) per layer.
Transformation rates, cellulose to extractives, extractives to lignin, humus to extractives, lignin to extractives, lignin to humus (fraction per time step)	Used when decomposition is turned on.	Five inputs when decomposition is turned on.
Mineralization rates for Ca, Mg, K (g nutr/(g nutr time step))	Used when decomposition is turned on.	Three inputs when decomposition is turned on.

Leaf senescence per time step (gC/time step)	Used when decomposition is turned on.	One input for the leaf senescence. Using the concentration of the nutrients in senescing leaves, the amount of each nutrient in senescence is calculated for an addition six inputs.
Root senescence per time step (gC/time step)	Used when decomposition is turned on.	One input for each soil layer for root senescence. Using the concentration of the nutrients in senescing roots, the amount of each nutrient in senescence is calculated for an additional six inputs.

5 EXAMPLES OF SIMULATIONS

Here are some examples of input and output for some demonstrations of chemical behaviors in YASE. The input and output files are described here and included with the software. The first examples illustrate the processes included in chemical equilibria: speciation in closed and open systems, equilibria with gaseous and solid phases, anion adsorption, and cation exchange. Subsequent examples include non-equilibrium processes: weathering, decomposition, and solution flux between soil layers.

Keep copies of the original input and output example files so that you can alter your working copies or compare your output to ours.

Example 1 - Carbonate speciation

The purpose of this example is to provide a simple introduction to the model and interface. The chemical system in this example is an aqueous carbonate solution that will be titrated with acid and base. There is no atmosphere (no gaseous CO₂) in this system. During this exercise the user should be focusing on the following goals:

- (i) construct a tableau given a set of reactions,
- (ii) navigate the menus to input the chemical reactions (tableau) and system description,
- (iii) run the model, and
- (iv) verify that the model output corresponds to the desired equilibrium solution.

Description. This first example serves as an introduction to the data input screens for the chemical equilibrium model. We will use the model to look at the equilibrium speciation of aqueous carbonate; we will also look at the effect of acid and base addition on the chemistry of this system. The basic chemical system is a solution of 1 mmol/liter NaCl and 1 μmol/liter of Na₂CO₃.

The first step for modeling a set of reactions is to formulate a tableau, as described in Section 2, Model Description. We are interested in the following reactions:

- (i) $\text{H}_2\text{O} = \text{H} + \text{OH}$
- (ii) $\text{NaCl(s)} = \text{Na} + \text{Cl}$
- (iii) $\text{CO}_3 + \text{H} = \text{HCO}_3$
- (iv) $\text{CO}_3 + 2\text{H} = \text{H}_2\text{CO}_3$

For this system, the list of species is Na, Cl, H, OH, H₂O, H₂CO₃, HCO₃, and CO₃. One set of components that can be selected for this system is H₂O, H, CO₃, Na, and Cl. With this selection of components all of the remaining species can be formed as products of reactions involving only other components, and no component can be formed as the product of reactions involving only other components. Since these are the only criteria that govern component selection, we can construct a tableau with these components. Other choices of components are equally valid, such as H₂O, OH, H₂CO₃, Na, and Cl. The choice of components makes no difference to the equilibrium concentrations calculated by the model, but it does affect the appearance of the tableau.

This simple system can be further simplified before we construct a tableau for the model. Since the dissolution of NaCl at these concentrations will not be limited by solubility, we can omit this reaction and simply provide the resulting Na and Cl concentrations to the model. Further, in dilute aqueous systems, water is always assumed to be present and the component H₂O does not need to be explicitly included in the tableau. Therefore a stoichiometric coefficient of -1 for H can be used to describe a hydroxyl (OH) group.

Table 5-1 : Tableau for reactions in Example 1.

Species	Components				Log K
	H	CO ₃	Na	Cl	
H	1	0	0	0	0
CO ₃	0	1	0	0	0
Na	0	0	1	0	0
Cl	0	0	0	1	0
OH	-1	0	0	0	-14
HCO ₃	1	1	0	0	10.25
H ₂ CO ₃	2	1	0	0	16.55

The list of species, the stoichiometric coefficients, and the equilibrium constants provide a description of the reactions that will occur in this system. The total concentration of each of the components in the tableau is the only additional information required for calculating the equilibrium chemistry.

Entering data. From the starting screen of the Hypercard interface (Figure 4-2) click on the "Select YASE Input Parameter File(s)" button to get to the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3). If the "single run" radio button is not set, click on it. If the file *Ex.1closedcarb.* is not the selected input file, select an input file by clicking on the space where the input file name is written. You will be asked to choose a "New" or "Existing" file; choose "Existing" then navigate through your hierarchy of files to find *Ex.1closedcarb.*. If you were to choose "New" you would have the opportunity to copy an existing file to a new file.

When the input file has been selected, click on the "Modify Parameter(s)" button to get to the **YASE Input Parameter Menu** screen (Figure 4-4). Click on the "System Definition" button and verify the following choices:

Table 5-2: Values in the YASE system definition input screen for Example 1.

<u>Parameter</u>	<u>Value</u>
Number of Layers	10
Number of Components	4
Number of Dependent Species	3
Number of Minerals	0
Number of Quickly Dissolving Phases	0
Detailed Output	No
Run the Decomposition Routines	No

Then click on the "Model Inputs" button to return to the **YASE Input Parameter Menu** screen (Figure 4-4).

We define 10 layers as a convenient way of using a single model run to generate solutions to 10 different chemical conditions. These "layers" do not communicate or influence one another in any way. To verify that there is no solution flux between layers, from the **YASE Input Parameter Menu** screen (Figure 4-4) click on the "Water and Nutrient Fluxes" button then the "Water Fluxes" button and see that all fluxes between layers are set to zero (Figure 4-40), then return to **YASE Input Parameter Menu** screen (Figure 4-4).

Click on the "General Parameters" button to get to the **General Parameters** screen (Figure 4-6), and verify that time step is set to 1 second and the number of time steps is set to 1. The soil area is set to 0.01 m² and the thickness is set to 0.1 m, giving a soil

volume of 1000 cm³ (1 liter). The bulk density is set to 1.0 g/cm³ so that the mass of soil is 1 kg. The volumetric soil moisture is also set to 1 m³/m³ so that the volume of soil solution is 1 liter. This volume is convenient because the analytical totals (mol) and the concentrations (mol/l) can be easily compared. The soil temperature is set to zero because it is only used during decomposition and decomposition is not running in this example.

Click on the “Components” button to access the **Define Components** screen (Figure 4-8). From this screen you can verify the component names, ionic charge, species type (Table 5-3), and analytical total concentrations (Table 5-4).

Table 5-3 : Component information for Example 1.

Component	Charge	Species Type
H	+1	AqMassBal
CO ₃	-2	AqMassBal
Na	+1	AqMassBal
Cl	-1	AqMassBal

The species type for these components is an abbreviated description identifying these components as aqueous and limited by mass balance. The mass balance limitation applies to situations where we know the total concentration of a component and we are asking the model to calculate its distribution among various forms.

Next, verify the total concentrations of each component by layer. An example of a series of acid and base additions is provided in Table 5-4.

Table 5-4 : Total concentrations (mol/L) for components in Example 1.

Layer	H	CO ₃	Na	Cl
1	1.0E-10	1.0E-6	1.00200E-3	1.000E-3
2	1.0E-6	1.0E-6	1.00200E-3	1.001E-3
3	3.0E-6	1.0E-6	1.00200E-3	1.003E-3
4	1.0E-5	1.0E-6	1.00200E-3	1.010E-3
5	1.0E-4	1.0E-6	1.00200E-3	1.100E-3
6	1.0E-3	1.0E-6	1.00200E-3	2.000E-3
7	-1.0E-4	1.0E-6	1.10200E-3	1.000E-3
8	-1.0E-3	1.0E-6	2.00200E-3	1.000E-3
9	-1.0E-2	1.0E-6	1.10020E-2	1.000E-3
10	-1.0E-1	1.0E-6	1.01002E-1	1.000E-3

The first layer is a simple NaCl and Na₂CO₃ solution. The second through sixth layers have additions of hydrochloric acid (HCl). To simulate the acid addition, the concentrations of H and Cl are increased. The remaining layers correspond to addition of increasing amounts of sodium hydroxide base (NaOH). Because the concentration of the component CO₃ is the same for all layers, it is convenient to check the box (|X|) to copy this information to all layers (Figure 4-8).

Note that for the base additions, the concentration of H ion input to the model is negative. Although negative concentrations seem impossible, remember that most of the H ion in any aqueous system is tied up in water molecules. By leaving the species H₂O out of our description, we have reduced the mole balance equation for H to the remaining species. In this problem, the concept of "total H ion concentration" can be equated to negative alkalinity (for example, compare the mole balance equation for the component H in this system to the equation for carbonate alkalinity). In this case, the addition of OH⁻ is accomplished by subtracting an equal number of H ions from the system. The equilibrium equations specified in the tableau (Table 5-1) controls the resulting concentrations.

Another point to consider is that for components with zero concentrations, it is usually better to input a very low concentration to the model. The use of a low but non-zero concentration will improve the efficiency of the model with negligible effect on the calculated equilibrium chemistry. Select a concentration low enough for the component in question to be much lower than the concentration of any species of interest in the output (three to five orders of magnitude lower is more than sufficient for this purpose).

After verifying the total concentrations for all layers, click on the "Model Inputs" button to return to the **YASE Input Parameter Menu** screen (Figure 4-4). Next, click on the "Dependent Species" button followed by the "Dependent Species Stoichiometry" button (Figure 4-10) to verify the stoichiometric coefficients (Figure 4-11) as they appear in the tableau for this system (Table 5-1). You will notice that the rows of stoichiometric coefficients for the component species are simply an identity matrix. Because of the way components are defined, this will always be the case for any tableau. Instead of requiring users to specify this information, it is simply hard-wired into the model code. Therefore, these coefficients do not appear on the input screen in the model.

When finished, return to the **Dependent Species** screen (Figure 4-10) and then click the "Dependent Species Species Type" button and verify the species types as all aqueous mass balance (Figure 4-12).

When finished, return to the **Dependent Species** screen and then click the "Dependent Species Equilibrium Constants, per layer" button and verify the equilibrium

constant (log K) information from the tableau. This information can be put in just once and then copied to all layers using the |X| button provided (Figure 4-13).

The activity coefficient choice is found by clicking on the "Activity Coefficients" button from the **YASE Input Parameter Menu** screen (Figure 4-4). All of the species in this example are aqueous species, so we can use the Davies equation for calculating activity coefficients.

Running the model. After all the data have been entered, it is time to run the model. From the **YASE Input Parameter Menu** screen (Figure 4-4) click the "Input Parameter Files" button and choose "Save Chgs." From the **YASE Input Parameter File(s)** screen (Figure 4-3) click on the "Main Menu" button to return to the startup screen (Figure 4-2). Click on the "Start a YASE Model Run" button to start the model.

Checking the output. The output is in the form of a formatted text file that can be imported to a spreadsheet program for additional calculations and graphing (Table 5-5). The concentrations of each species are given, followed by the total concentrations of each component. There are no solid phases in this example.

Table 5-5a: Model output for Example 1.

THE SPECIES CONCENTRATIONS (mol/l)							
LYR	H	CO ₃	Na	Cl	OH	HCO ₃	H ₂ CO ₃
1	1.05E-08	6.02E-09	1.00E-03	1.00E-03	1.02E-06	9.75E-07	1.90E-08
2	9.80E-05	3.64E-15	1.00E-03	1.10E-03	1.10E-10	5.47E-09	9.95E-07
3	2.98E-04	4.02E-16	1.00E-03	1.30E-03	3.63E-11	1.82E-09	9.98E-07
4	5.98E-04	1.02E-16	1.00E-03	1.60E-03	1.83E-11	9.14E-10	9.99E-07
5	1.07E-10	3.78E-07	1.10E-03	1.00E-03	1.01E-04	6.21E-07	1.23E-10
6	3.61E-11	6.47E-07	1.30E-03	1.00E-03	3.00E-04	3.53E-07	2.35E-11
7	1.82E-11	7.87E-07	1.60E-03	1.00E-03	6.00E-04	2.13E-07	7.09E-12
8	1.10E-11	8.61E-07	2.00E-03	1.00E-03	1.00E-03	1.39E-07	2.77E-12
9	1.24E-12	9.86E-07	1.10E-02	1.00E-03	1.00E-02	1.42E-08	2.83E-14
10	1.66E-13	9.99E-07	1.01E-01	1.00E-03	1.00E-01	1.07E-09	2.13E-16

Table 5-5b: Model output for Example 1.

THE KTs (mol)				
LYR	H	CO ₃	Na	Cl
1	1.00E-10	1.00E-06	1.00E-03	1.00E-03
2	1.00E-04	1.00E-06	1.00E-03	1.10E-03
3	3.00E-04	1.00E-06	1.00E-03	1.30E-03
4	6.00E-04	1.00E-06	1.00E-03	1.60E-03
5	-1.00E-04	1.00E-06	1.10E-03	1.00E-03
6	-3.00E-04	1.00E-06	1.30E-03	1.00E-03
7	-6.00E-04	1.00E-06	1.60E-03	1.00E-03
8	-1.00E-03	1.00E-06	2.00E-03	1.00E-03
9	-1.00E-02	1.00E-06	1.10E-02	1.00E-03
10	-1.00E-01	1.00E-06	1.01E-01	1.00E-03

A useful way to summarize the model output is with a Log concentration vs. pH diagram. Figure 5-1 shows the log concentration of the species in this example as a function of pH (you can construct this graph from *_Ex.1,closedCarb.Excel*). This type of graph is a useful way to look at changes in species distribution across a range of pH values.

The relevant checks on the equilibrium calculations are mole balance and mass action equations.

The mole balance equations are simply an accounting of material balance for each component in this system. The equations can be formed by summing down the column of the tableau under each component. The prefix "T." is used to indicate the total.

(Mole balance equations:)

$$T.H = [H] - [OH] + [HCO_3] + 2[H_2CO_3]$$

$$T.CO_3 = [CO_3] + [HCO_3] + [H_2CO_3]$$

$$T.Na = [Na]$$

$$T.Cl = [Cl]$$

where species in square brackets represent concentrations in moles/liter.

The mass action equations are the equilibria defined in the tableau (Table 5-1). The concentration of each species is found using eq. 1 (Section 2), in which the product of each component raised to the specified exponent is multiplied by the equilibrium constant (last column of the tableau). The first species (H) will be shown with the

uninvolved components (which have exponents of zero); these are omitted from the remaining calculations.

(Mass action equations:)

$$\{H\} = \{H\}^1\{CO_3\}^0\{Na\}^0\{Cl\}^0 \cdot 10^0 = \{H\}$$

$$\{CO_3\} = \{CO_3\} \cdot 10^0 = \{CO_3\}$$

$$\{Na\} = \{Na\} \cdot 10^0 = \{Na\}$$

$$\{Cl\} = \{Cl\} \cdot 10^0 = \{Cl\}$$

$$\{OH\} = \{H\}^{-1} \cdot K_{OH} = \{H\}^{-1} \cdot 10^{-14}$$

$$\{HCO_3\} = \{H\} \cdot \{CO_3\} \cdot K_{HCO_3} = \{H\} \cdot \{CO_3\} \cdot 10^{10.25}$$

$$\{H_2CO_3\} = \{H\}^2 \cdot \{CO_3\} \cdot K_{H_2CO_3} = \{H\}^2 \cdot \{CO_3\} \cdot 10^{16.55}$$

where species in braces represent ion activities. Obviously the mass action equations for components are trivial. However, the equations depend on activities rather than concentrations. Because only concentration information is available in the model output, you will notice that these equations are not exactly satisfied unless all species were defined with no activity coefficient calculation. If you wish to verify this output, you can specify that no activity coefficients be used and then the equations should be satisfied exactly. Another technique for checking these equations without changing the species definitions is to solve all of the mass action equations for the equilibrium constant and to substitute species concentrations for activities. The constants calculated this way are *apparent* constants and are dependent on the ionic strength of the system. However, these apparent constants can be checked against literature values for a given ionic strength.

Example 2 - Carbonate speciation in the presence of atmospheric CO₂(g)

The purpose of this example is to introduce solubility calculations and to examine the effect of the solubility of a gaseous phase on chemical speciation. During this exercise the user should be focusing on the following goals:

- (i) include gaseous solubility reactions in model simulations, and
- (ii) compare the chemistry of a carbonate solution with and without gaseous CO₂(g) equilibrium.

Description. This example is an extension of Example 1. The only difference is the addition of a reaction for gaseous CO₂ solubility. There are many possible ways to

write this reaction, but we use the one that uses the components we selected to define the system.



The solubility constant must be defined according to the reaction as written.

$$K_s = \{\text{H}\}^2\{\text{CO}_3\}/\{\text{CO}_2(\text{aq})\}$$

The solubility constant is dependent on the activity of aqueous CO_2 , which is equal to its partial pressure in the atmosphere with which it is in equilibrium. In order to express this solubility reaction using the concentration of components only, the value of the partial pressure is simply combined with the solubility constant. The partial pressure of atmospheric CO_2 is approximately $10^{-3.5}$ atm.

To the tableau from Example 1, we add a description of the gaseous phase (Table 5-6).

Table 5-6: Tableau for reaction in Example 2.

Species	Components				Log K
	H	CO ₃	Na	Cl	
H	1	0	0	0	0
CO ₃	0	1	0	0	0
Na	0	0	1	0	0
Cl	0	0	0	1	0
OH	-1	0	0	0	-14
HCO ₃	1	1	0	0	10.25
H ₂ CO ₃	2	1	0	0	16.55
<hr/>					
Phases					
CO ₂ (g)	2	1	0	0	-21.5

Entering Data. Since this example is similar to Example 1, it is easiest to start with the input file for Example 1 and add the additional information. (Alternatively, the example file for Example 2 can be loaded into the stack and the inputs simply verified

as described above for Example 1.) On the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3), click on the file name currently loaded. You will be asked if you want to create a new file or load an existing file. Choose "New." You will then be asked for the name of the new file (e.g. Example 2) and then for the name of the file to copy. Choose *Ex.1,closedcarb* as the file to copy. This is the file that was used for Example 1. Click on the "Modify Parameter(s)" button to get to the **YASE Input Parameter Menu** screen (Figure 4-4). Change the note here to indicate that this is now Example 2 and that the system is carbonate speciation with atmospheric CO₂(g). Click on the "System Definition" button to get to the **System Definition** screen (Figure 4-5). On the **System Definition** screen (Figure 4-5) change the number of quickly dissolving phases to 1, return to the **YASE Input Parameter Menu** screen (Figure 4-4) and click on the "Quickly Dissolving Phases" button. From the **Phases** screen (Figure 4-18), click on the "Phase Stoichiometry" button. The name of the phase, CO₂(g), and its solubility is entered just as it appears in the tableau (Figure 4-19; Table 5-6). Click on the "Back" button to return to the **Phases** screen (Figure 4-18), then click on the "Phase Equilibrium Constants, per layer" button and enter the solubility constant. Use the check box on the right to distribute the value over all layers. When you are finished, return to the **YASE Input Parameter Menu** screen (Figure 4-4) and click on the "Input Parameter File(s)" button. You will be asked if you want to save your changes; choose "Save Chgs." You will be returned to the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3), click on the "Main Menu" button to get to the startup screen. Now run the model.

Checking the output. All of the same mass action equations we applied to Example 1 can be used in this example. However, the mole balance equations must now consider the additional material contributed by the dissolution of CO₂(g). The revised equations are

$$\begin{aligned} T.H &= [H] - [OH] + [HCO_3] + 2[H_2CO_3] + 2MCO_2 \\ T.CO_3 &= [CO_3] + [HCO_3] + [H_2CO_3] + MCO_2 \end{aligned}$$

where MCO₂ represents the mass of CO₂ dissolved.

It is also instructive to compare the species distribution from these two examples using Log C vs. pH diagrams (Figure 5-2; from *_Ex.2,opencarb.Excel*). As you can see, the total concentration of dissolved carbonate is no longer fixed but is determined by the pH-dependent solubility of CO₂.

Since both of these examples involved acid and base additions, it is interesting to examine the effects of CO₂(g) solubility on pH buffering. This can be accomplished by plotting T.H vs. pH for both simulations (Figure 5-3; from *_Ex.2,opencarb.Excel*). Although there is little difference between the two simulations in the acid pH regions, in the alkaline region where CO₂ solubility is highest there is an approximately 3 pH value difference between the two simulations. The dissolution of CO₂ is responsible for a large increase in the buffering capacity of alkaline aqueous solutions.

Example 3 - Aqueous aluminum speciation with hydroxide and sulfate species

The purpose of this example is to introduce the use of fixed concentration components in model simulations. The aluminum speciation reactions that are introduced here will be used in a series of examples intended to demonstrate basic soil chemistry. The remaining examples in this section will incrementally add new types of reactions until a simulation complete with metal complexation, anion adsorption, and cation exchange is developed. During this exercise the user should be focusing on the following goals:

- (i) the use of fixed concentration components in model simulations,
- (ii) the use of chemical equilibrium models in describing metal complexation, and
- (iii) the effect of pH on aluminum speciation.

Description. This example can be constructed by loading the tableau used for the carbonate reactions, Example 1, and adding components and species necessary for simulating inorganic aluminum chemistry. The following reactions will be added in this example:

Reaction	Log K
(i) $\text{Al}^{3+} + \text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + \text{H}^+$	-4.92
(ii) $\text{Al}^{3+} + 2\text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	-9.30
(iii) $\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + 3\text{H}^+$	-15.0
(iv) $\text{Al}^{3+} + 4\text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + 4\text{H}^+$	-23.0
(v) $\text{Al}^{3+} + \text{SO}_4^{2-} = \text{Al}(\text{SO}_4)^+$	3.02
(vi) $\text{Al}^{3+} + 2\text{SO}_4^{2-} = \text{Al}(\text{SO}_4)_2^-$	4.92

In addition, the use of fixed concentration components is introduced in this example. It is sometimes convenient to specify the final equilibrium concentration of a component in a simulation rather than the analytical total. This convenience is especially useful for simulations involving H ion. The concentration of H ion from a chemical analysis of a water sample is usually specified as a pH value. This measured quantity is the negative log of H ion concentration. It is impossible to specify the total concentration of H ion unless a detailed chemical composition is known as well as the pH value. In Examples 1 and 2 the total concentration of H ion was calculated for a simple chemical system whose composition was completely specified. This information is not usually known. Therefore, total H ion is often not a useful quantity to use as an input for model simulations. It is more convenient in these simulations to specify the equilibrium H ion concentration as specified by a measured pH value and let the model calculate the total H ion concentration. For example, to simulate a pH of 4.2, fix the H concentration to 1E-4.2.

Entering Data. By now you should be familiar with organizing lists of reactions in tableau format. The list of reactions for this example are already organized so that all of the reactants are component species. To add these reactions, select a new parameter file by clicking on the input parameter file name currently listed on the **Names(s) of YASE Input Parameter File(s)** screen (Figure 4-3), selecting "New" from the dialog box, typing in a name for this new file and selecting the input file for Example 1 (*Ex.1,closedCarb*) for copying. When you are finished you can check your file against the Example 3 input file (*Ex.3,Al closed*) if you wish. To create the new system, increase the number of component species to 7 and the number of dependent species to 9. Add the information contained in Table 5-7 and 5-8 to the Define Components screen (Figure 4-8) for all the layers.

Table 5-7: Component information for Example 3.

<u>Component</u>	<u>Charge</u>	<u>Species Type</u>
H	+1	AqFixAct
CO ₃	-2	AqMassBal
Na	+1	AqMassBal
Cl	-1	AqMassBal
Al	+3	AqMassBal
SO ₄	-2	AqMassBal
Ca	+2	AqMassBal

Note that although the component Ca is not used in the above reactions it will be useful to include it now for subsequent example problems.

To use equilibrium H ion concentrations, enter the equilibrium value in place of the total concentration on the **Define Component** screen (Figure 4-8), and make sure to change the species type to "AqFixAct." In this example, we will change the pH from one layer to another and let all other component concentrations remain constant in order to see the effects of pH on aluminum speciation. Remember you can use the check boxes at the far right to set all layers to the same concentration.

Table 5-8: Component concentrations for Example 3.

<u>Layer</u>	<u>H</u>	<u>CO₃</u>	<u>Na</u>	<u>Cl</u>	<u>Al</u>	<u>SO₄</u>	<u>Ca</u>
1	1.0000E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
2	6.3096E-5	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
3	3.9811E-5	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
4	2.5119E-5	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
5	1.5849E-5	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
6	1.0000E-6	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
7	6.3096E-6	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
8	3.9811E-6	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
9	2.5119E-6	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5
10	1.5849E-6	1.00E-6	1.00E-3	1.00E-3	4.00E-5	8.00E-5	2.00E-5

Enter the data for the dependent species from Table 5-9 and 5-10. Access the necessary screens by clicking on the "Dependent Species" button on the **YASE Input Parameter Menu** screen (Figure 4-4), which leads to the **Dependent Species** screen

(Figure 4-10). Remember that hydroxyl groups are formed from negative coefficients for hydrogen.

Table 5-9: Stoichiometry for Example 3.

Species	Components						
	H	CO ₃	Na	Cl	Al	SO ₄	Ca
OH	-1	0	0	0	0	0	0
HCO ₃	1	1	0	0	0	0	0
H ₂ CO ₃	2	1	0	0	0	0	0
Al(OH)	-1	0	0	0	1	0	0
Al(OH) ₂	-2	0	0	0	1	0	0
Al(OH) ₃	-3	0	0	0	1	0	0
Al(OH) ₄	-4	0	0	0	1	0	0
Al(SO ₄)	0	0	0	0	1	1	0
Al(SO ₄) ₂	0	0	0	0	1	2	0

Table 5-10: Dependent species information for Example 3.

<u>Dependent Species</u>	<u>Species Type</u>	<u>Log K (same for all layers)</u>
OH	AqMassBal	-14.0
HCO ₃	AqMassBal	10.25
H ₂ CO ₃	AqMassBal	16.55
Al(OH)	AqMassBal	-4.92
Al(OH) ₂	AqMassBal	-9.30
Al(OH) ₃	AqMassBal	-15.0
Al(OH) ₄	AqMassBal	-23.0
Al(SO ₄)	AqMassBal	3.020
Al(SO ₄) ₂	AqMassBal	4.920

Input the data for activity coefficients by clicking on the "Activity Coefficients" button on the **YASE Input Parameter Menu** screen (Figure 4-4), which leads to the **Activity Coefficients** screen (Figure 4-21). Set all activity coefficients to "Davies."

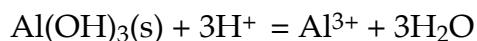
Checking the output. The output from this example can be summarized in a Log of concentration vs. pH diagram and should match Figure 5-4 (from *Ex.3, Al closed.Excel*). The pH values cover the range expected from acid forest soils to surface waters.

Example 4 - Aqueous aluminum speciation in the presence of an aluminum solid phase

The purpose of this example is to introduce solid phase solubility reactions, which are similar to the gaseous phase reactions introduced in Example 2. During this exercise the user should be focusing on the following goals:

- (i) use of solid phase solubility reactions, and
- (ii) understanding the effect of mineral solubility on aqueous aluminum concentrations.

Description. This example involves an addition of a solid phase aluminum hydroxide to Example 3. Solid phase dissolution and precipitation reactions are added in a manner similar to gaseous solubility reactions (Example 2). For this example we will use the solubility reaction:



In contrast with gaseous reactions, the activity of pure solid phases is equal to 1, and so the equilibrium constant is simply the solubility product for this solid phase. We will use Log Ks equal to 8.11 for all layers for this phase.

Entering Data. Create a new file by copying the file from Example 3. (The completed input parameter file is called *Ex.4,Al open*). Change the note on the **YASE Input Parameter Menu** screen (Figure 4-4) to indicate that this file is for Example 4. Increase the number of quickly dissolving phases to 1 on the **System Definition** screen Figure (4-5) and add the name of the phase and its stoichiometry as specified in Table 5-11 for the dissolution of this phase. Remember that the input screens for quickly dissolving phases are found by clicking on the "Quickly Dissolving Phases" button on the **YASE Input Parameter Menu** screen (Figure 4-4).

Table 5-11: Stoichiometry for the phase addition for Example 4.

Phase	Components						
	H	CO ₃	Na	Cl	Al	SO ₄	Ca
Al(OH) ₃ (s)	-3	0	0	0	1	0	0

Set the equilibrium constant for this reaction to 8.11 for all layers.

Checking the output. The same type of log of concentration vs. pH graph that was constructed for Example 3 can be used to compare the effects of an aluminum hydroxide solid phase on the speciation of aluminum. As shown in Figure 5-5, the total concentration of aluminum is now determined by the solubility of this solid phase, instead of being fixed.

Example 5 -Sulfate adsorption

The purpose of this example is to introduce soil surface species by simulating sulfate adsorption with a Langmuir adsorption equation. During this exercise the user should be focusing on the following goals:

- (i) understanding the use of surface species in model simulations, and
- (ii) application of a Langmuir adsorption isotherm in a reaction tableau.

Description. This example introduces soil surface species into chemical simulations. Reactions with surface species can be specified exactly the same way as for aqueous species. The treatment of surface species in the model differs from aqueous species in two ways. First, the amount of the species formed will depend not only on the amount of chemical reactants present, but also on the amount of soil present. Second, any substance bound to the soil will not be affected by hydrologic fluxes (see Example 9 below for an illustration of solution movement and cation retention).

The simulation will be used to examine the effects of sulfate adsorption on stoichiometric additions of Ca and SO₄.

Entering Data. This example can be created by creating a new file by copying the file created for Example 4 and adding a reaction for the adsorption of sulfate. (The completed input parameter file is called *Ex.5,sulfate ads.*)

Reaction	Log K
$>\text{MOH} + \text{SO}_4 = >\text{MOH}(\text{SO}_4)$	4.25

>M is used to describe a site of anion adsorption on the soil surface.

This problem will require defining an additional component (>MOH) and an additional species (>MOH(SO₄)). Both of these species must be added as SpMassBal species with no activity correction method specified.

To begin, on the **System Definition** screen (Figure 4-5) increase the number of components to 8 and the number of dependent species to 10. Next enter the data in Table 5-12 on the **Components** screen (Figure 4-8).

Table 5-12: Component information for Example 5.

Component Name	Charge	Species Type
H	+1	AqFixAct
CO ₃	-2	AqMassBal
Na	+1	AqMassBal
Cl	-1	AqMassBal
Al	+3	AqMassBal
SO ₄	-2	AqMassBal
Ca	+2	AqMassBal
>MOH	0	SpMassBal

Next, the total concentration of Ca and SO₄ can be incremented from one layer to the next to simulate a series of CaSO₄ additions as indicated in Table 5-13. The concentration for >MOH is constant over all the layers.

Table 5-13: Component concentrations for Example 5.

Lyr	H	CO ₃	Na	Cl	Al	SO ₄	Ca	>MOH
1	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	1.00E-10	1.00E-10	3.50E-3
2	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	6.00E-5	6.00E-5	3.50E-3
3	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	1.20E-4	1.20E-4	3.50E-3
4	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	1.80E-4	1.80E-4	3.50E-3
5	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	2.40E-4	2.40E-4	3.50E-3
6	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	3.00E-4	3.00E-4	3.50E-3
7	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	3.60E-4	3.60E-4	3.50E-3
8	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	4.20E-4	4.20E-4	3.50E-3
9	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	4.80E-4	4.80E-4	3.50E-3
10	1.00E-4	1.00E-6	1.00E-3	1.00E-3	4.00E-5	5.40E-4	5.40E-4	3.50E-3

Input the name and stoichiometry for the new dependent species as indicated in Table 5-14. The equilibrium constant is 4.25 for all layers. The species type is SPMassBal.

Table 5-14: Stoichiometry for dependent species for Example 5.

Dependent Species	H	CO ₃	Na	Cl	Al	SO ₄	Ca	>MOH
>MOH(SO ₄)	0	0	0	0	0	1	0	1

The activity coefficient for both the component >MOH and the dependent species >MOH(SO₄) is 'None'.

Checking the output. An adsorption isotherm is a convenient way to look at the response of adsorbed species to changing concentrations. A sulfate adsorption isotherm can be constructed by plotting the adsorbed sulfate species (>MOH(SO₄)) vs. the solution sulfate as shown in Figure 5-6.

Example 6 - Cation exchange

The purpose of this example is to introduce cation exchange reactions and show how they can be simulated using Kerr, Vanselow, or Gaines-Thomas type exchange reactions. During this exercise the user should be focusing on the following goals:

- (i) including cation exchange reactions in model simulations
- (ii) understanding the differences between theories of exchange and ion activity correction
- (iii) implementing multiple unattended runs

Description. This example is constructed from Example 5. The incremental additions of Ca and SO₄ used to examine sulfate adsorption can also be used to look at calcium exchange with sodium and aluminum. These relationships can be included with the addition of two new reactions.

Reaction	Log K
$2/3 X_3Al + Ca = X_2Ca + 2/3 Al$	0.00
$1/3 X_3Al + Na = XNa + 1/3 Al$	0.00

X is used to describe a site of cation exchange on the soil surface. The equilibrium constants describe ideal non-preference isotherms (Log K = 0). Empirical Log K's for soils can be calculated from measured concentrations of dissolved and exchangeable cations in equilibrium.

The model supports three different formulations for cation exchange. Each of these exchange theories results from a different assumption about the activity of ions on soil surfaces. The Kerr formulation assumes that species concentrations are good approximations for activity. The Vanselow exchange formulation (also known as Gapon) uses mole fractions of exchangeable ions as an approximation for ion activities, and the Gaines-Thomas formulation uses charge fraction. The mole fraction and charge fraction of the exchangeable species in the above reactions are calculated as:

Species	Mole Fraction (Vanselow)	Charge Fraction (Gaines-Thomas)
X ₃ Al	$[X_3Al]/([X_3Al] + [X_2Ca] + [XNa])$	$3 [X_3Al]/(3 [X_3Al] + 2 [X_2Ca] + [XNa])$
X ₂ Ca	$[X_2Ca]/([X_3Al] + [X_2Ca] + [XNa])$	$2 [X_2Ca]/(3 [X_3Al] + 2 [X_2Ca] + [XNa])$
XNa	$[XNa]/([X_3Al] + [X_2Ca] + [XNa])$	$[XNa]/(3 [X_3Al] + 2 [X_2Ca] + [XNa])$

Entering Data. Create a new file for the Kerr formulation by copying the input file for Example 5 (*Ex.5,sulfate ads*). (The complete input parameter file is called *Ex.6,Kerr*.) Change the note for this input file to indicate that this is Example 6, cation exchange, Kerr formulation. Increase the number of components to 9 and the number of dependent species to 12 and decrease the number of phases to zero. Input the component information specified in Table 5-15. Note that the new component X₃Al represents an exchangeable cation and must be defined with an SpMassBal species type. The analytical total for this new component is 3.00e-2 mol for all layers.

Table 5-15: Component information for Example 6.

Component Name	Charge	Species Type
H	+1	AqFixAct
CO ₃	-2	AqMassBal
Na	+1	AqMassBal
Cl	-1	AqMassBal
Al	+3	AqMassBal
SO ₄	-2	AqMassBal
Ca	+2	AqMassBal
>MOH	0	SpMassBal
X ₃ Al	+3	SpMassBal

Enter the stoichiometry for the new species as listed in Table 5-16.

Table 5-16: Stoichiometry for dependent species for Example 6.

Dependent Species	H	CO ₃	Na	Cl	Al	SO ₄	Ca	>MOH	X ₃ Al
X ₂ Ca	0	0	0	0	-0.6667	0	1	0	0.6667
XNa	0	0	1	0	-0.3333	0	0	0	0.3333

Both dependent species represent exchangeable cations and must be defined with a species type of SpMassBal. The equilibrium constant for both dependent species is zero for all layers.

For the Kerr formulation, the species X₃Al, X₂Ca, and XNa will have no activity correction method specified. For the Vanselow formulation, create a new input file by

copying the Kerr formulation input file and change the activity correction method to "Vanse." (The completed input parameter file is called *Ex.6,Vanselow.*) For the Gaines-Thomas formulation create a new input file by copying either the Kerr formulation input file or the Vanselow input file and change the activity correction method to the "Gain-Thom" method. (The completed input parameter file is called *Ex.6,Gaines-Thomas.*)

As an example of how to run multiple files, go the **Name(s) of YASE Input Parameter File(s)** screen (Figure 4-3). Click on the "Multiple, unattended runs" button and choose 3 runs. Most likely the Gaines-Thomas input file is the first file in the list, select the other two files you just created (Vanselow and Kerr) for the other two input files. The order of the files is unimportant. Click on the "Main Menu" button, then click on the "Start a YASE Model Run" button to run the three simulations in succession.

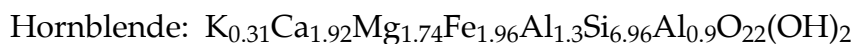
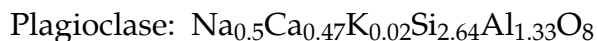
Checking the output. The output from each of these formulations results in different predictions for the distributions of cations on the exchange. Compare the concentration of soluble Ca, Al, and Na concentrations predicted by each of these formulations in Figures 5-7, 5-8, and 5-9 .

Example 7 - Weathering

The purpose of this example is to introduce the weathering routine in YASE. We will simulate the dissolution of two minerals, a feldspar and a hornblende. During this exercise the user should be focusing on the following goals:

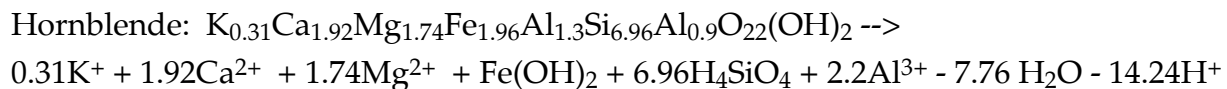
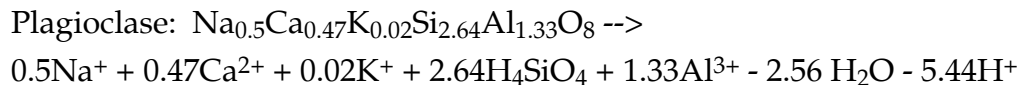
- (i) include weathering in a model simulation, and
- (ii) run the model for multiple time steps and examine output over time.

Description. Minerals are defined in YASE by a stoichiometry and a formula weight. We will be defining two minerals, a feldspar (plagioclase) and a hornblende, taken from an acid forest soil in the Adirondacks (April and Newton, 1992). The mineral compositions are as follows:



The formula weights (268.5 g and 881.7 g) are calculated by summing the weights of the elements in the formula (atomic weight of each element times the number of atoms in the formula).

The weathering reactions are written to produce the components used to define the soil system. A different selection of components would require conversion of the weathering reaction to the new components. For example, if OH⁻ were a component instead of H⁺, these weathering reactions would produce OH⁻ (and consume additional H₂O) instead of consuming H⁺.



The weathering rates can be made a function of the amount of mineral present and/or the acidity of the soil solution (see Section 2, Model Description). Weathering rates in soil are difficult to estimate: weathering rates in laboratory experiments can be orders of magnitude higher than those estimated in the field. For this example, we use weathering rates calculated by geochemical mass balance for a forested watershed in New Hampshire (Hyman 1993).

Entering Data. Create a new input parameter file by copying the parameter file from Example 6, Kerr Formulation (*Ex.6,Kerr*). (The completed input parameter file is called *Ex.7,Weathering*.) Change the note on the **YASE Input Parameter Menu** screen (Figure 4-4). On the **Define System** screen (Figure 4-5) decrease the number of components from 9 to 7. Because the last two components put into the system were the components that were added for the exchange and adsorption examples, this essentially erases them from the system. This works only because they were the last two components in the list of components. Change the number of dependent species from 12 to 9. This will remove the exchange and adsorption species added in the previous examples. Change the number of soil layers to 1.

On the **General Parameters** screen (Figure 4-6) change the time step to 31536000 seconds (one year) and the number of time steps to 101 (years). The first run will set up the soil system; the number of years that the model will actually run will be 100.

On the **Define Components** screen (Figure 4-8) overwrite Cl and Na with the information for K and Mg as specified in Table 5-17. Change the species type for H to AqMassBal and the analytical total to 1.00E-7 (mol). The initial amount of these components was set by soil solution concentrations measured in an experiment using red spruce saplings and soil collected from a forest in Maine (Sherman and Fahey 1990). The analytical totals are in units of mol, which have the same value as concentrations in units of mol/L, as the amount of solution present is 1 L (refer to **General Parameters** screen (Figure 4-6)).

Table 5-17: Additional component information for Example 7.

Component Name	Charge	Species Type	Analytical Total (mol)
K	+1	AqMassBal	1.13E-4
Mg	+2	AqMassBal	2.65E-4

On the **Dependent Species Stoichiometry** screen (Figure 4-11) make sure all positions in the matrix for K and Mg are zero for all dependent species.

Begin the definition for the two new minerals by clicking on the "Minerals" button on the **YASE Parameter Input Menu** screen (Figure 4-4). This will lead to the **Minerals** screen (Figure 4-14). Click on the "Mineral Stoichiometry" button to lead to Figure 4-15 where the names and stoichiometry for the minerals can be input according to Table 5-18. Notice that silica is present in both of these minerals but is not important to include as a component if we assume that dissociation of silicic acid (H_4SiO_4) can be ignored. Likewise, Fe can be omitted if we assume that it remains in the form $Fe(OH)_2$. Na is also omitted as a component. Although these components are not included in the tableau, the formula weight includes them because it is used to update the amount of the minerals present as weathering proceeds.

Table 5-18: Mineral stoichiometry for Example 7.

Mineral	H	Components					
		CO ₃	K	Mg	Al SO ₄	Ca	
Plagioclase	-5.44	0	0.02	0	1.33	0	0.47
Hornblende	-14.24	0	0.31	1.74	2.20	0	1.92

Return to the **Minerals** screen (Figure 4-14) and click on the "Mineral Fraction, per layer" button to get to the **Minerals Fraction Layer 1** screen (Figure 4-16). Set the mineral fractions (g/g soil) to the values indicated in Table 5-19. We only need one value for each mineral fraction because there is only one soil layer in the simulation. The initial amount of each mineral (called the Mineral Fraction) for this example is from the site in the Adirondacks (April and Newton, 1992); the amount of plagioclase feldspar is 34% by weight. Heavy minerals are 21% by weight at this site, of which 67% are reactive; hornblende is used to represent the reactive heavy mineral fraction (14%).

Return to the **Minerals** screen (Figure 4-14) and click on the "Molec. Wt., Weathering Rate, HOrder & MOrder" button to get to the **Minerals Miscellaneous** screen (Figure 4-17). Set the minerals' formula weight and weathering constants as defined in Table 5-19. Set the weathering rate to be independent of the amount of mineral present and the acidity of the soil solution (MOrder and HOrder are zero). The weathering rates are therefore in units of grams of mineral weathered per gram of soil per second. (The units for the weathering rates depend on the values of MOrder and HOrder (Figure 4-17). The rates in this example were converted from 153 mol/ha/yr for plagioclase and 2.31 mol/ha/yr for hornblende (Hyman 1993). The rates could be made higher to account for the higher fraction of these minerals at the Adirondack site.

Table 5-19: Mineral definitions for Example 7.

Mineral	Formula	Wt.	Weath. Rate	M Order	H Order	Mineral Fraction
Plagioclase	268.5	4.2E-13	0	0	0.34	
Hornblende		881.7	2.0E-14	0	0	0.14

Save the changes and run the model. The model will update the screen every 50 time steps to let you know that the model is still running. Depending on the speed of your machine you may have to wait a minute or so between updates, please be patient.

Checking the output. This is the first example in which we have followed the behavior of a system over time. The output file (*Ex.7,Weathering.Out*) has multiple lines, one for each time step. An excerpt of this file is shown in Table 5-20.

Table 5-20a: An excerpt of the weathering output file for Example 7.

THE SPECIES CONCENTRATIONS (C.) (mol/L), THE KTs (T.) (mol) AND THE PHASE MASS (M.) (mol)						
LAYER	C.H	C.CO3	C.K	C.Mg	C.Al	C.SO4

1	2.90E-05	3.94E-14	1.13E-04	2.65E-04	2.10E-05	9.85E-11
1	1.14E-06	1.75E-11	1.14E-04	2.66E-04	1.18E-07	1.00E-10
1	3.83E-08	1.54E-09	1.15E-04	2.67E-04	9.01E-12	1.00E-10
1	1.23E-08	5.05E-09	1.17E-04	2.69E-04	2.88E-13	1.00E-10
1	6.86E-09	9.15E-09	1.18E-04	2.70E-04	4.75E-14	1.00E-10

Table 5-20b: An excerpt of the weathering output file for Example 7 continued.

THE SPECIES CONCENTRATIONS (C.) (mol/L), THE KTs (T.) (mol) AND THE PHASE MASS (M.) (mol)						
LAYER	C.Ca	C.OH	C.HCO3	C.H2CO3	C.Al(OH)	C.Al(OH)2
1	1.00E-10	3.66E-10	1.80E-08	9.82E-07	7.74E-06	1.05E-05
1	2.46E-05	9.28E-09	3.17E-07	6.83E-07	1.11E-06	3.83E-05
1	4.91E-05	2.77E-07	9.31E-07	6.70E-08	2.51E-09	2.58E-06
1	7.37E-05	8.68E-07	9.73E-07	2.24E-08	2.49E-10	7.93E-07
1	9.82E-05	1.56E-06	9.78E-07	1.25E-08	7.30E-11	4.15E-07

Table 5-20c: An excerpt of the weathering output file for Example 7 continued.

THE SPECIES CONCENTRATIONS (C.) (mol/L), THE KTs (T.) (mol) AND THE PHASE MASS (M.) (mol)						
LAYER	C.Al(OH)3	C.Al(OH)4	C.Al(SO4)	C.Al(SO4)2	T.H	T.CO3
1	7.21E-07	2.64E-10	1.52E-12	1.05E-20	1.00E-07	1.00E-06
1	6.70E-05	6.22E-07	8.79E-15	6.22E-23	-2.78E-04	1.00E-06
1	1.34E-04	3.73E-05	6.60E-19	4.66E-27	-5.57E-04	1.00E-06
1	1.29E-04	1.12E-04	2.07E-20	1.45E-28	-8.36E-04	1.00E-06
1	1.21E-04	1.88E-04	3.34E-21	2.33E-29	-1.11E-03	1.00E-06

Table 5-20d: An excerpt of the weathering output file for Example 7 continued.

THE SPECIES CONCENTRATIONS (C.) (mol/L), THE KTs (T.) (mol) AND THE PHASE MASS (M.) (mol)						
LAYER	T.K	T.Mg	T.Al	T.SO4	T.Ca	
1	1.13E-04	2.65E-04	4.00E-05	1.00E-10	1.00E-10	
1	1.14E-04	2.66E-04	1.07E-04	1.00E-10	2.46E-05	
1	1.15E-04	2.67E-04	1.74E-04	1.00E-10	4.91E-05	
1	1.17E-04	2.69E-04	2.42E-04	1.00E-10	7.37E-05	
1	1.18E-04	2.70E-04	3.09E-04	1.00E-10	9.82E-05	

The elements that are weathered should all increase over time. This is demonstrated in Figure 5-10.

The amount of an element released by weathering can be checked against the user-defined stoichiometry and the weathering rate. For example, you can calculate the amount of calcium produced during the 100-year simulation by calculating the amount of calcium released from plagioclase and hornblende.

The soil volume is 1000 cm³ and the bulk density is 1 g/cm³, so the mass of soil is 1 kg. The weathering rate of plagioclase is 4.2E-13 of the soil mass/sec. This rate is

unaffected by the hydrogen ion concentration and the amount of mineral present (because HOrder and MOrder are zero), so the mass weathered is 1.32 g over 100 years. The formula weight for plagioclase is 268.5 g so the number of moles weathered over 100 years is $4.93\text{E-}3$ mol. The stoichiometry gave 0.47 moles of calcium per mole of plagioclase or $2.32\text{E-}3$ moles of calcium weathered from plagioclase.

The weathering rate of hornblende is $2.0\text{E-}14$ of the soil mass/sec, so the mass weathered is $6.43\text{E-}2$ g over 100 years. The formula weight for hornblende is 881.7 g so the number of moles weathered over 100 years is $7.30\text{E-}5$ mol. The formula gave 1.92 moles of calcium per mole of hornblende or $1.40\text{E-}4$ moles of calcium weathered from hornblende.

The total amount of calcium weathered is $2.46\text{E-}3$ moles, the sum of the $2.32\text{E-}3$ moles from plagioclase and the $1.40\text{E-}4$ moles from hornblende. The system is closed, and the total dissolved calcium (T.Ca) present at the beginning of the simulation was nearly zero ($1.00\text{E-}10$), so the T.Ca at the end of the system shows the $2.46\text{E-}3$ moles weathered.

As an additional exercise you can create a new file and set MOrder for each mineral to one, thereby making the amount weathered dependent on the amount of mineral present. The rate constants could be adjusted to give the same amount of weathering in 100 years. If you do not change the value of the weathering rates, you will find the contribution of plagioclase reduced to 34% of that in the original example, which is its fraction of the soil weight. Hornblende is 14% by weight; its contribution will be reduced accordingly, to simulate total Ca weathering of $8.07\text{E-}3$ moles. The amount weathered in 100 years is so small (0.45 g of plagioclase and 0.009 g of hornblende) that the rates do not decline significantly over the course of the simulation.

Example 8 - Decomposition

The purpose of this example is to introduce the decomposition routines in YASE. During this exercise the user should be focusing on the following goals:

- (i) include decomposition processes in model simulations,
- (ii) compare nitrogen mineralization and immobilization at two different soil temperatures.

Description. Decomposition in YASE is simulated differently for different nutrient elements. For N, we will use initial conditions and the rate constants from the original

data with which the decomposition algorithm was developed (Ryan, unpublished manuscript). Initial amounts of mineralizable nutrients other than N came from the ROPIS experiment (Sherman and Fahey 1994); Mg and S were estimated from Ca and P, respectively, using ratios from Hubbard Brook forest floor (Gosz et al. 1976). The contents of the Oa horizon in the ROPIS pots were converted to 1 kg of soil using the thickness and bulk density reported by Sherman and Fahey.

The decomposition routine is compatible with TREGRO; if run with TREGRO, senescing roots and leaves would add to the decomposable nutrient pools. These fluxes can be simulated by YASE when YASE is running alone. If running with these simulated fluxes or with TREGRO, decomposition must be parameterized with the six nutrients included in TREGRO as the first components and hydrogen as the seventh component.

Entering Data. Create a new input parameter file by copying the parameter file from Example 7, Weathering (*Ex.7, Weathering*). (The completed input parameter file is called *Ex.8, Decomp.*). Change the note on the **YASE Input Parameter Menu** screen (Figure 4-4). On the **Define System** screen (Figure 4-5), increase the number of layers to 2. Increase the number of components to 9. Change the number of minerals to 0. Turn on decomposition by clicking the "No" button following the query as to whether decomposition is to be used; the button will change to "Yes".

On the **General Parameters** screen (Figure 4-6) change the time step to 86400 seconds (one day) and the number of time steps to 730 (2 years). Soil layer two has the same information as soil layer one except for soil temperature. Change the soil temperature for soil layer one to 10C and soil layer two to 20C. The soil layers are not connected in any way; as in Examples 1 through 4, defining multiple layers is a shortcut to running multiple simulations. For this example, the only difference between the layers will be the temperature.

On the **Define Components** screen (Figure 4-8), enter information for all components in the order presented in Table 5-21. For a proper connection with TREGRO, the first six components must be Ca, Mg, P, N, K and S, in any order; the seventh component must be H. The component names PO₄, NO₃, and SO₄ are recognized as P, N, and S. It is also possible to simulate a tree with different elements as nutrients, but they must be the first six components. The analytical totals are in units of mol, which have the same value as concentrations in units of mol/L, as the amount of solution present is 1 L (refer to **General Parameters** screen (Figure 4-6)). Distribute the

data over both layers by clicking in the check box to the right of the input for analytical totals for all components.

Table 5-21: Component information for layers 1 and 2 for Example 8.

Component Name	Charge	Species Type	Analytical Total (mol)
Ca	+2	AqMassBal	3.408E-3
Mg	+2	AqMassBal	6.607E-4
PO ₄	-3	AqMassBal	6.452E-5
NO ₃	-3	AqMassBal	2.043E-3
K	+1	AqMassBal	2.897E-4
SO ₄	-2	AqMassBal	1.063E-4
H	+1	AqMassBal	1.000E-7
CO ₃	-2	AqMassBal	1.000E-6
Al	+3	AqMassBal	5.800E-5

On the **Dependent Species Stoichiometry** screen (Figure 4-11) enter the stoichiometric matrix shown in Table 5-22. A user interested in the speciation of phosphate could add dependent species for HPO₄²⁻, H₂PO₄⁻ and H₃PO₄.

Table 5-22: Stoichiometry for dependent species for Example 8.

<u>Dependent Species</u>	<u>Ca</u>	<u>Mg</u>	<u>P</u>	<u>NO₃</u>	<u>K</u>	<u>SO₄</u>	<u>H</u>	<u>CO₃</u>	<u>Al</u>
OH	0	0	0	0	0	0	-1	0	0
HCO ₃	0	0	0	0	0	0	1	1	0
H ₂ CO ₃	0	0	0	0	0	0	2	1	0
Al(OH)	0	0	0	0	0	0	-1	0	1
Al(OH) ₂	0	0	0	0	0	0	-2	0	1
Al(OH) ₃	0	0	0	0	0	0	-3	0	1
Al(OH) ₄	0	0	0	0	0	0	-4	0	1
Al(SO ₄)	0	0	0	0	0	1	0	0	1
Al(SO ₄) ₂	0	0	0	0	0	2	0	0	1

On the **Dependent Species Species Type** screen (Figure 4-12) ensure that all species types are aqueous mass balance (Figure 4-12).

On the **Equilibrium Constants for Dependent Species, Layer 1** screen (Figure 4-13) ensure that the equilibrium constants for dependent species are the same for all layers.

On the **Activity Coefficients** screen (Figure 4-21) set the activity coefficients for all components and dependent species to Davies.

On the **Decomposition** screen (Figure 4-22) there are two buttons, one to set parameters for nitrogen mineralization and the other for mineralization of other nutrients. Clicking the "Nitrogen Mineralization" button on the **Decomposition** screen (Figure 4-22) leads to the **Nitrogen Mineralization** screen (Figure 4-23). There are six buttons on this screen.

The first button, "Initial Amounts, per Layer" leads to the **Initial Amounts of Cellulose, Extractives, Lignin and Humus, Per Layer** screen (Figure 4-24). The initial amounts of these items is shown in Table 5-23. Both layers have the same initial amounts.

Table 5-23: Initial amounts of cellulose, extractives, lignin and humus in layer 1 and 2 for Example 8.

Cellulose (gC)	Extractives (gC)	Lignin (gC)	Humus (gC)
6.1	2.6	17.4	60.9

The second button, "C:N Ratios" leads to the **C:N Ratios** screen (Figure 4-25). Choose the default values for each ratio by clicking on the respective buttons, which will write the value into the field. You may have to click on the "Show default values" button in the lower left corner to make the default value buttons visible.

The third button, "Transformation Rates and Efficiencies" leads to the **Transformation Rates and Efficiencies** screen (Figure 4-26). Choose the default values for each input by clicking on the respective buttons. The rates are in units of day⁻¹, which is consistent with the one day time step of this example. To convert the default rates to another time step, use the following relationship, where a and b represent different time steps, in units of days, and R_a and R_b represent the rates at these time steps.

$$(1 - R_a)^{b/a} = 1 - R_b \quad (\text{eq. 26})$$

The fourth button, "Leaf Fractionation" leads to the **Leaf Fractionation** screen (Figure 4-27). Use the default values.

The fifth button, "Root Fractionation, per layer" leads to the **Root Fractionation Per Layer** screen (Figure 4-28). Use the default values for both layers.

The sixth button, "Soil Moisture Parameters" leads to the **Soil Moisture Parameters** screen (Figure 4-29). Use the default values.

The seventh and final button is "Miscellaneous Parameters" and leads to the **Miscellaneous Parameters** screen (Figure 4-30). Use the default values.

The mineralization of nutrients other than nitrogen is parameterized by selecting the button "Mineralization of Other Nutrients" (Figure 4-22) which leads to the **Mineralization of Other Nutrients** screen (Figure 4-35). Click the "Initial Amounts, per layer" to get to the **Initial Amounts of Calcium, Magnesium, Potassium, Phosphorus, Sulfur** screen (Figure 4-36). Input the initial amounts of nutrient elements as shown in Table 5-24. Both layers have the same initial amounts of nutrient elements.

Table 5-24: Initial amounts of calcium, magnesium, potassium, phosphorus and sulfur for layers 1 and 2 for Example 8.

Calcium (g Ca)	Magnesium (g Mg)	Potassium (g K)	Phosphorus (g P)	Sulfur (g S)
1.893	0.224	0.157	0.028	0.053

Selecting the "Mineralization Rates" button on the **Mineralization of Other Nutrients** screen (Figure 4-35) leads to the **Mineralization Rates** screen (Figure 4-37). Input the mineralization rates for calcium, magnesium and potassium as shown in Table 5-25. These rates were calculated from the annual rates of nutrient turnover in a northern hardwood forest floor (Gosz et al. 1976) using eq. 26.

Table 5-25: Mineralization rates for calcium, magnesium and potassium for Example 8.

Calcium (gCa/(gCa day))	Magnesium (gMg/(gMg day))	Potassium (gK/(gK day))
6.456E-4	8.246E-3	1.897E-3

Ensure that the concentration of all components in the rainfall is zero on the **Rainfall Concentration of Components** screen (Figure 4-38).

Ensure that all water and nutrient fluxes are zero by checking all the screens accessible from the **Water Fluxes** screen (Figure 4-40).

Save the changes and run the model. The model will update the screen every 50 days to let you know that the model is still running. Depending on the speed of your machine you may have to wait a minute or so between updates; please be patient.

Checking the output. The output file for this example contains information about multiple soil layers over multiple time steps. To graph this information, you may need to sort the output lines by soil layer. Add a variable for the time elapsed.

Decomposition releases mineralized N to the soil solution (Figure 5-11). The rate of N mineralization is higher at 20C than at 10C. This example does not allow leaching (movement of solution between soil layers is covered in the next example) or plant uptake, so all of the N mineralized remains in the system. Mineralization of P and S (not shown) are proportional to the mineralization of N and the amount of organic P

and S. Mineralization of cations is simulated by first-order decay; the appearance of mineralized Mg and K in soil solution is shown in Figure 5-12.

When decomposition is run, an additional output file is generated, called in this case *Ex.8,Decomp.DEC*. This file contains information about the amounts of C and N in the various fractions and the respiration and mineralization in each time step. In this example, without addition of organic matter, the greatest loss occurs from the lignin pool (Figure 5-13).

Example 9 - Solution flow

The purpose of this example is to introduce the routines that allow solution flow between soil layers in YASE. During this exercise the user should be focusing on the following goals:

- (i) parameterize the model for solution fluxes,
- (ii) simulate solution flux between layers with consequences for solution chemistry, and
- (iii) understand the output from multiple layers over time.

Description. This example uses a more realistic description of a soil column than the previous examples. The three horizons correspond to the Oa, Bs, and bulk B horizons of a Maine forest soil used in an experimental acidification of red spruce mesocosms. The initial conditions of the soil solution and exchangeable cations are those reported by Sherman and Fahey (1990), except that the volumes of the soil horizons and solutions are all set to 1 liter to simplify verification. The equilibrium constants or selectivity coefficients for cation exchange for each of the three soil layers are calculated from the dissolved and exchangeable cation concentrations. The solution added to the top of the soil column is an acid solution of pH 5, with sulfuric acid and nitric acid making equal contributions. There are no other components in the simulated rain.

The simulation demonstrates the movement of sulfate, nitrate, and H ion through the soil layers. It does not demonstrate acidification of the exchange complex because exchangeable H was not defined as a species (it could be added as X.H) and there is no source of additional exchangeable Al (gibbsite could be added as a solid phase). Extensions of this example to more realistic soil simulations are left as an exercise for the reader.

Entering Data. Create a new input parameter file by copying the parameter file from Example 8, Decomposition (*Ex8,Decomp*). (The completed input parameter file is called *Ex.9,Flow_pH5*). Change the note on the **YASE Input Parameter Menu** screen (Figure 4-4). On the **Define System** screen (Figure 4-5) increase the number of layers to 3, increase the number of components to 11 and increase the number of dependent species to 14. Turn off decomposition by clicking the "Yes" button following the query as to whether decomposition is to be used; the button will change to "No."

On the **General Parameters** screen (Figure 4-6) verify that the time step is 86400 seconds (one day) and change the number of time steps to 365 (1 year). For all layers, set the soil area to 0.01 m², the soil thickness to 0.1 m, and the soil moisture to 1 m³/m³. The soil temperatures are not used because decomposition is not turned on. You can use the buttons at the bottom of the screen to set a property for all layers at once. The bulk density for layer 1 is 0.4493 g/cm³ and the bulk density for layers 2 and 3 is 0.903 g/cm³.

On the **Define Components** screen (Figure 4-8), alter parameter values as necessary for the components presented in Table 5-26. The exchange sites are defined by the component X.Ca, which has a species type of SPMassBal (solid phase mass balance). The analytical totals for this component correspond to the cation exchange capacity of each layer. Because the amount of Ca in the system is less than the amount used to define the cation exchange sites, the analytical total of the component Ca is negative. The analytical totals for NO₄, SO₄ and CO₃ are the same for all layers because they are not based on measurements from this experimental system.

Table 5-26: Component information for layers 1, 2 and 3 for Example 9.

Component		Species Type	Analytical Totals (mol)		
Name	Charge		Lyr 1	Lyr 2	Lyr 3
Ca	+2	AqMassBal	-0.00906	-0.01385	-0.01031
Mg	+2	AqMassBal	0.005219	0.000593	0.001017
Mn	+4	AqMassBal	0.001542	0.000107	0.000134
NO ₃	-1	AqMassBal	7.00E-06	7.00E-06	7.00E-06
K	+1	AqMassBal	0.001895	0.000537	0.001251
SO ₄	-2	AqMassBal	8.00E-05	8.00E-05	8.00E-05
H	+1	AqMassBal	-9.81E-05	-3.93E-05	-3.93E-05
CO ₃	-2	AqMassBal	1.00E-06	1.00E-06	1.00E-06
Al	+3	AqMassBal	2.65E-04	0.008875	0.005985
X.Ca	0	SPMassBal	0.031	0.0166	0.016
Fe	+3	AqMassBal	6.23E-05	0.000188	0.000161

On the **Dependent Species Stoichiometry** screen (Figure 4-11) input the data as indicated in Table 5-27. The calculation of equilibrium constants for cation exchange must conform to the stoichiometry of the exchange reactions in this tableau. (See Equations under Model Description.)

Table 5-27: Stoichiometry for dependent species for Example 9.

Dependent Species	Ca	Mg	Mn	NO ₃	K	SO ₄	H	CO ₃	Al	X.Ca	Fe
OH	0	0	0	0	0	0	-1	0	0	0	0
HCO ₃	0	0	0	0	0	0	1	1	0	0	0
H ₂ CO ₃	0	0	0	0	0	0	2	1	0	0	0
Al(OH)	0	0	0	0	0	0	-1	0	1	0	0
Al(OH) ₂	0	0	0	0	0	0	-2	0	1	0	0
Al(OH) ₃	0	0	0	0	0	0	-3	0	1	0	0
Al(OH) ₄	0	0	0	0	0	0	-4	0	1	0	0
Al(SO ₄)	0	0	0	0	0	1	0	0	1	0	0
Al(SO ₄) ₂	0	0	0	0	0	2	0	0	1	0	0
X.Al	-1.5	0	0	0	0	0	0	0	1	1.5	0
X.Mg	-1	1	0	0	0	0	0	0	0	1	0
X.Mn	-2	0	1	0	0	0	0	0	0	2	0
X.Fe	-1.5	0	0	0	0	0	0	0	0	1.5	1
X.K	-0.5	0	0	0	1	0	0	0	0	.5	0

On the **Species Types for Dependent Species** screen (Figure 4-12) set the species type for the five new exchangeable dependent species to SPMassBal. All other species are AqMassBal.

On the **Equilibrium Constants for Dependent Species, Layer 1** screen (Figure 4-13), add the equilibrium constants for the five new exchangeable dependent species as specified in Table 5-28. The equilibrium constants are different for each layer for these new species but the same for each layer for the other 9 species.

Table 5-28: Equilibrium constants for additional dependent species for Example 9.

Dependent Species	Equilibrium Constants		
	Lyr 1	Lyr 2	Lyr 3
X.Al	-0.62349	2.798352	2.091713
X.Mg	-0.206525	-0.27377	-0.3426
X.Mn	-1.50576	-0.83457	-1.4339
X.Fe	-2.22779	-1.46628	-2.24427
X.K	0.500495	0.389072	0.617175

On the **Activity Coefficients** screen (Figure 4-21), set the activity coefficients for the exchangeable components and dependent species to None. All other components and dependent species are set to Davies.

On the **Water Fluxes** screen (Figure 4-40) set all fluxes to $3E-05$ L/(m^2 s) for a steady state flow of 0.02592 L/day, or 94.6 cm/year. Note that when YASE is run with TREGRO, the solution flow between the layers is controlled by TREGRO.

Ensure that all inputs are zero on the **Nutrient Uptake, Per Layer, For All Nutrients** screen (Figure 4-41).

Leaf and root senescence are not included in this example because decomposition is not turned on. Remember to look at these inputs if you turn decomposition on and remember that the first six components are considered the nutrients.

The chemical composition of the incoming solution is entered in the **Rainfall Concentration of Components** screen (Figure 4-38). To apply a solution of pH 5, set the concentration of H to $1E-5$ mol/L. To balance the charge with sulfate and nitrate, set the concentration of SO_4 to $2.5E-6$ mol/L and NO_3 to $5.0E-6$ mol/L.

Save the changes and run the model. The progress of the model is indicated by a message to the screen every 50 time steps. Depending on the speed of your machine you may have to wait a minute or so between updates; please be patient.

Checking the output. The movement of nitrate in soil solution between the soil layers can be seen by graphing concentration versus time (Figure 5-14). The initial concentration was the same in all layers. The incoming solution was less concentrated; the top layer is the first to decline in concentration and the succeeding layers are slower to equilibrate with the incoming solution.

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7 Flowcharts

Table 2-1. Variables used in describing the equilibrium submodel, CHESS.

A	coefficient used in Davies equation
$a_{i,j}$	stoichiometric coefficient of component j in formation reaction of species i
$c_{p,j}$	stoichiometric coefficient of component j in dissolution reaction of phase p
λ_i	activity coefficient for species i
i	array index used with species lists
I	ionic strength
j	array index used with component lists
K_i	equilibrium constant for the formation reaction for species i
cK_i	conditional equilibrium constant after applying activity corrections
K_{s_p}	solubility constant for phase p
M_p	Mass of phase p that dissolves or precipitates at equilibrium (moles)
N_c	Number of components
N_s	Number of species
p	array index used with phase lists
q	array index used to indicate a component selected by a phase
Q_i	concentration to mass conversion for species i (liters)
R_j	Residual for component j (moles)
S_i	Concentration of species i (moles/liter)
T_j	Total concentration of component j (moles)
W_j	Iterative adjustment to the free concentration of component j (moles/liter)
X_j	Free concentration of component j (moles/liter)
z_i	valence of species i
$Z_{j,k}$	Element of the Jacobian matrix for the partial derivative of residual j with respect to component k