

2 Interpretative Modelling Methods and Tools

*Adrian Bath, Jordi Delgado Martín, Luis Lomba Falcón, David Noy,
Fernando Recreo Jiménez*

2.1 GEOCHEMICAL EQUILIBRIUM MODELLING: PHREEQC

The widely-used PHREEQC program from the US Geological Survey is based on an ion-association aqueous model and on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. It performs a wide variety of low-temperature aqueous geochemical calculations. Its main capabilities of relevance for present applications are (i) mixing of waters with speciation and saturation-index calculations, (ii) batch-reaction and mass transfer calculations of reversible and irreversible reactions involving aqueous, solid and gas phases, and (iii) one-dimensional advective mass transport. PHREEQCI v2.8 (Parkhurst and Appelo, 1999) was used with the PHREEQC rev2.3 thermodynamic database. This expansion of the code includes capabilities to simulate dispersion and diffusion in 1D-transport calculations including matrix exchange in a dual porosity medium, to model kinetic reactions, and to model the formation or dissolution of binary solid solutions, plus some improved flexibility in the input and output of data.

In batch-reaction calculations, PHREEQC is oriented toward system equilibrium so that all of the moles of each element are distributed among the aqueous phase, pure phases, solid solutions, gas phase, exchange sites, and surface sites to attain system equilibrium. The p_e is calculated initially by a mass balance on hydrogen and oxygen. Distribution of redox elements among their valence states can be based on a specified p_e or any redox couple for which data are available.

The framework for numerically efficient 1D advective transport modelling coupled iteratively with reversible and irreversible chemical reactions is provided by PHREEQC's capability to define multiple solutions and multiple assemblages combined with the capability to determine the stable phase assemblage. The input to PHREEQC is completely free format and is based on chemical symbolism. Balanced equations, written in chemical symbols, are used to define aqueous species, exchange species, surface-complexation species, solid solutions, and pure phases.

2.2 FLOW AND REACTION MODELLING: PRECIP AND CORE-2D

2.2.1 PRECIP: 1D flow and reactive transport code (BGS)

The general conceptual approach of the reactive transport code PRECIP is of a one dimensional flow path along which flow is Darcian and on which precipitation and dissolution reactions can take place amongst a number of components. The flow field is defined by either fixed head values at each end of the path or by a specified flow rate along it. The chemical reactions are described by kinetic rate laws and the aqueous components are transported by advection and dispersion. As the chemical reactions proceed, the masses of precipitates change at each point on the path with consequent changes in the porosity. These porosity changes may be related to changes of permeability by a user defined function, thereby affecting the flow field. The reactions may be dependent upon a user specified temperature variation along the flow path and optional aqueous phase speciation and solution-mineral equilibria may also be included. The transport and reaction equations are fully coupled and solved simultaneously.

The mathematical development of the model starts with equations for the description of the precipitation and dissolution of minerals as kinetic processes. A second set of equations describing the transport of multiple reacting aqueous species is then developed. Finally, a form of the groundwater flow equation which explicitly takes account of the changing of porosity with time is added. These three mathematical components form a complete description of the coupled system and can be solved using spatial discretization based on simple central finite differences. Numerical integration over time of the resulting system of coupled non-linear ordinary differential equations is achieved using Gear's method. A detailed description of the code, together with input data specifications and verification examples, are found in Noy (1998). Thermodynamic data have been selected, appropriately for the reactions being modelled, from the EQ3NR/EQ6 database version data0.com.V8.R6.

2.2.2 CORE^{2D}: Flow and reactive transport Code (ENRESA-UDC)

CORE^{2D} is a finite element code which solves for groundwater flow, heat transport and multi-component reactive solute transport under the following conditions:

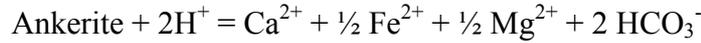
1. 2-D confined or unconfined, saturated or unsaturated, steady or transient groundwater flow with general boundary conditions (Dirichlet, Neuman and Cauchy)
2. Transient heat transport considering conduction, convection and heat dispersion processes.
3. Chemical processes occurring at the equilibrium or kinetically controlled, including homogeneous and heterogeneous reactions
4. Radioactive decay

CORE^{2D} is based on the sequential iteration approach (SIA) to solve the coupled hydrological transport processes and hydrogeochemical reactions. In this approach the transport and chemical equilibrium equations are considered as two different subsystems. These subsystems are solved separately in a sequential manner following an iterative procedure. At any given iteration, the chemical sink/source term is assumed known (or taken equal to the value at the previous iteration) for the purpose of solving the transport equations. This renders the differential equations linear which allows the use of fast numerical methods for solving the linear system of equations. After solving the transport equations, the set of chemical equations is solved on a node-basis. Solution of these non linear equations is carried out using Newton-Raphson iterative procedures. After convergence, the chemical source term is updated. The whole iterative process (transport + chemistry) is repeated until overall convergence is attained. The finite element method is used for spatial discretization, while implicit, explicit and general finite difference schemes are used for time discretization. CORE^{2D} can cope with heterogeneous systems having irregular internal and external boundaries. The code can handle heterogeneous and anisotropic media in: (1) two-dimensional horizontal planes for confined or unconfined flow, (2) two-dimensional vertical planes and (3) three-dimensional problems having axial symmetry for confined aquifers and variably saturated porous media.

Both steady-state and transient flow regimes can be simulated. Prescribed head and water flux as well as mixed boundary conditions are included. Both point and areal fluid sources can be specified. In addition, free drainage boundary condition (unit gradient type) is allowed for variably saturated flow. Solute transport processes included in the code are: advection, molecular diffusion and mechanical dispersion. Solute transport boundary conditions include: (1) specified solute mass fluxes, (2) specified solute concentrations and (3) solute sources associated with fluid sources.

Heat transport is solved at each time step. Computed temperatures are used for updating equilibrium constants and the constants for calculating activity coefficients.

The input of aqueous species, minerals, gases, and adsorbed/exchanged species only requires specifying their names. Thermodynamic data and stoichiometric coefficients of the reactions are read directly from a database modified from the EQ3NR/EQ6 software package (data0.com.V7.R22a; Wolery, 1992). The thermodynamic database of CORE^{2D} has a different structure to that of EQ3/EQ6, but identical thermodynamic data (log K's) and associated reactions, etc (Samper et al., 2000). For the purpose of PADAMOT, the database was supplemented with a new equilibrium constant for the solubility of the ideal stoichiometric ankerite $\text{Ca}(\text{Fe}_{0.5}\text{Mg}_{0.5})(\text{CO}_3)_2$, based on data by Langmuir (1997) and the reaction:



2.3 HYDROLOGICAL BALANCE MODELLING: VISUAL-BALAN

VISUAL BALAN is code designed to compute hydrological water mass balances. Typically, it is employed within the soil (edaphic) zone, the non-saturated zone and the aquifer.

Water transferences among these reservoirs are summarized in Figure 3.1. Precipitation plus irrigation (P) are split into interception (I_n), runoff (E_s) and infiltration (I). A given amount of the total water might be affected by evapotranspiration (ETR) while a part of the remaining water contributes to soil water reserve and to the in transit recharge or effective rain (P_e).

Within the unsaturated zone, water can flow laterally towards the surface as hypodermic flux (Q_h) or contribute to the aquifer via vertical movement as recharge (Q_p). Finally, the underground discharge (Q_s) represents the natural water exit towards streams and rivers.

In order to make the mass balance, it is necessary to consider an aggregated model where the properties of the three groundwater reservoirs are assumed to be homogenous throughout the entire catchment. Thus, the representativity of the water balance will depend on the degree of homogeneity of the catchment and its size.

The water balance is based on the application of the mass conservation law within a given region of known volume and boundary conditions. In the time frame considered, the change in the amount of water stored in the aquifer is related to the differences between the total water input and output.

The basic equation for water balance in the soil is usually integrated between two given times t_i and t_f ($\Delta t = t_f - t_i$):

$$P + D - I_n - E_s - \text{ETR} - P_e = \Delta\theta \quad (1)$$

where P , D , I_n , E_s , ETR , P_e and $\Delta\theta$ represent precipitation, irrigation, interception, runoff, real evapotranspiration, in transit recharge (which is identical to recharge when lateral flow through the unsaturated zone does not occur) and change in moisture content, respectively.

Because water balances are performed on a surface basis, the unknowns in equation (1) are expressed as volume per unit surface area or equivalent water height (i.e. mm). Strictly speaking, the water balance equation should incorporate an explicit term accounting for infiltration (I). Then:

$$I - (\text{ETR} + P_e) = \Delta\theta \quad (2)$$

where

$$P + D - I_n - E_s = I \quad (3)$$

One of the key points of a successful water mass balance model is the computation of ETR, which is, in turn, related to a model to compute the potential evapotranspiration, ETP. Thus, both

ETP and ETR are mutually related and connected with the moisture conditions prevailing in the soil.

Because the earlier water mass balance models were developed for humid regions, their applicability to arid or semi-arid regions cannot be taken for granted. They are most successful if the region in question has a well developed soil layer, the moisture content is higher and, therefore, when ETR and ETP have similar values.

An additional point to take into account is the preferential movement of water through macropores. It is a well known fact that there might be recharge even in the case of soil water deficiency (Rushton and Ward, 1979). In order to account for that, there are a number of available empirical formulations. The simplest one considers that it is directly proportional to the amount of precipitation beyond a given threshold.

The major part of the components participating in the water mass balance (I , E_s , ETR , P_e) depend on soil's moisture content on a non-linear way. Thus, the exact resolution of equation (1) would require the implementation of numerical iterative procedures. However, for common applications it is enough to consider sufficiently small time increments, Δt , and constraints so that the moisture content of the soil does not exceed given values (wilting point and full saturation).

In the application for PADAMOT, the water mass balances have been computed with VISUAL-BALAN following four consecutive stages:

First stage (A): Definition of the geographical situation of the studied area; properties of soil, non saturated zone and aquifer; climatic information from the available weather stations (one single time series).

Second stage (B): Preliminary evaluation of ETP, which is needed whether the Thornthwaite, Turc, Makkink, Blannay-Criddle or Penman models are selected. Then, a number of climatic parameters are given (theoretical daily sunny hours; monthly heat index for Thornthwaite's method; ratio between the monthly averaged maximum time of insolation and the corresponding yearly averaged value according to Blannay-Criddle's method; global radiation according to Makkink's method; and extraterrestrial radiation and altitude anemometer correction following Penman's method).

Third stage (C): Here the hydrometeorology balance is done. For each single day the code performs a series of sequential calculations. Firstly, and only when irrigation is considered, it computes the amount of water applied to the soil. Then, the ETP is computed according to one of the four methods originally implemented in the code. After that, VISUAL BALAN computes the interception and the amount of flow through preferential channels which is the followed by the calculation of runoff, ETR and outflow. Once the water soil balance is completed, the water balance in the non-saturated zone is performed, computing first the hypodermic flow and the aquifer recharge. Finally, the change in piezometer levels is accounted.

Fourth stage (D): The results for each considered catchment (main and secondary) are provided by the code, including: daily, monthly and yearly values; results of the sensitivity analyses; cumulative and averaged values; computed and measured water levels; computed and measured water flux; recharge and/or leakage functions; and results related to automatic calibrations.

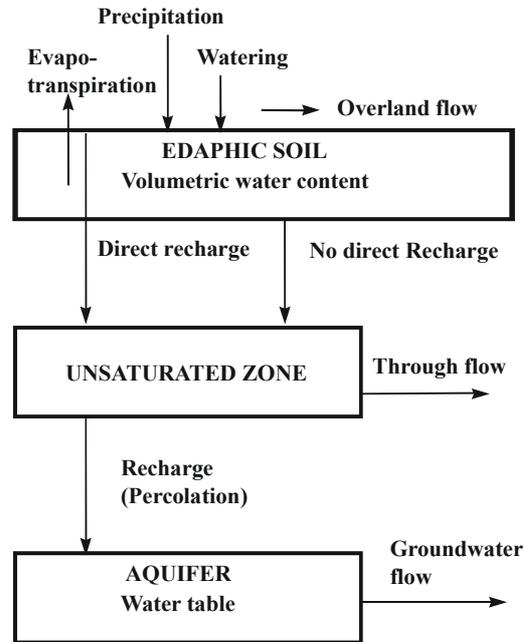


Figure 2.1. Summary of the major components of the hydrologic cycle considered by VISUAL-BALAN.

2.4 GROUNDWATER TRAVEL TIME MODELLING: MODFLOW

The Ground Water Vistas (GWV) modelling package by J. and D. Rumbaugh, Environmental Simulation, Inc. was used (Rumbaugh and Rumbaugh, 1998). The flow solver MODFLOW (McDonald and Harbaugh, 1988), which is a part of the GWV package, was used for groundwater flow and groundwater travel time modelling.

The well known MODFLOW solver uses the finite difference method for solving the equation governing flow:

$$\frac{\partial}{\partial x} \left(k_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(k_{zz} \frac{\partial h}{\partial z} \right) - W = S_s \frac{\partial h}{\partial t} \quad [1]$$

where k_{xx} , k_{yy} and k_{zz} ... hydraulic conductivity along x, y and z axis, parallel with main tensors of permeability (L/t),

h ... piezometric head (L),

W ... infiltration and evapotranspiration (1/t),

S_s ... specific value of material storativity (1/L),

t ... time (T)

Equation [1] describes three dimensional groundwater flows in a heterogeneous and anisotropic environment. This equation, together with boundary and initial conditions, represents a numerical expression of transient groundwater movement.