



Block-Centered Transport (BCT) Process for MODFLOW-USG Transport *(continued)*

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PHT-USG module of BTN Package

Sorab Panday¹, Hiroko Mori¹, Chin Man Mok¹, Jungho Park², Henning Prommer³, Vincent Post⁴

1. GSI Environmental, USA
2. Australia
3. CSIRO, Floreat, Australia
4. BGR, Germany

Introduction

PHT-USG is a module included in the Basic Transport (BTN) package to couple the USG-Transport code that solves for flow and transport of heat and solute species using an unstructured grid, with PHREEQC, the U.S. Geological Survey (USGS) geochemical code for the quantification of reactive processes. The PHT-USG module was designed to be flexible such that newer versions of PHREEQC or of the BTN package can be readily accommodated. This version of PHT-USG implements PHREEQC-2 (Release 2.17). Also, USG-Transport Version 1.4.0 which includes heat transport, was used to implement the integration.

PHREEQC was developed by D.L. Parkhurst at U.S. Geological Survey and C.A.J. Appelo (Parkhurst and Appelo, 1999). It was designed to perform a wide variety of low-temperature aqueous geochemical calculations and is based on an ion-association aqueous model. PHREEQC has capabilities for (1) speciation and saturation-index calculations; (2) batch-reaction and one-dimensional (1D) transport calculations involving reversible reactions, which include aqueous, mineral, gas, solid-solution, surface- complexation, and ion-exchange equilibria, and irreversible reactions, which include specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and temperature changes; and (3) inverse modeling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters, within specified compositional un- certainty limits.

USG-Transport continues to be developed with partial support from GSI Environmental. Development of PHT-USG was supported by funding from DOE-LM.



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Background

A study of the various methods available in literature for coupled reactive transport modeling was conducted to evaluate the state-of-the science in geochemical reactive transport modeling. The PHREEQC code from the USGS was chosen as the candidate geochemical reaction model as it had the required capabilities. The benefit of PHREEQC coupled with USG-Transport is the ability to limit these numerically intense, focused reactive computations within required bounds using unstructured grids.

Several versions of PHREEQC are available publicly. Version 2 was released by the USGS (Parkhurst and Appelo, 1999). Version 3 was released by the USGS in 2013 (Parkhurst and Appelo, 2013). The version 3 modules were also released as PHREEQC RM, which are a set of functions used by PHREEQC, that may be called from any available transport simulator.

Henning Prommer and Jungho Park were involved in development of PHT3D Version 2.174 which uses PHREEQC Version 2, coupled to the MT3D transport code (Prommer and Post, 2010), with MODFLOW-2000 (Harbaugh et al, 2000) providing the groundwater flow field. They had also attempted integration of PHREEQC RM modules into MT3D for an updated version of PHT3D (unpublished). Upon evaluation of both approaches, it was determined that the Version 2 approach was modular and provided all the required capabilities for this work. Therefore, PHT3D Version 2.174 was used to initiate the development with PHREEQC-2 for the geochemical code.

Numerical Implementation of PHT-USG

PHT-USG has been designed in a modular manner. Following the MODFLOW code design implemented in USG-Transport, the PHT-USG module creates an interface between MODFLOW-USG, the transport routine and PHREEQC, to allocate array space, read and prepare PHREEQC-related data, perform the PHREEQC reaction calculations, and calculate mass budgets. The module has been designed as a wrapper such that component models can be



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interchangeable and newer versions of USG-Transport or PHREEQC can be readily accommodated.

The sequential iterative solution method was used to interface PHREEQC with USG-Transport. Thus, an iterative loop was included within USG-Transport after transport computations were completed for all component species. A pure operator splitting approach is simulated when maximum number of iterations, NSEQITR = 1. The computations continue to the next time step if the maximum number of iterations is exceeded. Experience has shown that results are stable and reasonably accurate with NSEQITR = 2 to 5 even with large time steps with Courant Numbers exceeding unity.

The PHREEQC reaction time-step is the same as the time-step for transport computations. USG-Transport has been designed such that there is no interpolation in time and therefore the transport time-step is also the same as that for flow calculations when the flow field is transient. USG-Transport uses an implicit total variation diminishing (TVD) scheme for solution to the transport equations. Use of an implicit scheme removes time-step size stability constraints and therefore provides flexibility in time-step size selection. However, the first-order-in-time solution may provide more dispersed solutions for very large time step sizes and therefore selection of a maximum time step size for a simulation should consider time scales of all processes involved.

PHT-USG was created from PHT3D Version 2.174 with solution files created by Jungho Park. Message Passing Interface (MPI) routines are included to allow for parallel processing of the PHREEQC routines on multiple cores or multiple computers. Other efficiencies are also under consideration to speed up the otherwise computationally intense reactive transport computations.

Input

The PHT-USG module is activated by opening the datafiles for PHREEQC portion of the computations in the NAME file with the keyword PHC. The data is identical to what was contained in the parallel dataset for PHT3D and can



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therefore a PHT3D datafile can be directly used for the PHREEQC portion of the information. The PHREEQC database should also be available for the simulation, along with the other USG-Transport datasets.

Output

Output from PHT-USG includes the regular transport output as well as the reactions computed by PHREEQC. The Listing file reflects input parameters, transport iteration behavior and output of solute concentrations, mass balance, (also temperature and energy balance for a thermal component to the simulation) along with other data of the simulation.

Component species that are not transported are included in USG-Transport to accommodate immobile species (IMCOMP) that may be involved in geochemical reactions. The total number of components NTCOMP, is equal to the total number of mobile components, MCOMP (plus temperature if heat is solved), plus the total number of immobile components, IMCOMP. The variables are also ordered in the same manner – i.e., the mobile components are first, followed by the temperature if the heat equation is simulated, followed by the immobile components. Input concentrations are provided for these additional species which may then be changed by a reaction or geochemical package. Output of the reacted immobile concentrations is then also provided by USG-Transport so that all species are tracked and reported in the listing file and associated binary concentration files.

Since geochemical reactions may involve several species, the concentration output file has been further optionally split into multiple files. Specifically, the default approach was to write all species concentrations to a single .CON file. An option is now provided whereby each species is written to a separate .CON file. With this option, MULTIFILE, the output of each species goes to a separate file. The root name of the file is defined with the MULTIFILE option, and each species number (CONC01, CONC02, etc) gets concatenated to the root filename with the extension .CON. For temperature output, the MULTIFILE option appends the word “TMPR” to the root filename followed by the extension “.CON”.



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Verification Examples

The first three example problems from the PHT3D document were used to compare the results between PHT3D and PHT-USG to verify that the integration is done appropriately. The tests and results are documented below. Only a brief part of each example describes the geochemistry and the dynamics of the geochemical changes. Users are encouraged to familiarize themselves with the other PHT3D example problems as well as with geochemistry afforded by the PHREEQC-2 software.

Example 1: Single Species Transport with Monod Kinetics

This example simulates one-dimensional, purely advective transport coupled to kinetically controlled biodegradation. A steady-state flow-field introduces solute species from the left end of the column and its migration through the column was computed. The simulation time was set to 1826 days, divided into 200 time steps of equal length (9.13 day time-step size). This example problem demonstrates the major steps that are involved in setting up a reactive transport model with the PHT-USG module and the USG-Transport code. The analytical solution to the Monod Kinetics associated with this example was originally given by Parlange et al. (1984). Solute transport and reaction parameters used for the simulations were provided by Essaid and Bekens (1997) and are shown on Table 1 below.



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Table 1: Parameters and chemical concentrations used in Example 1.

Flow simulation	steady state
Total simulation time (<i>days</i>)	1826
Stress period	1
Time steps	200
Model length <i>L</i> (<i>m</i>)	150
Pore water velocity v_p ($m\ d^{-1}$)	0.1
Porosity n_e	0.25
Dispersivity α_l (<i>m</i>)	0
Maximum uptake rate $v_{max}\ d^{-1}$	4.77×10^{-3}
Half-saturation concentration <i>K</i> (mol L ⁻¹)	0.5
Inflow concentration of specie 1 (at <i>x</i> = 0 and for <i>t</i> > 0) (mol/ <i>L_w</i>)	1
Initial concentration of specie 1 (at <i>x</i> = 0 and for <i>t</i> = 0) (mol/ <i>L_w</i>)	1
Initial condition of pH in layer 1	7.0
Initial condition of pe in layer 1	4.0

Files that were created for USG-Transport included:

- .bas (MODFLOW-USG Basic Package)
- .bcf (Block-Centered Flow Package)
- .bct (Block-Centered Transport Package)
- .chd (Time-Variant Specified-Head Option)
- .dis (Discretization File for an unstructured grid)
- .nam (MODFLOW Name File)
- .oc (Output Control Option)
- .sms (Matrix Solver Package)



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These files were created by modifying the associated MT3D files of PHT3D. The files include a basic simulation file (BAS) with a discretization file (DIS) for the 1-D column. A steady-state flow-field within the column is developed from left to right by the flow (BCF) and boundary (CHD) packages. The BCT file for this problem includes one mobile component (MCOMP = 1) with two immobile species (IMCOMP = 2) for 'pH', and 'pe'. Also, the adsorption flag is turned off (IADSORB = 0) since adsorption related reactions, if present, are simulated by PHREEQC. The SMS and OC files are for solver and output control of the simulation.

Files that were available for the PHREEQC reaction module included:

- pht3d datab.dat (PHREEQC database)
- pht3d ph.dat (PHREEQC chemical data file)

These PHREEQC related files are the same files used in the PHT3D simulation. The PHT-USG simulation of this example was compared with the PHT3D solution (which was compared with the analytical solution of Parlange et al, 1984 by Prommer and Post, 2010). Figure 1 shows the comparison of PHT-USG with PHT3D indicating a good match.



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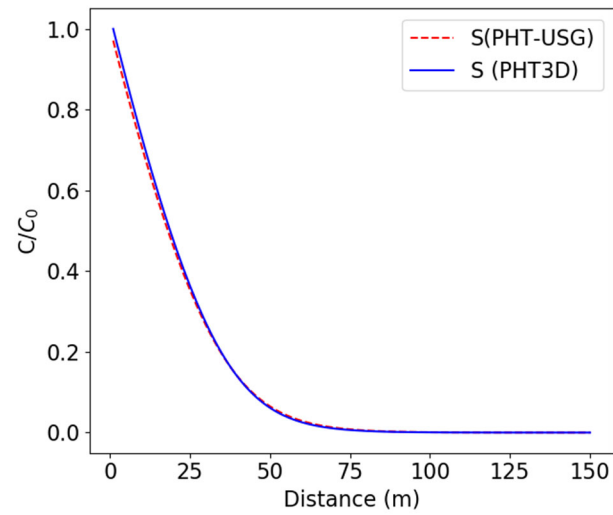


Figure 1: Single-species transport with Monod-type biodegradation – comparison of PHT-USG with PHT3D solution.



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Example 2: Transport and mineral precipitation/dissolution

This example simulates one-dimensional, reactive transport including mineral dissolution and precipitation. The model simulates the mineral fronts of chemically equilibrium aqueous solution replaced by a steady-state flow introduced from the left end of the column. The simulation time was set to 0.2430 days, divided into 210 time steps of equal length (0.001157 day time-step size). This example problem was originally presented by Engesgaard and Kipp (1992). Flow and transport parameters and chemical and mineral concentrations used for the simulations are shown on Table 2 and Table 3, respectively.

Table 2: Parameters and chemical concentrations used in Example 2.

Flow simulation	steady state
Total simulation time (<i>days</i>)	0.2430
Stress period	1
Time steps	210
Model length L (<i>m</i>)	0.50
Pore water velocity v_p ($m\ d^{-1}$)	0.083
Porosity n_e	0.32
Logitudinal dispersivity α_l (<i>m</i>)	0.0067
Transverse dispersivity	0.00067



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Table 3: Chemical and mineral concentrations used for Example 2.

Chemical	Initial Concentration (mol/ L_w)	Inflow Concentration (mol/ L_w)	Mobility*
C(4)	0	1.23×10^{-4}	M
Ca	0	1.23×10^{-4}	M
Mg	1.0×10^{-3}	0	M
Cl	2.0×10^{-3}	0	M
pH	9.9	7.0	IM
pe	4.0	4.0	IM
Calcite	0	3.91×10^{-5}	IM
Dolomite	0	0	IM

*M and IM refer to mobile and immobile components, respectively.

The BCT file for this problem includes four mobile component (MCOMP = 4) with four immobile species (IMCOMP = 4) for 'pH', 'pe', 'Calcite', and 'Dolomite'. Also, the adsorption flag is turned off (IADSORB = 0).

The PHT-USG simulation of this example was compared with the PHT3D solution (which was compared with the analytical solution of Engesgaard and Kipp (1992) by Noorishad (1987)). Figure 2 shows the comparison of PHT-USG with PHT3D indicating a good match for all mobile components and minerals.



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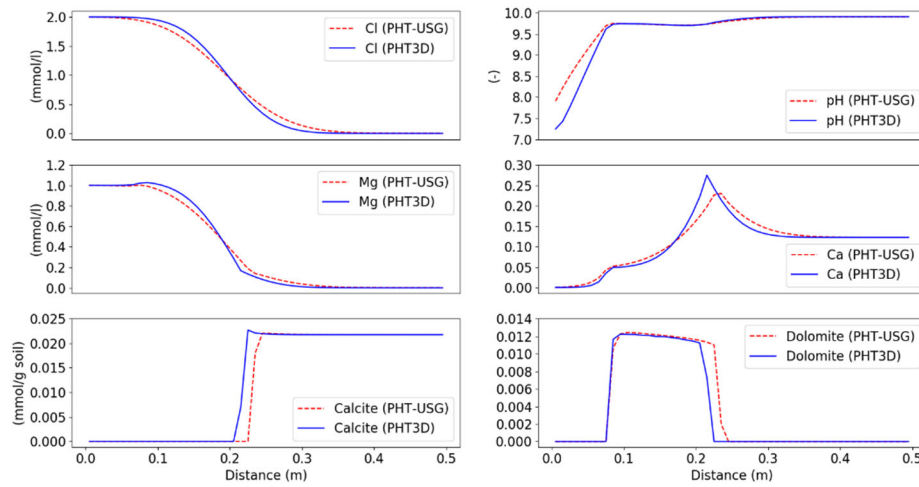


Figure 2: Transport and mineral precipitation / dissolution – comparison of PHT-USG with PHT3D solution.



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Example 3: Migration of Precipitation/Dissolution Fronts

This example simulates a one-dimensional, inorganic redox problem that was first presented by Walter et al. (1994). The model simulates the geochemical reaction of acidic mine tailings in a carbonate aquifer. The simulation time was set to 24 days, divided into 192 time steps of equal length (0.125 day time-step size).

Solute transport parameters used for the simulations are shown on Table 4 below and initial and inflow concentrations of both aqueous components and minerals are listed in Table 5.

Table 4: Parameters and chemical concentrations used in Example 2.

Flow simulation	steady state
Total simulation time (<i>days</i>)	24
Stress period	1
Time steps	192
Model length L (m)	0.40
Pore water velocity v_p ($m\ d^{-1}$)	0.02
Porosity n_e	0.35
Longitudinal dispersivity α_l (m)	0.005
Transverse dispersivity (m)	0.0005



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Table 5. Initial concentration and inflow of aqueous and mineral components

Chemical	Initial Concentration (mol/ L _w)	Inflow Concentration (mol/ L _w)	Mobility*
C(4)	3.94×10^{-3}	4.92×10^{-4}	M
Ca	6.92×10^{-3}	1.08×10^{-2}	M
Cl	1.03×10^{-3}	1.19×10^{-4}	M
Mg	1.96×10^{-3}	9.69×10^{-4}	M
Na	1.30×10^{-3}	1.39×10^{-3}	M
K	6.65×10^{-3}	7.93×10^{-4}	M
Fe	5.932×10^{-5}	3.06×10^{-2}	M
Mn(2)	4.73×10^{-5}	9.83×10^{-6}	M
Al	1.27×10^{-7}	4.30×10^{-3}	M
Si	1.94×10^{-3}	2.08×10^{-3}	M
S(6)	7.48×10^{-3}	5.00×10^{-2}	M
pH	6.96	3.938	IM
Pe	1.67	7.69	IM
Calcite	1.95×10^{-2}	0.0	IM
Siderite	4.22×10^{-3}	0.0	IM
Gypsum	0.0	0.0	IM
SiO ₂ (a)	4.07×10^{-1}	0.0	IM
Gibbsite	2.51×10^{-3}	0.0	IM
Fe(OH) ₃ (a)	1.86×10^{-3}	0.0	IM

* M and IM refer to mobile and immobile components, respectively.

The BCT file for this problem includes 11 mobile component (MCOMP = 11) with seven immobile species (IMCOMP = 8) for 'pH', 'pe', and minerals. Also, the adsorption flag is turned off (IADSORB = 0).

The PHT-USG simulation of this example was compared with the PHT3D solution for concentrations of selected components and minerals at day 6, 12, and 24.

Figure 3 shows the comparison of PHT-USG with PHT3D.



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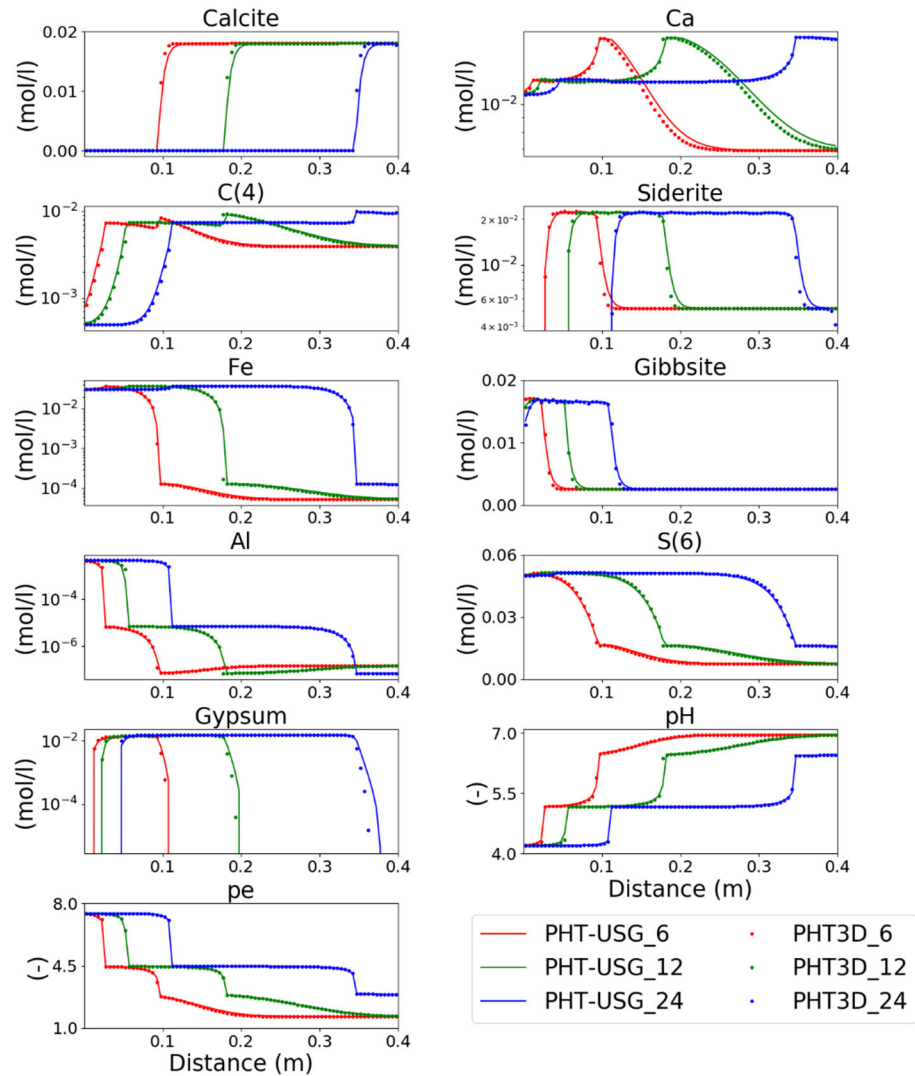


Figure 3: Migration of Precipitation/Dissolution Fronts – comparison of PHT-USG with PHT3D solution.

In addition, the original document from PHT3D manual lists Fe(2) and Fe(3) as input data for pht3d_ph.dat. However, the files provided in the example manual list Fe instead of Fe(2) and Fe(3); therefore the following figures only list Fe for



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comparison between PHT-USG and PHT3D. It is noted that results from PHT-USG at 24 days match those from PHT3D for all mobile components and minerals.

Input Instructions for PHT-USG Module

The PHT-USG module is used by a simulation if the keyword PHC is included in the NAME file that runs USG-Transport. The datafile for the PHREEQC interface package is opened and linked to the unit number attached to the PHC keyword. This file carries information about the number, names and types of chemicals included in a PHT-USG simulation, reaction rate constants, (and other reaction parameters. In addition, a file called PHT3D-DATAB.DAT is also used by PHREEQC. This is database file analogous to the original PHREEQC-2 database files.

The input data for the interface file and the PHREEQC database are identical to what was contained in the respective PHT3D geochemical data files. Therefore, the input instructions from the PHT3D documentation may be used to create these datasets. The flow and transport portions of the datasets of USG-Transport are not impacted by the PHT-USG modifications and would replace any of the MT3D datasets from a PHT3D simulation.



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