

# PHT3D: A Reactive Multicomponent Transport Model for Saturated Porous Media

reviewed by C.A.J. Appelo<sup>1</sup> and Massimo Rolle<sup>2</sup>

This column reviews the general features of PHT3D Version 2, a reactive multicomponent transport model that couples the geochemical modeling software PHREEQC-2 (Parkhurst and Appelo 1999) with three-dimensional groundwater flow and transport simulators MODFLOW-2000 and MT3DMS (Zheng and Wang 1999). The original version of PHT3D was developed by Henning Prommer and Version 2 by Henning Prommer and Vincent Post (Prommer and Post 2010). More detailed information about PHT3D is available at the website <http://www.pht3d.org>.

The review was conducted separately by two reviewers. This column is presented in two parts.

**PART I** by C.A.J. Appelo

## Introduction

PHT3D is a computer code for general reactive transport calculations, coupling MODFLOW/MT3DMS for transport and PHREEQC for chemical reactions. It was developed by Henning Prommer in the 1990s and has been applied by him and his coworkers to various groundwater problems of practical interest. The resulting publications ([http://www.pht3d.org/pht3d\\_public.html](http://www.pht3d.org/pht3d_public.html)) show an impressive applicability of the code and illustrate the underlying understanding of quite complicated interactions (e.g., Prommer and Stuyfzand 2005; Prommer et al. 2008, 2009). In the original version, transport is calculated during a time step, an input file is written for PHREEQC for calculating reactions such as ion exchange and precipitation or dissolution of minerals, and these steps are repeated for subsequent time steps until finished. This

loose coupling has the advantage that updates of the master programs can be installed without much effort. A disadvantage is that the calculation of the chemical reactions needs to be initialized time and again for each cell in the model, which adds another time-consuming step to calculations that are already computer-intensive. Another disadvantage is that surface complexation reactions need to be calculated first using the water composition from the previous time step and then reacted with the changed water concentrations. This procedure was not implemented in the original version of PHT3D, and surface complexation reactions could not be calculated.

Prommer and Post recently released the second version of PHT3D that resolves the shortcomings and works very well. The improvement is owing firstly to the implementation of total-variation-diminishing (TVD) scheme that MT3DMS uses for calculating advective and dispersive transport (Zheng and Wang 1999). Secondly, it is because PHREEQC is now being used for storing the chemical data of the model, including the chemical activities and the composition of surface complexes from the previous time step. In addition, the procedure to transport total oxygen and hydrogen has been adapted from PHAST (PHAST is the 3D reactive transport model developed by Parkhurst et al. 2004, based on HST3D and PHREEQC). This enables the user to obtain the redox state of the solution without having to transport individual redox concentrations of the elements (e.g., C being distributed over carbon-dioxide, C(4), and methane, C(-4)). The tighter coupling quickens the calculations twofold at least, but probably by an order of magnitude for the more interesting cases. In this review, the background of the new implementation is presented and illustrated with examples and compared with results from PHREEQC and PHAST.

## How Are pe and pH Calculated in the New Version

The calculation of pe and pH from total hydrogen and oxygen, and charge balance has been implemented in the

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new version of PHT3D. The procedure can be understood by considering a set of reactions for pure water.

First, the dissociation reaction:



with the mass action and charge-balance equations:

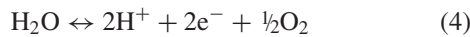
$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 10^{-14} \quad (2)$$

and

$$m_{\text{H}^+} = m_{\text{OH}^-} \quad (3)$$

where brackets and  $m_i$  indicate dimensionless activity and concentration in mol/(kg H<sub>2</sub>O), respectively.

Second, the oxidation reaction:



with the mass action equation:

$$\frac{[\text{H}^+]^2[\text{e}^-]^2[\text{O}_2]^{0.5}}{[\text{H}_2\text{O}]} = 10^{-43} \quad (5)$$

And third, the mass balance equations:

$$\text{tot}_{\text{H}} = 2\text{tot}_{\text{H}_2\text{O}} + \text{tot}_{\text{H}^+} + \text{tot}_{\text{OH}^-} \quad (6)$$

$$\text{tot}_{\text{O}} = 2\text{tot}_{\text{O}_2} + \text{tot}_{\text{H}_2\text{O}} + \text{tot}_{\text{OH}^-} \quad (7)$$

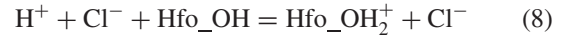
where  $\text{tot}_i$  is total moles of  $i$ .

For this set of reactions of seven variables and five equations (2, 3, 5 to 7), a solution can be found when two more unknowns are defined; thus, if total hydrogen and oxygen are known (and transported, the concentrations in Equation 3 are given by  $m_{\text{H}^+} = \text{tot}_{\text{H}^+} / \text{tot}_{\text{H}_2\text{O}} \times (\text{mol H}_2\text{O}/\text{kg H}_2\text{O})$ , etc.). Adding H<sub>2</sub> to the set gives another mass action equation, and its concentration can be solved then as well. The concentrations of H<sup>+</sup> and OH<sup>-</sup> are in the order of 10<sup>-7</sup> M, and the charge-balance equation 3 needs to be solved with 11 digits precision when other solutes are present at higher concentrations. Moreover, chemical analysis may not have produced an exactly balanced result, surface complexation reactions can impart a charge imbalance to the solution, and therefore, also the charge balance must be transported.

## Charging Surfaces and Solutions

Sorption of heavy metals with strong pH dependence is often modeled as a surface complexation reaction. The essence of surface complexation theory is that the electrical potential at the surface, which develops when the surface is charging as a result of sorption, is accounted for in the sorption of charged species. However, it is usually dismissed that charging of the surface also implies that the solution will obtain a countercharge. For example,

the reaction of HCl with ferrihydrite (Hfo, amorphous iron-hydroxide),

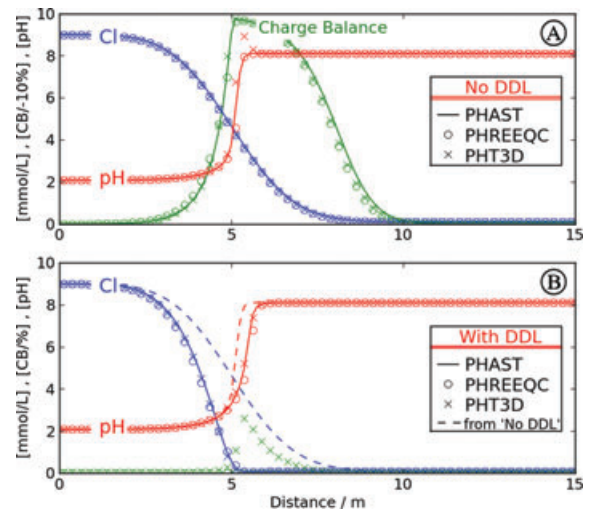


shows that the surface turns positive while the solution becomes negative.

A numerical column experiment can illustrate the implications. Water along a 15-m flow line is in contact with ferrihydrite-coated quartz at a concentration of 0.89 g Hfo/L water. The water contains 0.1 mM NaCl and the pH is brought to 8.11 with NaOH. At this pH, ferrihydrite has zero charge (Dzombak and Morel 1990). The dispersivity is 0.2 m, the diffusion coefficient is zero. Injected is a 9 mM HCl solution (pH = 2.1). Figure 1 shows pH, Cl<sup>-</sup>, and charge balance when the front has traveled 5 m, calculated with PHREEQC (60 cells), PHAST (120 cells), and PHT3D (60 cells).

Both codes give almost the same results (PHAST needs at least twice finer grid than PHREEQC and PHT3D to counter numerical dispersion). Because H<sup>+</sup> is lost to ferrihydrite, the solution is left with an impossible negative charge of almost -100%. PHT3D shows small pH deviations in the front, probably because the charge balance is transported with insufficient precision. However, a neutral pH is buffered by carbonate species in groundwater, and the effect may disappear in normal cases.

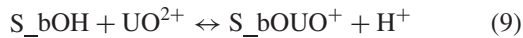
PHREEQC can counterbalance the surface charge with a diffuse double layer (DDL) that stays with the surface. Figure 1B shows the results when this option (“-donnan”) is invoked for the surface, and illustrates,



**Figure 1.** Effects of surface complexation and charging on transport of Cl<sup>-</sup> and H<sup>+</sup> calculated with PHT3D, PHAST, and PHREEQC. Protons from an HCl solution, entering the flow line from the left, sorb on ferrihydrite, which imparts the solution with a strongly negative charge (charge balance, CB, expressed as % and normalized by dividing by -10% before plotting in A, and by +1% in B). The surface charge can be compensated in a diffuse double layer (DDL) that is fixed to the surface (option -donnan in PHREEQC), leading to correct charge balance in PHREEQC and PHAST (Figure 1B).

first, that the transported solution remains uncharged, second, that  $\text{Cl}^-$  has not traveled as far as before (compare dashed and full lines), and third, that the three codes give the same results. Chloride is retarded because it is taken up in the DDL where it compensates the positive surface charge. The small jump in pH that PHT3D calculated before is absent, but a charge imbalance has appeared instead.

The charging effects of surface complexation have been neglected in most of the literature in which surface complexation is used to model sorption of heavy metals or metalloids. For example, Kohler et al. (1996) modeled a column experiment in which U(6) was sorbing on quartz with the surface complexation reaction (among others):



Example 12 of the PHT3D manual (Prommer and Post 2010), using the case as a benchmark, shows that PHT3D calculates very much the same results as depicted by Kohler, that is, without accounting for charging of the solution and its adverse effects on the calculated pH. However, because the pH affects sorption of  $\text{UO}_2^{2+}$  according to Equation 9, the results become different if a DDL is included when the surface is defined in the model. Figure 2 illustrates that different profiles for pH and solute U(6) are calculated with and without a DDL on the surface of quartz.

Of course, transport of a charged solution is physically impossible unless an electrical field is present. Accordingly, the solutions should be charge balanced exactly to at least  $10^{-11}$  eq/kg  $\text{H}_2\text{O}$ , and the charge balance should be transported with at least 11 digits accuracy. If this is not done, the solution may be endowed with chemically improbable properties that will prevent PHREEQC from finding a correct solution, especially

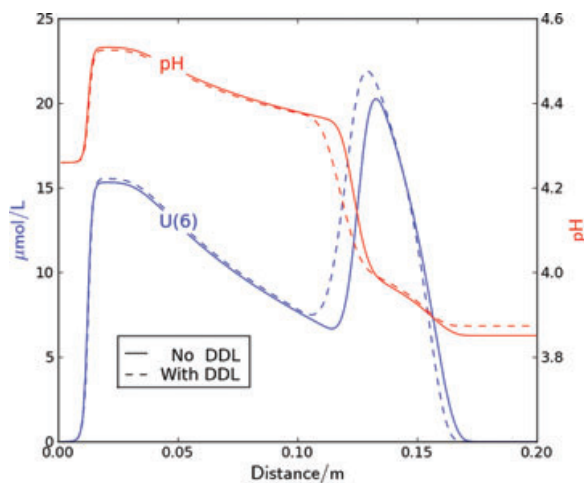


Figure 2. Modeled profile of U(6) and pH in a column experiment described by Kohler et al. (1996). The profile is depicted 3 h after the start of the experiment, with surface and solution charging (“No DDL,” the original simulation), and with surface charge counterbalanced by a diffuse double layer (“With DDL”).

when small concentrations of redox-sensitive elements are present. Usually, this results in the unpleasant note that the model “failed to converge.”

## A 2D Case: Uranium Release and Capture by Reduction

How much time will it take to build a model with PHT3D compared with PHAST? For hydrogeologists familiar with MODFLOW, the hydrological model may be easy, but the definition of the chemical data in MT3DMS will require quite some time. Solutions associated with wells and constant head boundaries need to be input in a complicated manner in different files and concentrations must be given with many digits to obtain a solution with zero charge balance. In the new version, a “postfix.phrq” file can be written with initial solutions in the model domain that can be charge balanced by PHREEQC, but the definition of zones must be done cell-by-cell. On the other hand, PHAST allows inputting zones easily by defining boxes in real-space coordinates. Both models were tested by calculating transport of heavy metals from a former uranium mine, with surface complexation and reduction of U(6). The case was described by Appelo and Dimier (2004).

The model is for a 50-m thick and 2000-m wide cross section of the aquifer, discretized in  $40 \times 100$  cells. Acid leachate from the mine enters the section from the lower left at  $1.5 \text{ m}^3/\text{day}$  and is accompanied by the same amount of natural background water from the upper left (Figure 3). The aquifer contains 10 mmol ferrihydrite/L pore water which sorbs U(6), but there is competition by  $\text{H}^+$  and other solutes. In the lower quarter, from the mine until the outflow cells in the middle right, pyrite is present. The pyrite will reduce U(6) to U(4), which then precipitates readily as coffinite ( $\text{USiO}_4$ ). The pyrite zone was defined in the postfix file with a python script, which was somewhat time-consuming, so that modeling this case, together with graphic display of the results, took about 1 day with PHT3D. The model for PHAST could be generated in less than 1 h, and the results can be displayed without effort in 2D with ModelViewer, which is included with PHAST. The input files for PHAST are easy to

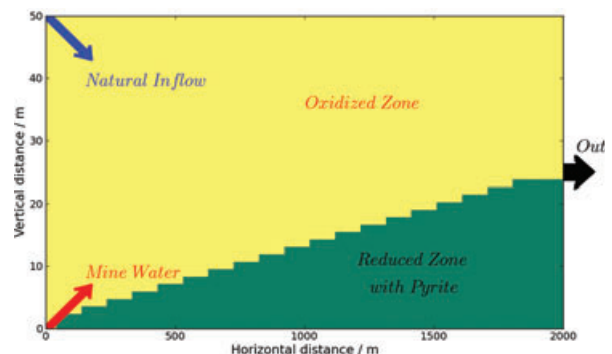
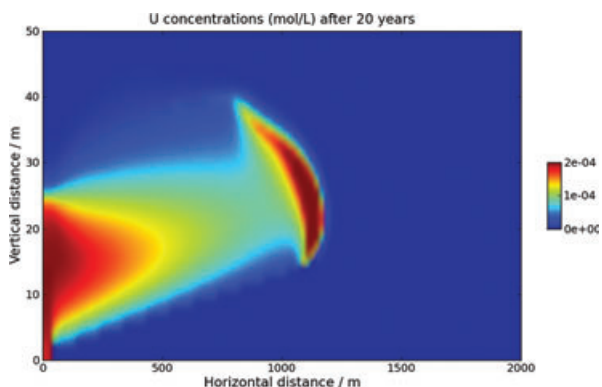


Figure 3. Outline of the aquifer in which U(6) is spilled with mine water.



**Figure 4.** U-concentrations after 20 years in the aquifer shown in Figure 3.

read and present all the details of the model; they are available at <http://www.xs4all.nl/~appt/exmpls/uran.html>, specifically in files `u2.trans.dat` and `u2.chem.dat`. Both models give essentially the same results and need the same time for calculating transport and reactions during 20 years (1 h on a 2.6 MHz PC). However, with equal cells and time steps, PHAST shows more smeared-out concentrations as a result of higher numerical dispersion.

Results for the U-concentrations after 20 years spilling (Figure 4) illustrate the special features of U transport in an aquifer in which both sorption and desorption, as well as redox and precipitation play a role. Uranyl has a concave sorption isotherm on ferrihydrite (the slope of the isotherm lies below the curve), which gives a sharpening front when U desorbs in the acid mine water (Appelo and Postma 2005). The sharpening results in a concentration enhancement of U(6) at the front. At the same time, part of the U(6) is lost to the reduced zone by dispersion, where it is reduced and precipitated as coffinite. All in all, the Uranyl concentration pattern in the aquifer displays the typical mushroom shape that has become so ominously associated with this element.

## Summary

Both PHT3D Version 2 and PHAST enable the user to calculate transport of chemicals in aquifers with the suite of complicated reactions that are commonly observed in nature. Both models are open source and use the same chemical solver PHREEQC, and can do the same chemical problems. However, the two models will probably address different users.

PHT3D is based on MODFLOW and uses a complicated Fortran-type input style in various text files that need to be written precisely and coordinated exactly. In the version tested, the charge balance is transported with insufficient precision. This may give pH deviations, but these will probably not occur when carbonate species buffer the pH. The good points of the code are the small numerical dispersion thanks to MT3DMS' TVD scheme, and many hydrogeological options provided by the various MODFLOW modules. The documentation, on the

other hand, is still very much oriented to the first version of the code and a good graphical interface is lacking. However, this will not be much of a problem for a hydrogeologist who is already familiar with the MODFLOW procedures.

In contrast, PHAST can be readily applied to groundwater transport problems thanks to a well-structured definition of input and a fine user's guide. A hydrogeologist, unfamiliar with the details of MODFLOW, will find PHAST easier than PHT3D for doing chemical transport problems. Unfortunately, PHAST has more numerical dispersion than PHT3D. PHAST needs a finer grid and smaller time steps, which will extend its execution time compared with PHT3D. It would help if the code would issue warnings, for example, list the largest Courant number in the model domain (which MT3DMS does). Numerical dispersion will play a role when column- or injection tests are modeled, but it can be abated by a finer discretization. As the chemical and physical details of aquifers are mostly unknown anyhow, PHAST is excellent for gaining rapid insight into the interplay of complicated transport phenomena in aquifers.

## Further Information

<http://www.pht3d.org/>

[http://www.brr.cr.usgs.gov/projects/GWC\\_coupled/phast/](http://www.brr.cr.usgs.gov/projects/GWC_coupled/phast/)

<http://www.xs4all.nl/~appt/exmpls/uran.html>

## PART II by Massimo Rolle

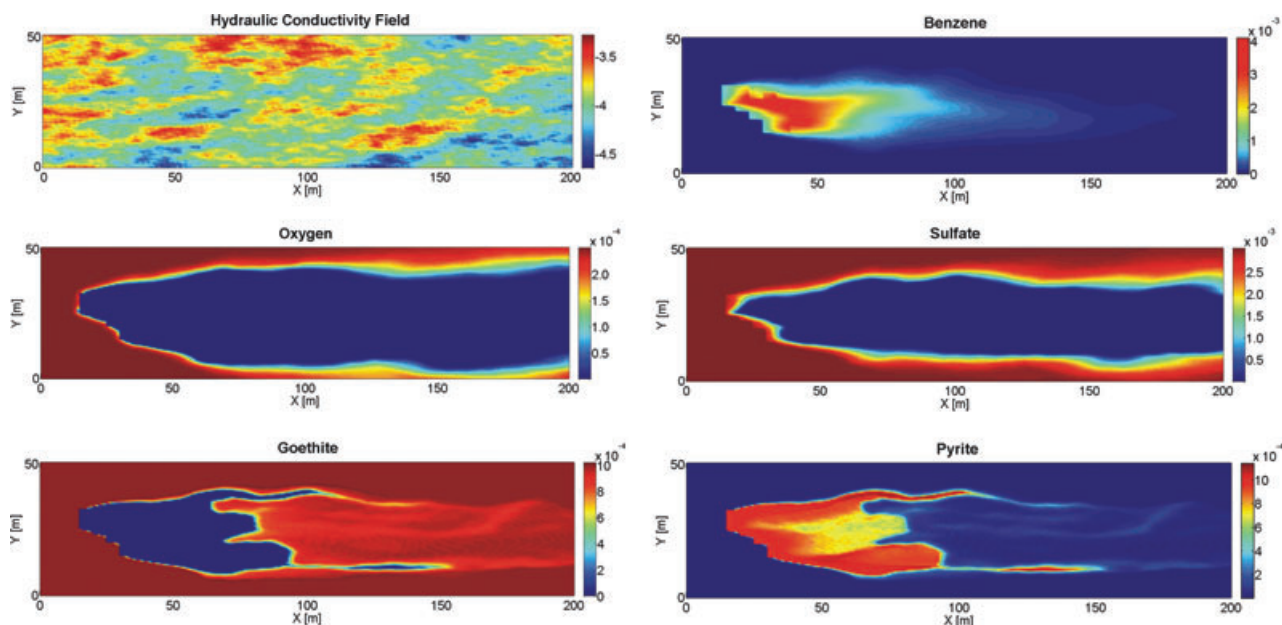
I reviewed PHT3D Version 2.0, incorporating MT3DMS (Release 5.2) and PHREEQC-2 (Release 2.15), on a Windows XP Laptop Dual Core 2.8 GHz with 3.0 GB RAM. The code was tested with and without a graphical user's interface (GUI). The selected GUI was Processing Modflow for Windows (PMWIN). Another GUI available for use with PHT3D is Visual MODFLOW (VM).

The installation of the code required only a few seconds. It provided the source code, executable programs, the user's manual, and the input files of a number of benchmark test examples described in detail in the user's manual.

## What I Found

I tested some of the examples described in the manual and focused my attention on example 10, a problem dealing with reactive transport of aromatic hydrocarbons (BTEX, i.e., benzene, toluene, ethylbenzene, and xylenes) including dissolution from a non-aqueous phase liquid (NAPL) source, degradation and geochemical interaction with reactive minerals present in the solid matrix. Successively, I applied the groundwater chemistry and reactions described in example 10 to my own scenario, where reactive transport and geochemical interactions occurred in a randomly generated two-dimensional heterogeneous porous medium (Figure 5).

PHT3D is built on the modular structure of MODFLOW/MT3DMS for the solution of the flow



**Figure 5. Hydraulic conductivity field (log scale) and computed molar concentrations of dissolved and solid species.**

and transport problem. Input instructions are provided through different input files according to the structure of MT3DMS. The coupling of the transport and the geochemical simulator PHREEQC-2 is realized through a series of subroutines and an interface package. The user needs to provide two additional input files: pht3d\_datab and pht3d\_ph. The first file is a geochemical database, with the same structure of the original PHREEQC-2 database (phreeqc.dat), where the aqueous components (master species), the reactions taking place in the aqueous phase and involving mineral or gaseous phases and the rates of kinetically controlled processes are defined. The file pht3d\_ph contains instructions about the number, names, and properties of the species included in the PHT3D simulation.

The output of the program maintains the structure of MT3DMS and the computed concentrations of the different species at the selected output times can be saved both as binary files (.UCN) and as ASCII files (.ACN). External applications, such as Matlab<sup>®</sup>, can be used to visualize the results as done, for example, in Figure 5.

The GUI simplifies the creation of the input files and allows a basic visualization of the simulation outcomes. It also allows the extraction of selected simulation results for more sophisticated post-processing.

### What I Liked

The software performance was good. I was particularly impressed by the flexibility offered by PHT3D in solving complex groundwater quality problems. The code, based on the robust transport simulator MT3DMS and its options of solution techniques (including particle-tracking based Eulerian-Lagrangian and Eulerian higher-order finite volume methods), allows the user to tackle

multidimensional transport problems coupled to a wide variety of equilibrium and kinetically controlled reactions. Moreover, the tested new version of PHT3D gives an increased flexibility in taking advantage of the capabilities of the geochemical simulator PHREEQC-2, such as the possibility to simulate multi-site cation exchange and surface complexation reactions.

A feature that I found useful for applied reactive transport modeling is the possibility, in PHT3D, to carry out reactive and conservative transport simulations. In the latter case the reactive module is switched off and the defined species undergo conservative transport. A direct comparison between the simulated concentrations of conservative and reactive species allows the modeler to quantitatively assess the influence of different reactive processes on the fate and transport of dissolved compounds (e.g., contaminants undergoing degradation reactions).

I found the PMWIN interface to be a basic but quite intuitive environment to handle input and output data. The part of GUI concerning PHT3D maintains basically the original modular structure of the code, thus facilitating the management of input instructions and computed results. In my opinion, the main advantage of PMWIN is the possibility to directly visualize and edit input data in a matrix format. This feature is particularly useful when a fine discretization grid is adopted and the assignment of input data by drawing on the model domain area can become cumbersome.

### What I Did Not Like

In my opinion, the use of the code can be quite difficult if the user has no experience in modeling with MT3DMS and PHREEQC-2. Some basic knowledge of MT3DMS helps to understand the structure of PHT3D

and some experience in geochemical modeling with PHREEQC-2 is a necessary prerequisite to use PHT3D. In fact, the user trained to PHREEQC-2 data structure and syntax will find it easier to understand the data organization in PHT3D and will be able to create his or her own reactive module. The latter task can be challenging for a new user of PHT3D.

In terms of software capabilities, problems of reactive transport in unsaturated systems cannot be solved with the present version of PHT3D. Moreover, similar to MT3DMS, flow problems have to be solved in advance with a flow simulator (typically MODFLOW). Therefore, effects on hydraulic properties caused by reactive processes cannot be taken into account.

Although the PMWIN GUI is probably the most intuitive among the ones I have tested, some aspects can be improved. In particular, the visualization of the simulation results could be given a “more appealing look” and the quality of the figures could be improved. Moreover, some graphical features such as representing different contour lines or color scales could be made less laborious.

## Overall

My overall impression is positive. PHT3D can be adopted by groundwater professionals and geochemists to solve an impressive number of water quality problems in saturated porous media. A user with sound process knowledge of groundwater transport and reactive processes can fully take advantage of the rich features of PHT3D. The code is particularly suited for researchers or experienced modelers who want to address rather complex multicomponent reactive transport processes including kinetic and equilibrium geochemical reactions that cause changes in the water chemistry and liquid-solid matrix interactions.

## Our Mission

The goal of Software Spotlight is to help readers identify well-written, intuitive, and useful software. Independent reviewers from government, industry, and academia try out full working versions of software packages and provide readers with a concise summary of their experiences and opinions regarding the capability, stability and ease-of-use of these packages.

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