Coupling PhreeqcRM with GoldSim: New perspectives for the Mining Industry

Benoît Paris (bparis@intera.com) and Ken Esposito (KEsposito@intera.com) from INTERA Inc.

Abstract

This paper illustrates the use of PhreeqcRM for computing various low-temperature aqueous geochemical calculations in GoldSim via an external dynamic link library (DLL). This coupling has been successfully benchmarked against examples from the PhreeqC manual and tested on a complex acid rock drainage conceptual case. While being completely dynamic and seamless, this implementation runs nearly as fast as native PhreeqC simulations allowing Monte Carlo calculations to fully propagate uncertainty in transport models. Furthermore, the approach is highly flexible and efficient as it enables the user to run numerous types of simulations without the need to change the DLL, thus saving potentially significant model preparation time. This tool offers mine operators the possibility to evaluate potential mine impacts and make operational decisions in real time using scientifically-defensible mechanistic models in a probabilistic framework.

1. Introduction

In the mining industry, GoldSim has been extensively used for various purposes, some of which include: environmental impact assessment, water management, production planning, operation optimization, and risk analysis (GTG, 2017). GoldSim is typically used to understand (or design) complex fluid or material movement by tracking the quantities of material moving around a system. When GoldSim is used to track fluid flow, operators and regulators are frequently concerned about aqueous chemical reactions as well as solution volumes. Although GoldSim can model mass transport and simple chemical reactions (using the Contaminant Transport Module), it cannot simulate complex geochemical reactions such as mineral precipitation and dissolution.

PhreeqC (Parkhurst and Appelo, 2013), on the other hand, is a computer program written by the USGS that is designed to perform a wide variety of aqueous geochemical calculations. PhreeqC can be used for speciation and saturation-index calculations, as well as reaction-path and 1D advective-transport calculations (including, irreversible reactions, mixing of solutions, mineral and gas equilibria, surface-complexation reactions, and ion-exchange reactions). The use of both GoldSim and PhreeqC together can in principle allow modelers to simulate solution flow and complex geochemical reactions, but until now, passing data back and forth between the two programs has been a challenge (Eary, 2007; Johnson et al., 2018).

The solution to this issue lies with the use of Dynamic Link Libraries (DLLs). GoldSim allows the user to develop separate program modules that can then be directly coupled with the main GoldSim algorithm. These user-defined modules are referred to as external functions and are linked into GoldSim as DLLs. Integrating an external program module into GoldSim requires the development of a "wrapper" or "shell" around the function to compile it into a DLL.

It is thus possible to access PhreeqC subroutines from GoldSim to solve complex geochemical problems. Such a coupling has already been described by Johnson et al. (2018). In the Johnson et al. approach, the DLL performs the following sequence to communicate between the programs, it: (1) pauses the GoldSim model and writes component concentrations received from GoldSim into a PhreeqC input file, (2) opens DOS, (3) runs PhreeqC to produce an output file, (4) closes DOS, (5) extracts results from the PhreeqC

output file and finally, (6) sends the information back to GoldSim. This process is repeated during all geochemical time-steps. The DLL provides basic approach for integrating the two programs. For example, the user must change the DLL source code to add a component, output parameters, or boundary conditions, while the periodic pausing of GoldSim to run PhreeqC causes the coupled program to run slowly.

PhreeqcRM (Parkhurst and Wissmeier, 2015) is a newer version of PhreeqC released in 2015 by the USGS. The geochemical modeling of PhreeqcRM is similar to PhreeqC; however, PhreeqcRM contains a "shell" of additional libraries that allow PhreeqC to interface with other computer codes. INTERA used this PhreeqcRM feature to develop a fully integrated GoldSim and PhreeqcRM water-balance and geochemical model. INTERA's model is similar to the previous coupling attempts in that a DLL is used to link the two programs. INTERA's DLL provides continuous communication between GoldSim and PhreeqC. Therefore, GoldSim does not need to stop running to run PhreeqC separately, resulting in runs up to 100 times faster than past DLL solutions.

2. Methodology

INTERA developed a DLL in C++ for performing geochemical calculations with PhreeqcRM which returns the results to GoldSim and carries out other transport processes (e.g. diffusion, advection).

The DLL executable, as well the entry function name within the DLL, are identified in the tab "Definition" of the GoldSim DLL element. The "Interface" tab specifies the input and output arguments exchanged between GoldSim and the DLL program. This coupling functions as follows:

(1) The DLL runs the PhreeqC input file and initializes the simulation.

(2) The chemical species are defined within the GoldSim file using the dedicated Species array.

(3) Boundary and initial conditions are defined in the PhreeqC input file and remain available in GoldSim during the simulation using PhreeqcRM dedicated functions. The GoldSim file dynamically assigns these conditions as vectors to each cell or medium constituting the model.

(4) User-defined outputs are specified in the "SELECTED_OUTPUT" block of PhreeqC input files. These values can be dynamically transferred as an array of values to GoldSim through the DLL.

(5) At the start of each GoldSim time step, GoldSim processes the calculations defined by the user (mixing of water, transport, etc.).

(6) The new aqueous concentrations information and speciation conditions are passed as input arguments to the DLL interface which calls the dedicated PhreeqcRM functions to initialize the speciation calculation in each cell.

(7) The PhreeqcRM DLL speciates the solution in each cell and returns updated aqueous concentrations to GoldSim as outputs of the DLL Element using the PhreeqcRM dedicated functions. All reaction cell solution concentrations are transferred to GoldSim as concentration vectors (of size number of components times the number of cells). The output results (i.e. pH, pe, etc.) selected by the user are also returned in the DLL by the corresponding PhreeqcRM function. All non-aqueous concentrations (precipitated, sorbed, etc.) are stored in the DLL for later use.

(8) The concentrations updated by PhreeqcRM are assigned to each cell of the GoldSim model before being processed by GoldSim through the cell network.

(9) Steps (5), (6), (7) and (8) are performed sequentially at each time step until the end of the simulation.

Our procedure allows a continuous communication between GoldSim and PhreeqC so that GoldSim does not need to stop running to launch PhreeqC separately. This results in runs up to 100 times faster than the previous DLL solution while the user can still use all GoldSim features such as visualization or pausing simulations. Furthermore, the approach is highly flexible and efficient as it enables the user to run numerous types of simulations without any need to change the DLL, thus saving potentially significant model preparation time.

3. Verification

Our PhreeqcRM DLL, and its implementation within GoldSim, has been benchmarked against the Phreeqc code (Version 3.5.0) using several examples (#7, 11 & 14) from the PhreeqC manual (Parkhurst & Appelo, 2013) to check the validity of our approach for simulating the following various coupled reactive processes:

- Formation of gas bubble during reduction of organic matter under fixed pressure or fixed gas phase volume in example 7;
- Ion exchange through advection in example 11;
- Phase-equilibrium, cation-exchange and surface-complexation reaction during advection in example 14.

For each test case, there was significant agreement between PhreeqC results and those obtained with our DLL coupling PhreeqcRM to GoldSim. The agreement between models can be demonstrated by comparing the results obtained for the ion exchange through advection example (Example 11). This example simulates the chemical composition of the effluent from a column containing a cation exchanger. Initially, the column contains a Na-K-NO_3 solution in equilibrium with the exchanger. The column is flushed with three pore volumes of $CaCl_2$ solution. Ca, K, and Na react to equilibrium with the exchanger at all times. Chloride is set as a conservative solute. The exercise considers 40 grid blocks of 0.002 m length in PhreeqC. The coefficient of dispersivity is set to 0.002 m.

For the comparison, a 15-cell model (plus one injection cell and one extraction cell) is built using the GoldSim software (**Figure 1**). The flow velocity is set at one pore volume per day. The simulation is carried out over 3 days to reproduce the 3 pore volumes simulated in the PhreeqC example. The DLL is called to update cell aqueous concentrations computed by PhreeqcRM before being advected by GoldSim.

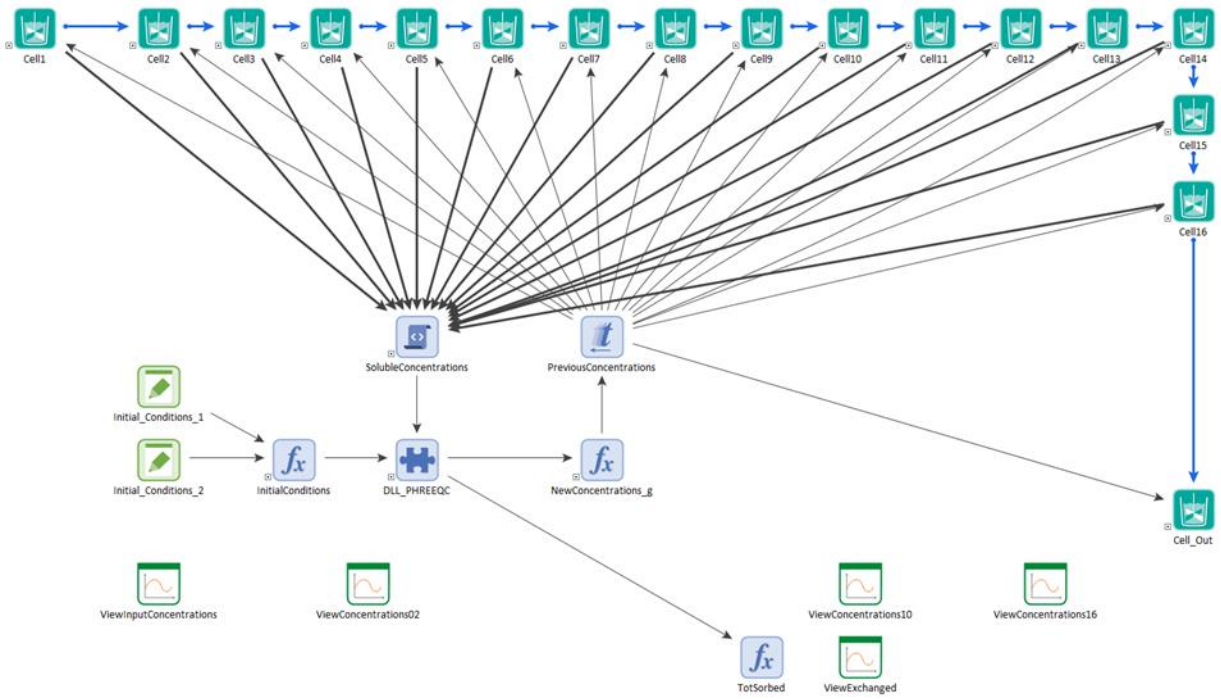

Figure 1. Network of GoldSim cells for simulating Example 11 of Parkhurst & Appelo, 2013

The simulation is performed using the thermodynamic database contained in the phreeqc.dat file. The simulation results are compared with the data provided in the PhreeqC output files according to the Figure 12 of the PhreeqC manual (Parkhurst & Appelo, 2013).

The GoldSim input file simulates mass transport as being purely convective. However, the numerical dispersion generated by GoldSim naturally adds a dispersion term which depends on the number of cells and on the duration of the time step. A similar dispersion to the one obtained with Phreeqc was achieved using a time step of 0.05 day in GoldSim.

Figure 2 presents a comparison of the PhreeqC results with those obtained in GoldSim using the PhreeqcRM DLL. At the beginning of the simulation, the sodium initially present in the column exchanges with the incoming calcium and is eluted as long as the exchanger contains sodium. Because potassium exchanges more strongly than sodium in the exchange reaction, potassium is released after sodium. Once all the potassium has been released, the concentration of calcium increases to the steady-state concentration in the effluent.

Figure 2 shows that GoldSim results are in good agreement with PhreeqC as GoldSim reproduces the Na depletion curve, and Cl and Na breakthrough curves as well as the potassium peak with good accuracy.

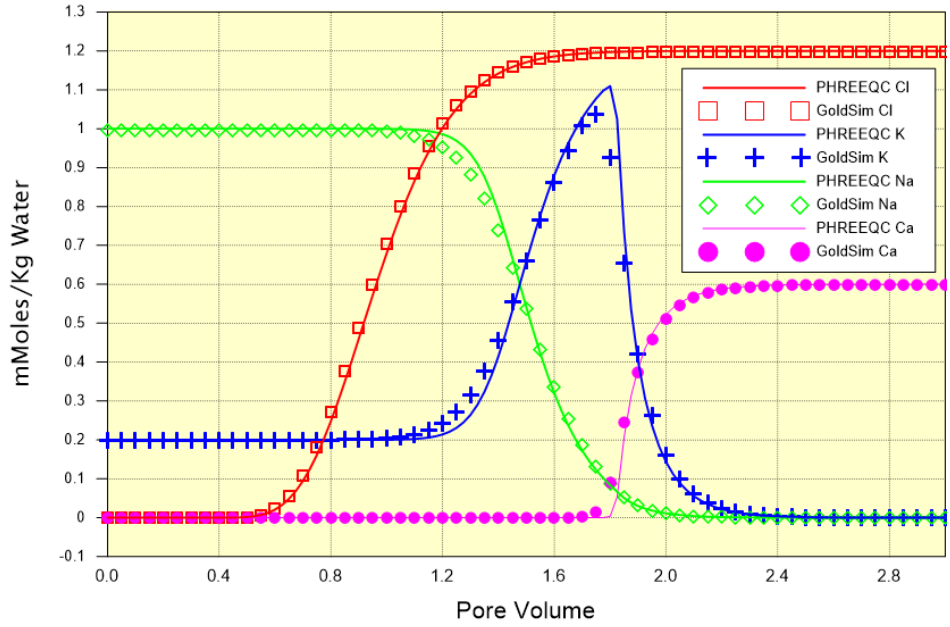

Figure 2. Comparison of Cl, K, Na and Ca aqueous concentrations (mmol/kg w) simulated by GoldSim coupled to PhreeqcRM to those simulated by PhreeqC considering Example 11 of (Parkhurst & Appelo, 2013)

4. Example Application

An example of the PhreeqcRM-GoldSim DLL in the context of an environmental impact assessment of a mining site is illustrated by considering a complex conceptual example taking advantage of the strength of both codes, that is, (i) the flexible probabilistic simulation framework of GoldSim and (ii) the ability to model complex geochemically-based release processes with PhreeqcRM.

In this test case, two in-pit backfill disposal facilities are assumed at a hypothetical mining site at closure (Figure 3). The backfill is assumed to be located entirely within the site vadose zone (VZ) with the groundwater table located at the bottom of each pit. In both cases, the mineralogy of the backfilled waste rock is identical, containing pyrite, K-Feldspar, quartz and minor amount of calcite, gypsum and amorphous $Fe(OH)_3$. Pyrite contains a probabilistic variable content of impurities (Zn and Cu). The scenario is designed to estimate the concentrations of Cu and Zn in groundwater downgradient of the second pit.

Backfill leaching is simulated considering:

- Infiltration of meteoric water (recharge) at a constant rate;
- Infiltration of O_2 through the backfill considering two different processes: (1) gaseous O_2 flux diffusing from the atmosphere and (2) aqueous O_2 flux dissolved in meteoric waters in equilibrium with the atmosphere. The two processes are simulated simultaneously;
- Acid rock drainage (ARD) due to pyrite oxidative dissolution controlled by a rate law;
- Release of Zn and Cu as a ratio of the amount of pyrite dissolved at every time step. This ratio is proportional to the initial metal content of the block within pyrite.

The leaching and transport processes resulting in Zn and Cu releases in groundwater is represented in GoldSim considering:

- Two 1-D vertical cell networks (VZ columns) corresponding to each tailing disposal where: (1) aqueous advection with a fixed recharge rate and (2) gas diffusion with a top boundary condition corresponding to equilibrium with the atmosphere;
- A horizontal 1-D cell network corresponding to the aquifer receiving in 2 mixing cells discharges from the VZ columns, which are next transported by advection at a constant flow rate.

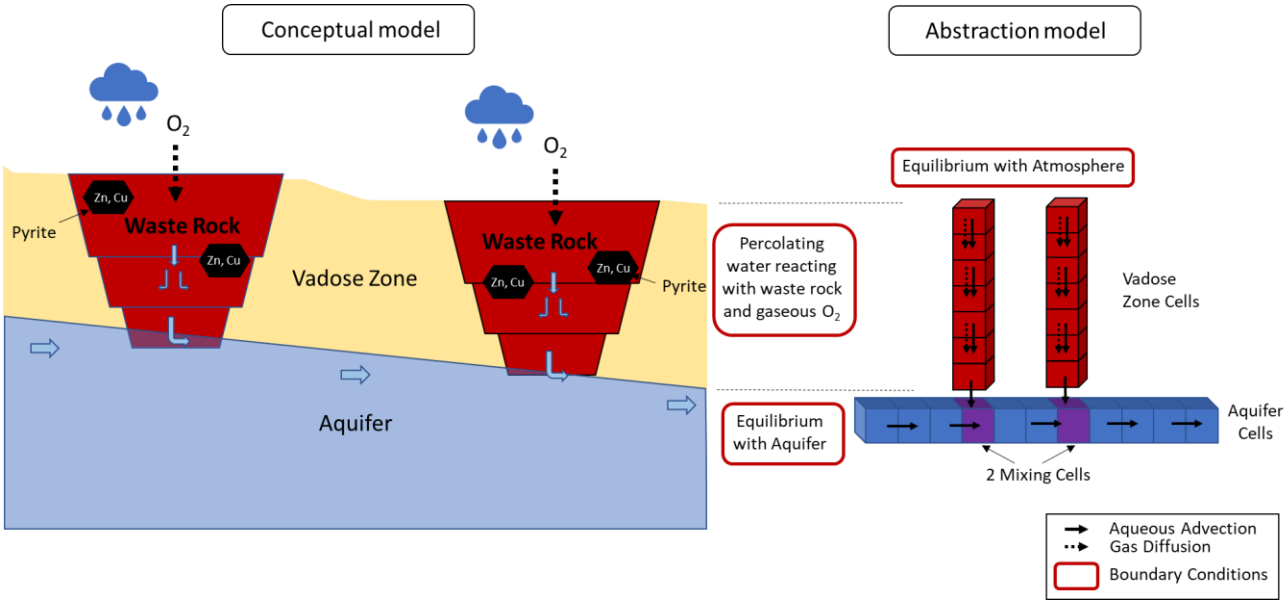

Figure 3. Conceptual model and corresponding abstraction model built in GoldSim for illustrating the simulation of ARD on a complex conceptual example using the PhreeqcRM DLL

This abstraction model aims at capturing the main physical and chemical processes controlling Cu and Zn releases as well as transport of these constituents to evaluate the possible impact of mine waste disposal through the groundwater pathway.

The development of this abstraction model in GoldSim coupled to PhreeqcRM with our DLL allows simulating breakthrough of acidic discharges due to oxidative weathering of pyrite in the vadose zone (Figure 4) reacting to O_2 diffusion through the backfill (Figure 5). The simulation results reflect the progress of the acidic front through the waste rock and its dilution in the aquifer. As expected, the downstream pile generates an additional load of acid resulting in a lower pH.

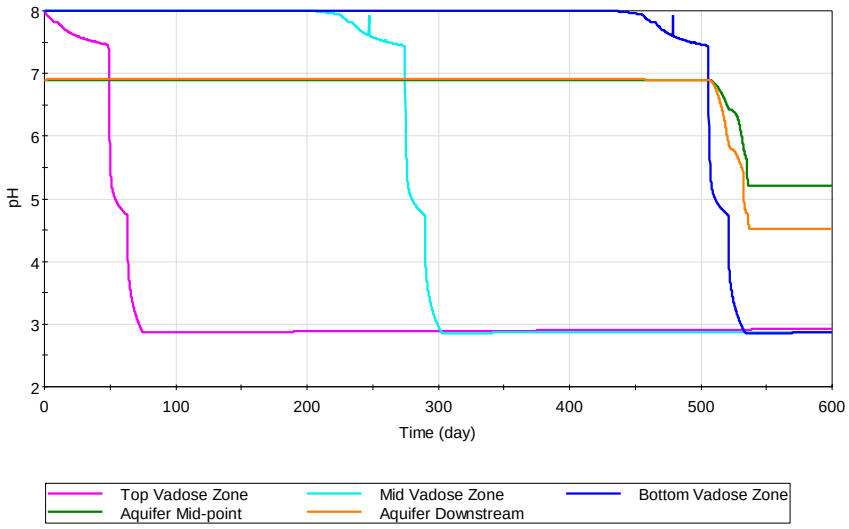

Figure 4. Simulated pH in the ARD test case in different GoldSim cells of the tow Vadose Zone columns and the aquifer cell network

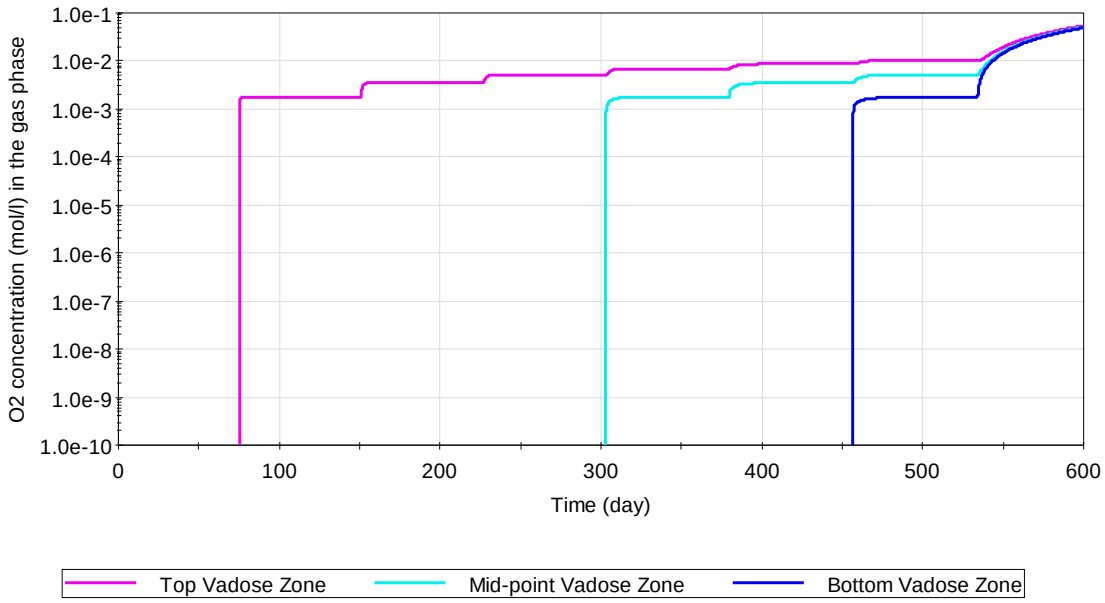

Figure 5. Simulated amount of O_2 (mol) in the gas phase in the ARD test case in different Vadose Zone GoldSim cells

A defensible evaluation of their environmental impact would require an uncertainty analysis associated with the Cu or Zn ratios (or of any other component of concern) in pyrite. Thus, a log normal probability distribution is next assigned in GoldSim to the ratio of both Cu and Zn concentrations within the pyrite. A hundred Monte Carlo simulations are performed for evaluating aqueous metal concentration in the vadose zone and in the aquifer. The results of these 100 simulations are provided in Figure 6 for Cu which shows that the order of magnitude range in Cu concentrations in both the vadose zone and the aquifer highly depends on the Cu ratio in pyrite.

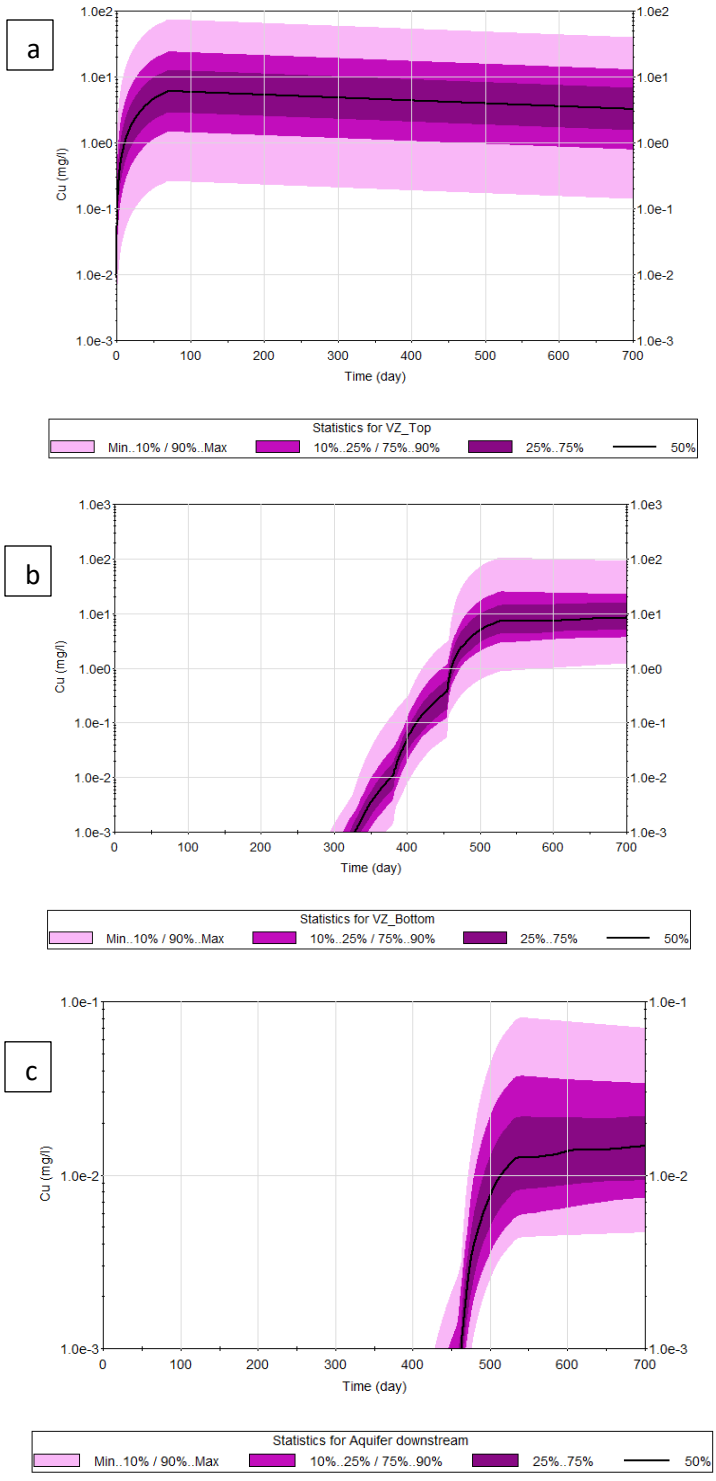

Figure 6. Simulated aqueous Cu concentration (mg/L) statistics (10%, 25%, 50%, 75% and 95% percentiles) in the ARD test case in different GoldSim cells of the Vadose Zone (VZ) columns (a: top cell, b: bottom cell) and the aquifer (c: downgradient cell).

5. Conclusion

The integrated simulation tool presented in this paper allows the site-specific flow system data to be combined with a geochemical model to depict geochemical reactions that will likely occur in dynamic, real-world water balance and mixing scenarios. Our integrated model is ideal for solving mixing, chemical equilibrium and aqueous speciation problems in complex systems at operating or planned facilities. This seamless approach largely simplifies the model setup while minimizing calculation times compared to previous DLL approaches. This tool can be used to evaluate mine or nuclear waste disposal concepts and to make real-time operational decisions using scientifically defensible, mechanistic models through a probabilistic framework.

References

Eary, T. (2007). Linking GoldSim with the PHREEQC Geochemical Model with a Dynamic Link Library. *GoldSim User's Conference.* San Francisco, California: GoldSim Technology Group LLC.

GTG. (2017). *GoldSim: Engineering and Environmental Simulation Software for the Mining Industry.* Seattle, Washington: GoldSim Technology Group LLC.

Johnson, B. C., Rohal, P., & Eary, T. (2018). Coupling PHREEQC with GoldSim for a More Dynamic Water Modeling Experience. *11th ICARD | IMWA | MWD Conference – "Risk to Opportunity"*, (pp. 1081-1086). Pretoria, South Africa.

Parkhurst, D. L., & Wissmeier, L. (2015). PhreeqcRM: A reaction module for transport simulators based on the geochemical model PHREEQC. *Advances in Water Resources, 83*, 176-189.

Parkhurst, D., & Appelo, C. (2013). Description of input and examples for PHREEQC Version 3 - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. In U. G. Methods, *book 6, chap. A43* (p. 497). Denver, Colorado: USGS.