

# Linking a Simulated Annealing Based Optimization Model with PHT3D Simulation Model for Chemically Reactive Transport Processes to Optimally Characterize Unknown Contaminant Sources in a Former Mine Site in Australia

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## Abstract

Historical mining activities often lead to continuing wide spread contaminants in both groundwater and surface water in previously operational mine site areas. The contamination may continue for many years after closing down the mining activities. The essential first step for sustainable management of groundwater and development of remediation strategies is the unknown contaminant source characterization. In a mining site, there are multiple species of contaminants involving complex geochemical processes. It is difficult to identify the potential sources and pathways incorporating the chemically reactive multiple species of contaminants making the source characterization process more challenging. To address this issue, a reactive transport simulation model PHT3D is linked to a Simulated Annealing based the optimum decision model. The numerical simulation model PHT3D is utilized for numerically simulating the reactive transport process involving multiple species in the former mine site area. The simulation results from the calibrated PHT3D model are illustrated, with and without incorporating the chemical reactions. These comparisons show the utility of using a reactive, geochemical transport process' simulation model. Performance evaluation of the linked simulation optimization methodology is evaluated for a contamination scenario in a former mine site in Queensland, Australia. These performance evaluation results

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illustrate the applicability of linked simulation optimization model to identify the source characteristics while using PHT3D as a numerical reactive chemical species' transport simulation model for the hydro-geochemically complex aquifer study area.

### Keywords

Groundwater Contamination, Source Characterization, PHT3D, Linked Simulation Optimization Methodology, Chemically Reactive Transport Simulation, Mine Site Contamination, Simulated Annealing

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## 1. Introduction

Characterization of unknown contaminant sources is an essential first step for effective remediation and management of contaminated groundwater resources. Linked optimization methodologies are widely used for characterization of unknown groundwater contaminated source, in terms of flux magnitude, location and activity history in contaminated aquifers [1] [2]. Transport of contaminants comprising of multiple chemically reactive species, in contaminated groundwater systems, is complex and highly non-linear process. Therefore, robust numerical simulation models incorporating chemical reactions of the contaminant species in the transport process are necessary in linked simulation-optimization methodology. The purpose of the present study is to propose and evaluate a linked simulation optimization methodology, linking a multiple species' reactive transport simulation model to an optimization model for unknown groundwater source characterization. The methodology is evaluated for a former mine site in Queensland, Australia involving multiple reactive contaminant species undergoing complex geochemical reactions.

PHREEQE [3], a reactive, chemical transport model, is a widely used computer code using the two-step procedure for solution. Tebes-Stevensa, Valocchia [4] developed a reactive transport simulation code (FEREACT) to investigate the chemical reaction-based transport for cobalt and EDTA (Ethylene Diamine Tetra-acetic Acid) through an iron oxide-coated sand column. Prommer, Barry [5] presented numerical computation results for both reactive and non-reactive chemical species transport in an aquifer site contaminated by hydrocarbons. They used the PHT3D [6] model, coupling the non-reactive part of MT3DMS [7] model with the reactive geochemical model PHREEQC-2 [8]. Moreover, MT3DMS is widely used in various chemical reactive transport simulators such as RT3D [9], SEAM3D [10], BioRedox [11], DART [12], PHAST [13] and PHWAT [14]. These models have been coupled with saturated media flow simulation models. On the other hand, one-dimensional movement simulators such as HP1 [15] and RICH-PHREEQ [16] have been used in recent years as unsaturated porous media flow models incorporating detailed geochemistry. The numerical model HYDROGEOCHEM 5.0 [17] [18] for simulating transport of

reactive chemical species in an aquifers, has also gained popularity in recent years [19] [20] [21] [22]. Wissmeier and Barry [23] presented a software tool for groundwater flow and transport movement in combination with geochemistry in two and three-dimensional systems. Their study coupled the reaction-based transport equations used in IPHREEQC [24], to the finite element method solver COMSOL [25] for the simulation of flow and transport processes in the form of a computer code. In this study, the PHREEQC/MT3DMS-based reactive multi-component transport model PHT3D [26] is used to simulate the reactive transport process and it is linked to Simulated Annealing (SA) based optimization algorithm to identify the optimal source characteristics.

Initial attempts for identifying the flux magnitude, location and activity duration of unknown groundwater pollution sources utilized linear optimization model based on linear response matrix approach [27] and statistical pattern recognition [28]. Other methodologies proposed latter include: determining optimal estimates of the unknown model parameters and source characteristics using non-linear maximum likelihood estimation based inverse models [29]; source identification using embedded nonlinear optimization technique [30] [31] [32]; classical optimization based approach [33]; Genetic Algorithm (GA) based optimization approach [34] [35]; Artificial Neural Network (ANN) approach; heuristic harmony for source identification [36]; Simulated Annealing (SA); and Adaptive Simulated Annealing (ASA) based linked optimization algorithm for source identification [1] [22] [37] [38] [39]; and differential evolution algorithm for groundwater source identification [40] [41]. Optimization techniques for solving source identification problems are reviewed in Chadalavada, Datta [42], Ketabchi and Ataie-Ashtiani [43] and Sreekanth and Datta [44].

A linked simulation optimization approach is implemented in the present study. This approach links multiple species reactive transport simulation model with SA based optimum decision model. Performance of its efficiency and reliability is evaluated for a contaminated aquifer site hydro-geologically representing an abandoned mine site in Queensland, Australia.

## 2. Methodology

In this study, chemically reactive transport process is simulated using PHT3D, and is compared with non-reactive transport process in complex study area, such as mine site area. The proposed simulation model is then utilized in the linked simulation-optimization based methodology for simulating the transport process of the contaminant species in the aquifer for unknown groundwater source characterization in the contaminated aquifer. The following two main steps explain the proposed methodology development and its application to a mine site in Queensland, Australia. The first step comprises of implementing the flow and transport simulation model based on the estimated hydrological and geochemical properties of the mine site area. MODFLOW is used as a flow simulation model. PHT3D as a numerical coupled physical and chemical transport process simulator is utilized to simulate the reactive chemical transport

processes in the contaminated aquifer. The flow simulation results are compared with field measurement data [45] to obtain acceptable calibration results based on measured flow data. In the second step, the simulation model is linked to Simulated Annealing (SA) optimization algorithm within a linked simulation-optimization framework to obtain the optimal source characteristics in terms of location, flux magnitude and time of activity.

## 2.1. Simulation of Groundwater Flow and Physical Transport

The widely used three-dimensional numerical flow simulation model MODFLOW [46] is used for simulation of the flow in the selected aquifer study area. The MODFLOW can simulate steady and transient flow. As several variables affect the groundwater flow, it is generally modelled by the spatial and temporal governing partial differential equations.

MT3DMS [7] is a modular three-dimensional transport model used to simulate the transport process. It is capable of incorporating dispersion, advection, and chemical reactions of dissolved chemical species in groundwater systems. MT3DMS utilizes the flow simulation MODFLOW to compute the pollutants transport processes. In this study, MT3DMS is used for physical transport process. Equation (1) [47] represents the three-dimensional reactive transport process in groundwater systems:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial c}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C) + \frac{q_s}{\theta} C_s + \sum_{k=1}^N R_k \quad (1)$$

where

$C$  is the pollutant concentration ( $M \cdot L^{-3}$ );

$t$  is time (T);

$x_i$  is the Cartesian coordinate axis  $i$  (L);

$D_{ij}$  is the hydrodynamic dispersion coefficient tensor ( $L^2 \cdot T^{-1}$ );

$v_i$  is the linear pore water or seepage velocity ( $L \cdot T^{-1}$ );

$q_s$  is volumetric flux of water per unit volume of aquifer (positive for source and negative for sinks ( $T^{-1}$ ));

$C_s$  is the source or sinks concentration ( $M \cdot L^{-3}$ );

$\theta$  is the porosity of the porous medium (dimension less);

$R_k$  is the chemical reaction term representing each of the  $N$  species ( $M \cdot L^{-3} \cdot T^{-1}$ ).

The multiple component multiple species reactive transport model PHT3D [48] is utilized in this study or linking with the optimal source characterization model. PHT3D combines MT3DMS and PHREEQC [49]. The PHREEQC component allows for a variety of low temperature aqueous geochemical reactions. The PHT3D is used in this study to simulate both physical and chemical transport processes in the contaminant aquifer. In PHT3D several species can be integrated. The number of species and their initial concentrations on basic transport package need to be changed compared the MT3DMS module. It is also required to add the concentrations for each new species in the source/sink package. The chemical equations [48] which are solved by PHREEQC are:

$$\frac{\partial c}{\partial t} = r_{\text{reac}} \quad (2)$$

$$C = c + \sum_{i=1,n} Y_i^s s_i \quad (3)$$

where

$r_{\text{reac}}$  is a source/sink chemical reaction rate term;  $c$  is the concentration (molar) of the uncomplexed aqueous component,  $s_i$  is the concentration (molar) of the  $i^{\text{th}}$  complexed species,  $n$  is the number of dissolved chemical species  $t$  complexed with the aqueous component,  $Y_i^s$  is the stoichiometric coefficient of the aqueous component in the  $i^{\text{th}}$  complexed species.

## 2.2. Source Characterization Model Using Simulated Annealing Algorithm

The evolutionary optimization algorithm Simulated Annealing (SA) [50] is used as the optimization algorithm for optimal solution of the contaminant source characterization model linked with PHT3D as the reactive transport simulation model. The SA is based on analogy with thermodynamics. The analogy is with the process of slowly cooling (annealing) molten metals to a state of low energy. The important features of SA which make it a potentially powerful optimization algorithm are: it can handle multiple optima and the algorithm can move uphill, thus escaping from local optima to find global optima. The capability of SA for convergence to a global optimal solution in complex, multivariate problems involving higher degree non-linear functions makes it an ideal choice for solving unknown groundwater pollution source characterization problems.

In the search process of the SA algorithm, a random nearby solution is replaced utilizing the probability depending on the difference between the corresponding function values and algorithm control parameters (initial temperature, temperature reduction rate, etc.). Here, SIMANN a FORTRAN code developed by [51] is utilized as the optimization algorithm.

A new linked simulation optimization model linking SIMANN, the SA based optimization algorithm with reactive transport simulation model (PHT3D) is developed for this study. **Figure 1** shows the schematic linking of the reactive transport simulation model (PHT3D) with the SA based optimization model in a linked simulation-optimization framework. The reactive transport simulation model PHT3D utilizes the flow field simulated by MODFLOW.

In order to achieve computational efficiency, the SA algorithm parameters need to be suitably specified. The SA parameters needed to be specified include the following:

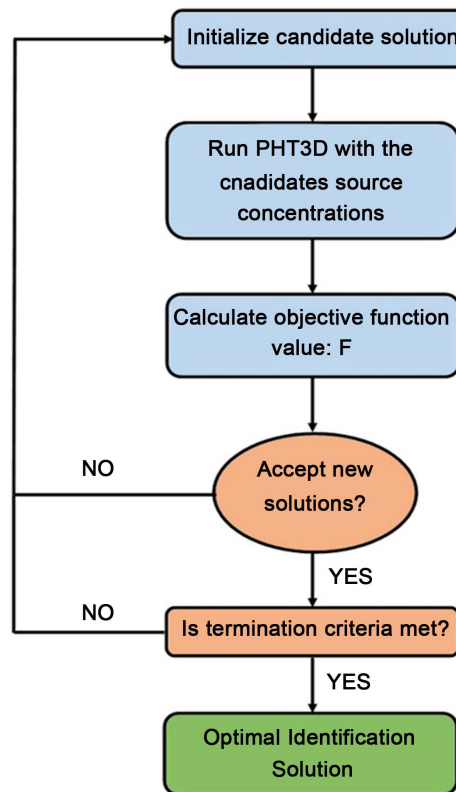
The initial temperature (T);

The error tolerance for termination (called EPS);

The temperature reduction factor (RT).

The objective function of the optimal source characterization model can be described as [38] [39]:

$$\text{Minimize } F1 = \sum_{k=1}^{n_k} \sum_{job=1}^{n_{ob}} \text{Abs}(C_{\text{est}iob}^k - C_{\text{obs}iob}^k). \quad (4)$$



**Figure 1.** Representative flowchart of the linked simulation-optimization model using simulated annealing algorithm.

Subject to the implicit constraints defining the simulation model of the flow and reactive transport processes [38],

where

Abs is the absolute difference;

$C_{estiob}^k$  is the estimated concentration simulated by the transport model at monitoring point  $iob$  and at end of the time period  $k$  (mole/L);

$n_k$  is the number of time steps for monitoring;

$n_{ob}$  is the total number of monitoring points;

$C_{obsiob}^k$  is the observed concentration at monitoring location  $iob$  and at the end of the period  $k$  (mole/L).

### 3. Performance Evaluation

Performance of the proposed source characterization methodology is evaluated for a polluted aquifer study area hydrogeologically resembling the Mount Morgan, a former mine site in Queensland, Australia. The hydrogeological and geochemical parameters for the study area is obtained from previous studies [Esfahani and Datta 22; Wels and Findlater 45].

#### 3.1. Polluted Aquifer Site Description

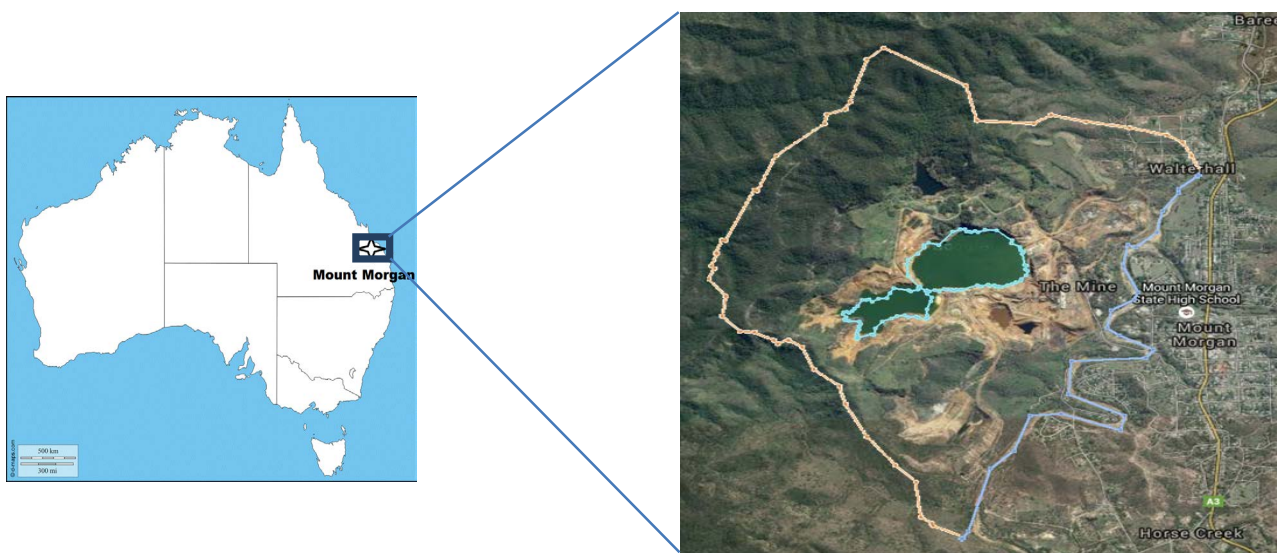
Mount Morgan deposit is situated in the Calliope Block, which is an important tectonic zone, and occurs along the eastern margin of Australia [52]. The geolo-

gy of Mount Morgan mainly constitute of volcanic and metamorphic rocks (quartz, feldspar, basalt etc.). Mount Morgan mine site was operational for a period close to 100 years starting 1889 till 1990. It was once a large mine located in Queensland, Australia (Figure 2). It is surrounded by Dee River on the downstream of the mine site which flows into the Fitzroy River. The ground topography generally slopes from north east towards the river in south. Gold, silver, and copper ores were primarily mined during its operational life time.

The climate at the site show seasonal variation with average maximum monthly temperatures ranging from 32°C in January to 23.1°C in July. The average annual rainfall is approximately 815.5 mm of which a large portion is received during the wet season from November until March. During the winter season the average rainfall is in between 22 and 43 mm, while, from October to March, the rainfall may exceed 100 mm [53].

Hazardous contaminants which mainly remain buried deep in the earth's crust are exposed to the atmosphere due to open cuts, waste deposits from the ore and the created tailing dams. These hazardous compounds travel through the drainage path and contaminate the groundwater as well as surface water in the vicinity of the mine site. Once these hazardous contaminants and their components interact with water (in from of rainfall or get collected in the tailings dam as a result of overland flow), generate Acid Rock Drainage (ARD) and Acid Mine Drainage (AMD). Although several remediation measures were undertaken for this area, accurate contaminant sources characterization of ARD and AMD, physical and chemical behaviors of the contaminants in the groundwater system all along the transport pathway are required to achieve effective and efficient remediation strategies, and for optimal groundwater management.

During the early 1900s there was little or no environmental regulation. Heightened mining activities with no environmental regulations have left a legacy of impacts on the Dee River and the site itself. The current environmental pollution



**Figure 2.** Plan view of the contaminated aquifer area in Queensland, Australia.

can possibly be attributed to acid and metalliferous drainage also known as acid mine drainage. Such pollution occurs when sulfidic rocks, such as pyrite, are exposed to atmospheric water and oxygen rather than being isolated as crystalline rock underground [54]. This exposure leads to the formation of sulfuric acid, which in turn dissolves high concentrations of salts and hazardous materials, such as copper, arsenic, nickel, cadmium, zinc, aluminum, iron and many more. Acid mine drainage is a very toxic concoction of hazardous chemicals threatening aquatic ecosystems and biodiversity [19]. Starting in 1982, tailings were dredged from Sandstone Gully and treated using the Carbon-In-Pulp (CIP) process for recovery of gold, before being backfilled into the open cut. After final closure in 1990, the partially backfilled open cut (and Sandstone Gully) were allowed to flood by natural inflows (surface runoff and groundwater inflow) [54].

A major part of the waste rock deposit from the open cut is acid-forming as it contains up to 10% sulphur with sulphide minerals such as pyrite ( $\text{FeS}_2$ , also called fool's gold). The term "Mundic" describes a copper ore that begins to melt. Historically, the Mundic tailings were placed into Mundic Creek drainage channel and the other tailings were placed into tailing dams. Geochemical tests carried out [55] show that the Mundic Red tailings were unreactive whereas the Mundic Grey tailings are highly reactive releasing sulphate ( $\text{SO}_4^{2-}$ ), iron (Fe), aluminum (Al) and copper (Cu). If tailings were deposited without proper containment, this would be a real environmental issue [54] [56]. Thus, it is evident that the mining activity at Mount Morgan throughout its period of operation produced many chemically reactive hazardous pollutants in large quantities leading to environmental pollution issues.

The major ore at the site is Devonian Mount Morgan Tonalite which is almost impermeable. Devonian rhyolitic volcanic deposits have provided Au-Cu mineralization. Permeability of the porous medium comprise of primary permeability resulting from the formation of rocks (mostly considered negligible in rock formations in Australia) and secondary permeability controlled by the presence of faults and fractures in the rock strata. Compartmented dykes in the area causes groundwater discharge deeper into the mine site [56]. Mining activities for extracting Pyrite ore mineral has resulted in large waste deposit comprising mainly of quartz-pyrite waste rocks. Sulphide oxidation, pyrite waste rock exposition, and also tailings at the site generate hazardous acidic and metal-rich drainage. The absence of carbonate rocks to naturalize groundwater pH has exacerbated this situation [57]. The geology of the site has been described in detail in [56] [58] [59].

The high pH values as associated with AMD result in dissolution of metals (e.g., copper, iron, aluminum) in the water. As and when the pH value rises and become closer to neutrality, the dissolved metals precipitates leaving behind a yellow-orange substance or a light-blue substance as in **Figure 3**.

The groundwater flow occurs mainly in the permeable mine waste dumps and in shallow bedrocks that may have been fractured by mining and have become permeable. The area consists of 4 layers [45]: waste rock dumps and tailing; highly





**Figure 3.** Acid mine drainage consequences in the dee river.

weathered bedrock; partially weathered bedrock; and tight bedrock. Groundwater flow is simulated with specified hydrogeological parameters as given in **Table 1**. An aerial view of the mine site is shown in **Figure 4**.

The flow model is calibrated against the available head data. The flow models were calibrated with the aim to assign proper head boundary conditions, and estimate the spatially and temporally averaged recharge. The calibration was partially based on the earlier flow model calibration for the same study area as reported in [60]. The flow model was calibrated against limited and sparse measured hydraulic head field data available for the site. Hydraulic head measurement data recorded between 2002 and 2003 [45] from 11 observation locations spread across the impacted area were used for model calibration. A portion of the average rainfall intensity per year is specified as recharge to the groundwater aquifer for calibration of the flow simulation model. Calibration targets were set to be within two meter intervals of the observed hydraulic head value with a confidence level of 90 percent. The model boundary conditions were manually adjusted based on best judgment of the existing boundary conditions, to achieve the calibration targets. **Figure 5** shows the calibration results in form of box plots. More rigorous calibration can be undertaken if a large number of spatiotemporal field measurement data is available.

This study only serves as a demonstration, which includes the implementation of the flow and multispecies reactive transport simulation model in a hydrogeologic contaminated site with multiple sources of contamination. Copper and sulfate are considered as two representative chemically reactive species, although more species and more complex chemical activities are present in this site. This illustrative application is used to demonstrate the limited application of the linked simulation optimization based methodology for unknown source charac-

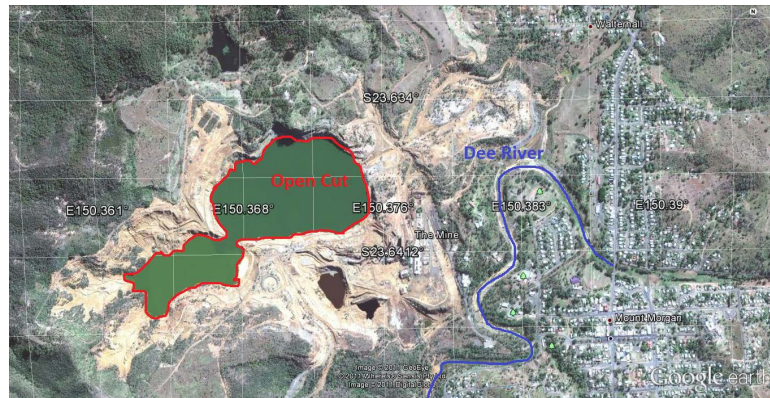


Figure 4. Open cut and dee river illustration at mount morgan site.

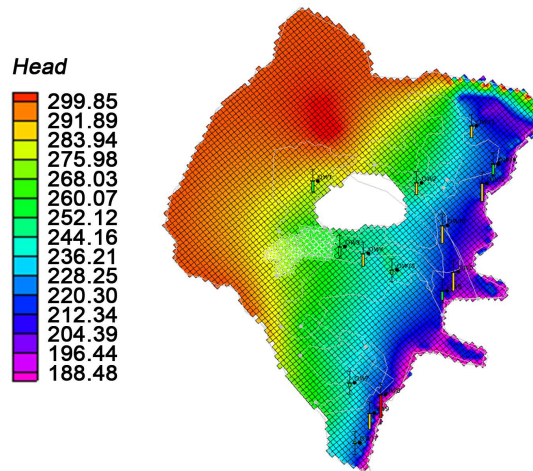


Figure 5. Flow simulation and calibration results [21].

Table 1. Hydrogeologic parameters used in flow and transport models of the study area [21].

Parameters	Unit	Values
Length of study area	m	4000
Width of the study area	m	4000
Saturated thickness	m	variable
Grid spacing in $x$ direction	m	40
Grid spacing in $y$ direction	m	40
Number of layer in $z$ direction	-	4
Horizontal $K$ :	-	
Layer 1	m/d	0.98673
Layer 2	m/d	0.163555
Layer 3	m/d	0.014369
Layer 4	m/d	0.009365
Vertical $K$ all layers	m/d	0.2
Effective porosity all layers		0.28
Longitudinal dispersivity	m	20
Transverse dispersivity	m	4
Initial [pollutant]	mg/L	0

terization in such a complex aquifer system, while incorporating chemically reactive transport processes. **Table 2** shows the chemical equations related to the contaminant transport processes in the contaminated aquifer.

### 3.2. Pollutant Transport Simulation in the Mine Site Area

To demonstrate the role of chemically reactive transport process with chemical reactive multi-species in the contaminated aquifer, the reactive contaminant transport simulation results are compared with the simulation model results incorporating only the physical and chemical transport processes (MT3DMS). PHT3D is utilized to simulate the chemically reactive transport process in the contaminated aquifer. For the purpose of implementation, and to synthetically generate simulated concentration measurement data at specified monitoring locations, specified pollutant concentrations are specified along the boundary of the mining pit. The transport model uses the flow field generated by the flow simulation model to predict the movement of the pollutants in the impacted area of the aquifer over a specified five year period.

The Dispersion Package in MT3DMS and PHT3Dis utilized to simulate the effect of advection, longitudinal dispersion, transverse dispersion and the effective molecular diffusion. The relevant parameter values are given in **Table 1**. Advection and dispersion occur in every transport process for both non-reactive contaminants and chemical reactive contaminants. But for transport of the reactive species, chemical reactions also impact the spreading and movement of the pollutant plume. These reactions are handled by using PHT3D reactive species transport simulation model.

Since advection and dispersion are not impacted by reactions, the input parameters for these two aspects of the transport are the same as in advective and dispersive transport process. PHT3D handle the reactions that the user need to consider. In the developed linked simulation optimization model developed incorporating PHT3D, the chemical reactions need to be specified in a database file, which will be used by the model during the simulation process.

There are certain norms for creation of the reactions input data base for PHT3D. This reaction database enables consideration of the specified reactions.

**Table 2.** Copper reactions and constants of reaction [22].

Reactions	Constant rate (log K)
$\text{Cu}^{2+} + \text{e}^{-} = \text{Cu}^{+}$	2.72
$\text{Cu}^{2+} + \text{H}_2\text{O} = \text{Cu}(\text{OH})^{+} + \text{H}^{+}$	-9.19
$\text{Cu}^{2+} + 2\text{H}_2\text{O} = \text{Cu}(\text{OH})_2 + 2\text{H}^{+}$	-16.19
$\text{Cu}^{2+} + 3\text{H}_2\text{O} = \text{Cu}(\text{OH})_3^{-} + 3\text{H}^{+}$	-26.9
$\text{Cu}^{2+} + 4\text{H}_2\text{O} = \text{Cu}(\text{OH})_4^{2-} + 4\text{H}^{+}$	-39.6
$\text{Cu}^{2+} + \text{SO}_4^{2-} = \text{CuSO}_4$	2.36

In this study, reaction databases were utilized to simulate copper related contamination. Once the database is created, it has to be linked to PHT3D in order to launch the simulation. In the Basic Transport Package for PHT3D, defining species also implies choosing a reactions database. This is where the database can be linked to the simulation program. The different active species existing in the databases is then considered in the simulation (Table 2).

Since every species (even the products of the reaction) are considered, the initial concentration must be defined for every species in all the areas and in the pit (a potential source of contamination). As only copper is considered in this study, the species that are considered for the reactions are  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$  and water for the reagents. Water does not have to be defined as a species; indeed it is part of the flow model. Then the products of the reactions between copper and water and copper and sulphate are:  $\text{Cu}(\text{OH})^+$  (named Cu(3) in the database),  $\text{Cu}(\text{OH})^2$  (named Cu(4)),  $\text{CuOH}_3^-$  (named Cu(5)),  $\text{Cu}(\text{OH})_4^{2-}$  (named Cu(6)) and  $\text{CuSO}_4$  (named Cu(7)). There is also  $\text{Cu}^+$ , which is called Cu(1) in the reaction database, which is formed due to the presence of electrons.

Initial value for these species in the study area is defined in Figure 6. A concentration of  $1.0 \times 10^{-30}$  Mole/L is set in order to avoid numerical error because of a zero concentration for all the compounds. pH and pe also have to be defined. An arbitrary value of 6 is set for the pH because the media is rather acidic than neutral with heterogeneous values. The pe is set at 13.5. The Source/Sink Mixing Package also need to be change.

### 3.3. Comparison of Advection Dispersion and Reaction

The concentrations of all the reaction products in the pit are the same as in all the rest of the study area. Indeed, only copper (II) is assumed to originate from the pit for this simulation. When these parameters are defined, the simulation is

The screenshot shows the 'Point sources/sinks' configuration window. It includes a 'Recharge...' button, an 'Evapotranspiration...' button, and a dropdown menu for selecting species. Below this is a table with the following data:

row	col	layer	type	S(6)	Cu(2)	Cu(1)	Cu(3)	Cu(4)	Cu(5)	Cu(6)	Cu(7)	pH	pe
1	49	22	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5
2	48	22	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5
3	44	22	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5
4	49	23	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5
5	48	23	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5
6	47	23	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5
7	45	23	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5
8	44	23	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5
9	43	23	2	constant concentration	0.137	0.0007	1.0e-030	1.0e-030	1.0e-030	1.0e-030	1.0e-030	2.76	13.5

Figure 6. Screen shot of the Source/Sink Mixing Package concentrations input for the reaction part.

ready to be launched. The plume contours in the study area are obtained based on advection, dispersion, and chemical reaction in the transport process. To show the contaminant transport contours with better resolution, adjust the area close to the pit it showed in Figures 7-9. Figure 7 shows the contaminants spreading with time from North to South. Indeed, with advection, the pollutants spread following the direction of flow, thus from North to South.

Figure 8 represents the simulation results obtained at the beginning and at the end of the simulation based on advection and dispersion. Figure 8 shows the ef-

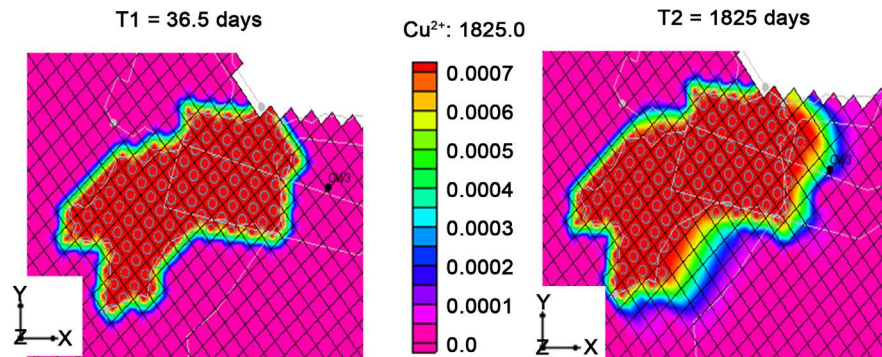


Figure 7. Evolution of the contaminant plume from the Open Pit between T1 = 36.5 days and T2 = 1825 days with only advection.

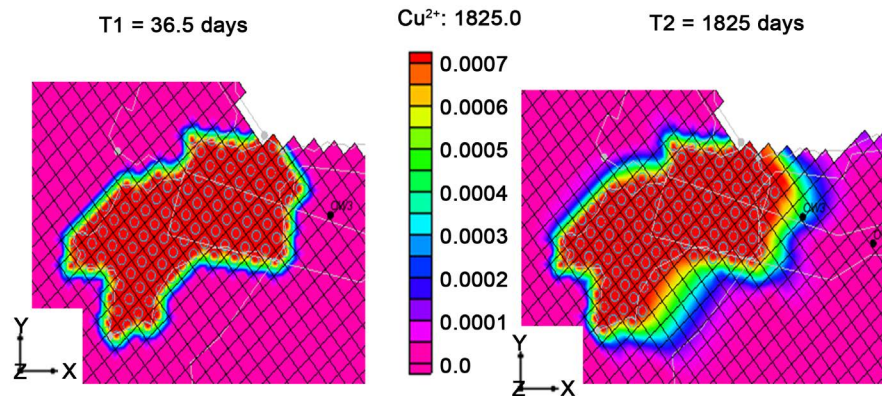


Figure 8. Evolution of the contaminant plume from the Open Pit between T1 = 36.5 days and T2 = 1825 days with advection and dispersion.

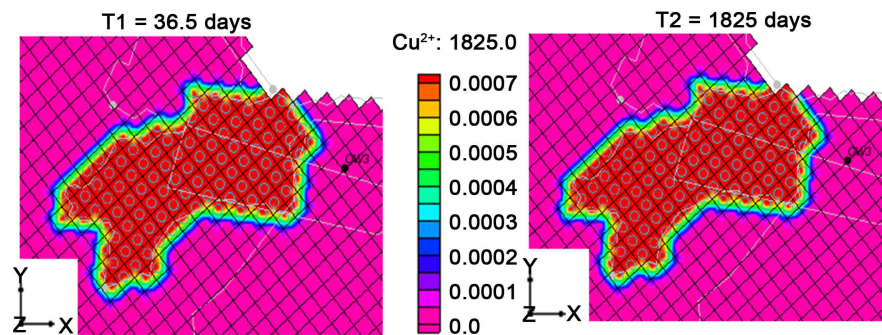


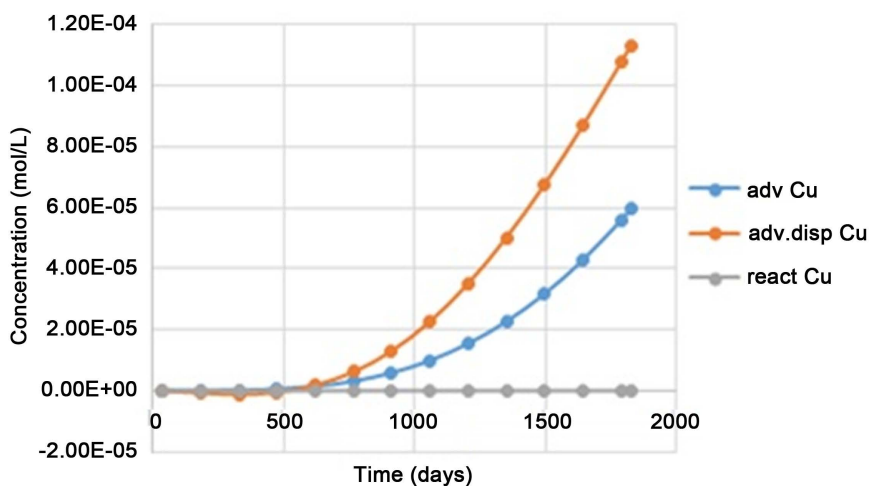
Figure 9. Evolution of the contaminant plume from the Open Pit between T1 = 36.5 days and T2 = 1825 days with advection, dispersion and chemical reaction.

fect of dispersion as well. The spread of the pollutant plume is similar to that observed with advection, meaning that the spread occurs generally from North to South, following flow direction. However, with the added effect of dispersion the plume is more diffuse compared to that with only advection. Indeed, with dispersion, the contaminant spreading follows the general direction of flow as well as the longitudinal and transverse directions. Thus the dispersivity allows the contaminant to reach locations in the site further than that with advection.

Subsequently, the reaction process is added to the simulation process, in order to see the effect of reactive chemical species transport with  $\text{Cu}^{2+}$ . **Figure 9** show the simulation results at the beginning and at the end of the simulation time span. **Figure 9** shows that the contaminant spread is smaller compared to that for advection and dispersion without reaction. The contaminant concerned in this study is the  $\text{Cu}^{2+}$ . However,  $\text{Cu}^{2+}$  chemically reacts with water and sulphate in the site. Thus it is because copper ( $\text{Cu}^{2+}$ ) is transformed to other forms of copper or products, and there is an associated loss of mass resulting in smaller concentrations when the reactive transport process is incorporated.

To illustrate a better comparison of different transport processes (Advection, Dispersion, and Chemical Reaction), the  $\text{Cu}^{2+}$  concentration in particular at different times is considered using each variation in the transport process. For this purpose, the point A (layer (L) 2, row (R) 53 and column (C) 30) is selected. This point is chosen because it is situated east of the open pit, where the contaminant spread is evident and the distinction between the advection, dispersion and reaction is prominent (**Figure 10**).

As shows in **Figure 10**, for the same point, the  $\text{Cu}^{2+}$  concentration is larger with advection and dispersion and smaller with copper reactions. Indeed, the advection allows the contaminants to be spread following the flow direction in the site. However, due to dispersion in addition to advection, at certain locations and time, larger total quantity of contaminant species may be transported, compared to advection alone. Thus, at the point A, the dispersion advection process

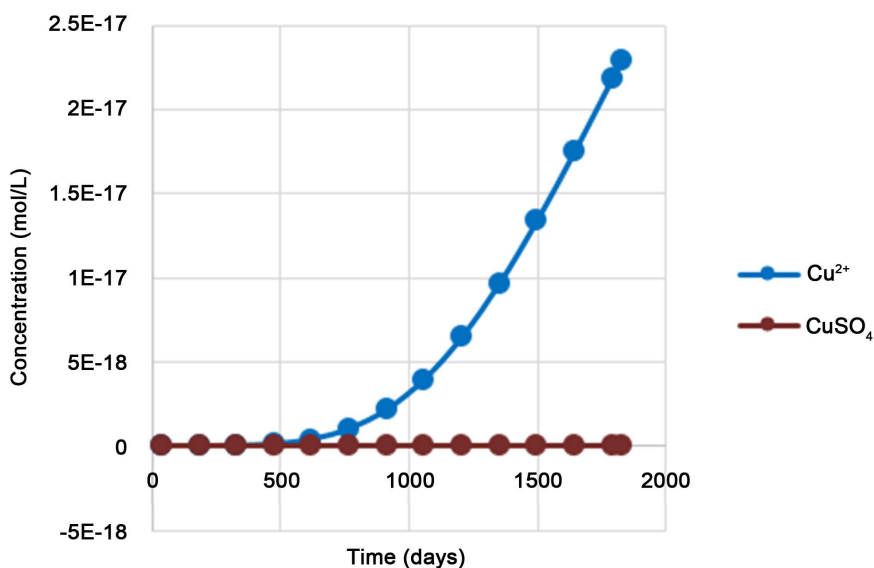


**Figure 10.** Graph representing the copper concentration (Mole/L) as a function of time at the point A, with advection, dispersion or reaction.

results in more contaminant quantity than the advection process alone. Moreover, the addition of reaction package to the dispersion transport model incorporates the copper product formation following the reactions presented in **Table 3**. A very small amount of Cu is produced from the chemical reaction equations. There are some reasons for it such as all equations are equilibrium and without any changes in the ion balance the Cu production is very low. Only the  $\text{Cu}^{+2}$  transport is shown here.

### 3.4. Copper Products Repartition

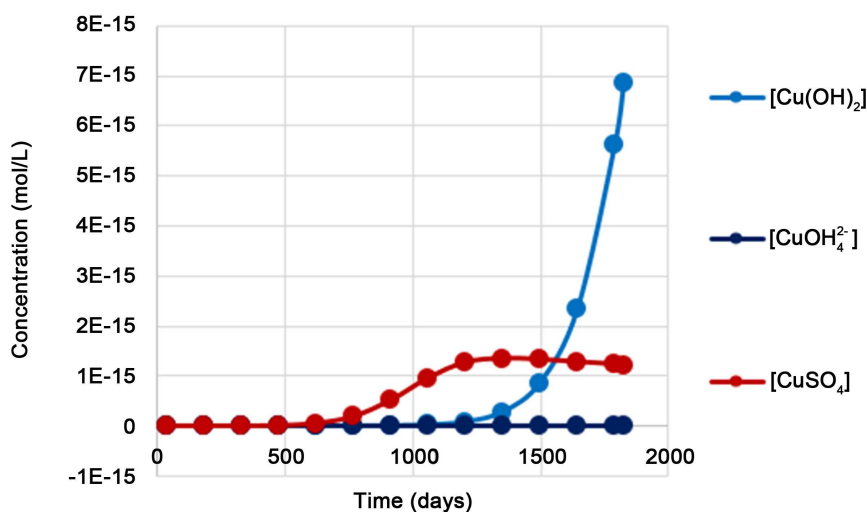
The different forms of copper are studied at the location A (L: 2, R: 53, C: 30). This point is located on the right hand side (east) of the open pit, in the area where the copper is prominently present and most spread out of the source. Therefore at this location, the  $\text{Cu}^{2+}$  reactive transport is likely. **Figure 11** and **Figure 12** show the different copper forms as a function of time. As shows in **Figure 11**, the majority of copper at the point A is in the form of  $\text{Cu}^+$  at a concentration of  $2.34\text{E}-6$  Mole/L at 1825 days. The reaction allowing the formation



**Figure 11.** Graph representing the concentrations of the different forms of copper (Mole/L) as a function of time at the point A.

**Table 3.** Results of the SA algorithm and comparison with real concentrations in the open pit.

Species	Optimal estimated concentrations from linked SA model (mole/L)	Actual concentrations in the Open Pit (mole/L)	Error (%)
$\text{SO}_4^{2-}$	0.14622	0.137	6.73
$\text{Cu}^{2+}$	0.00067	0.0007	4.3
$\text{Cu}^+$	0.00004	$1\text{E}-30$	<100
$\text{Cu}(\text{OH})_2$	0.00004	$1\text{E}-30$	<100
$\text{CuSO}_4$	0.00006	$1\text{E}-30$	<100



**Figure 12.** Graph representing the concentrations of the different forms of copper (Mole/L) as a function of time at the Point A without  $\text{Cu}^+$ .

of  $\text{Cu}^+$  from  $\text{Cu}^{2+}$  (Table 2) has a reaction constant of 2.72 that means a strong tendency to form  $\text{Cu}^+$  at the detriment of the  $\text{Cu}^{2+}$ . The  $\text{Cu}^+$  is presented with the most concentration on this point but other products are presented in smaller concentrations (Figure 12).

As shown on Figure 12, two other species are major forms of copper at the point A are:  $\text{Cu}(\text{OH})_2$  and the  $\text{CuSO}_4$  at concentrations of  $6.87\text{E}-15$  Mole/L and  $1.22\text{E}-15$  Mole/L respectively at 1825 days. The formation constant for the  $\text{CuSO}_4$  is 2.36, that is higher than that for  $\text{Cu}(\text{OH})_2$  which is  $-16.19$ . But the water is in excess that could explain why the  $\text{Cu}(\text{OH})_2$  concentration is more important than  $\text{CuSO}_4$  concentration. The other copper forms such as  $\text{CuOH}^+$ ,  $\text{Cu}(\text{OH})^{3-}$  and  $\text{Cu}(\text{OH})_4^{2-}$  are not in large enough concentration to be considered as major copper forms. Indeed, their formation constants are lower than the  $\text{Cu}^+$ ,  $\text{Cu}(\text{OH})_2$  and  $\text{CuSO}_4$ . That is why they are almost not traceable. Moreover,  $\text{Cu}(\text{OH})_2$  is the product of the reaction between water and  $\text{Cu}^{2+}$  the most stable. Thus if formed,  $\text{CuOH}^+$  is transformed to  $\text{Cu}(\text{OH})_2$ . Very small amount if any, of  $\text{Cu}(\text{OH})^{3-}$  and  $\text{Cu}(\text{OH})_4^{2-}$  are formed. The four major forms of copper in the site are  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Cu}(\text{OH})_2$  and  $\text{CuSO}_4$ . These four species are considered as the relevant contaminants for the groundwater pollution source identification using the linked SA algorithm and PHT3D reactive transport simulation model

#### 4. Source Characterization Using PHT3D as the Reactive Chemical Species Transport Model

PHT3D model is used as simulators of the flow and transport processes in the linked simulation-optimization model for optimal source characterization of distributed sources in the contaminated mine site area. For evaluation purpose, concentration measurements are simulated using the calibrated numerical flow and transport simulation model to generate synthetic concentration measurement data at specified monitoring locations. These concentration measurement



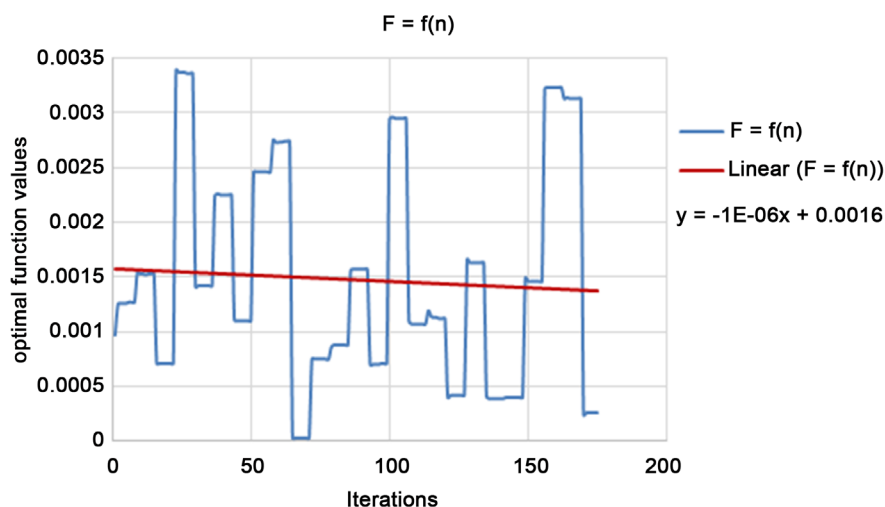
data are generated for the study area for specified source characteristics. Then these synthetic concentration measurement data are utilized together with the linked simulation-optimization models, to evaluate the potential applicability, accuracy and feasibility of the developed methodology. The Cp it is considered as a distributed source of reactive contaminants. For simplification, it is assumed that the unknown contamination source characterization problem can be represented by using unknown concentrations on the periphery of the open pit. Therefore discharge into the aquifer from the pit with specified water surface elevation (estimated by the calibrated flow model) and the unknown concentrations to be estimated as the source concentration by using the linked optimization simulation model, will determine the unknown contaminant mass flux. Therefore, the liked source characterization model essentially needs to estimate the unknown concentrations along the periphery of the open pit in order to characterize the unknown contaminant sources.

## 5. Results and Discussion

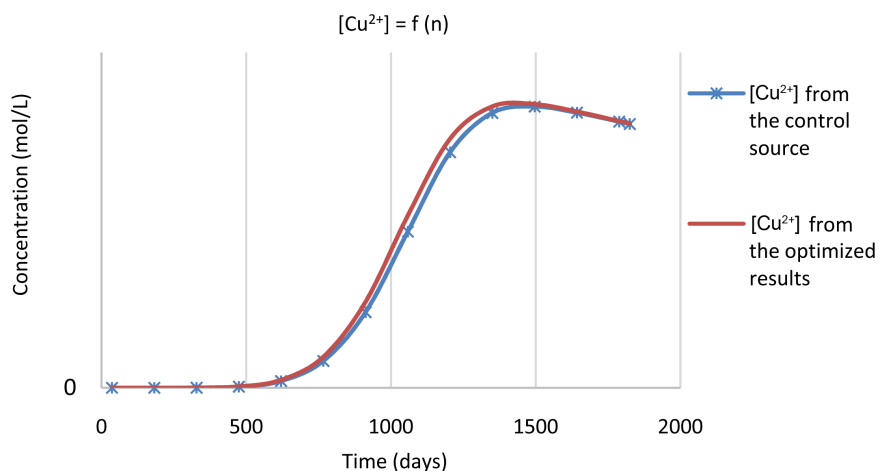
The performance evaluation results of source characterization using PHT3D model linked SA optimization algorithm are presented in **Table 3**. The contaminant source concentration magnitude is in mole per liter. In **Table 3**, the linked optimization model solution results for reactive transport process are compared with synthetically simulated actual concentrations at the observation wells for specified pollution sources. The errors associated with source characterization using the PHT3D model linked optimization model are very small. However, source magnitude results is comparatively large for some Cu components due to site complexity with associated chemically reactive multiple species. These performance evaluation results demonstrate that the developed methodology with PHT3D models is capable of optimally identifying the actual source magnitudes and locations in the mine site area with small estimation errors. **Figure 13** illustrates the number of iteration in source characterization optimization model and the corresponding objective function value. The objective function value should converge to nearly a zero value for an optimal solution. The objective function value trend line, by decreasing, indicates that the optimal function value converges towards zero that should mean that the estimated sulphate and copper concentrations converge towards their respective actual values related to the open pit source.

In order to verify if the optimal concentration values given by SA algorithm correspond to the real initial concentrations integrated in the Open Pit, these values are used as input to the PHT3D simulation model to simulate the resulting concentrations at the monitoring locations. A typical solution result obtained for the Copper (II) at the point A (L = 2, R = 57, C = 28) is presented on **Figure 14**.

**Figure 14** shows that the  $\text{Cu}^{2+}$  concentrations obtained for different times at location A (L = 2, R = 57, C = 28) are very close to the concentrations measured at this location. Indeed, the difference between the actual concentrations and the



**Figure 13.** Graph representing the objective function values as a function of the number of iterations for one typical trial.



**Figure 14.** Graphs representing the concentrations of  $\text{Cu}^{2+}$  obtained from the control source and the concentrations of  $\text{Cu}^{2+}$  obtained when the source concentrations correspond to the concentrations given by the SA simulation, as a function of times in the point 2.

concentrations obtained by using the estimated source does not exceed 16%. Thus, this trial shows that the linked simulation optimization model incorporating reactive chemical species transport is potentially useful for estimating the unknown contaminant source accurately. No doubt more rigorous performance evaluations are necessary to establish this beyond doubt, or to determine the limitations.

## 6. Conclusions

Mount Morgan, a former gold, copper and silver mine in Queensland, Australia, has an impact on groundwater surface water quality. Indeed, because of the mixture of pyrite, water and oxygen in the site, Acid Rock Drainage is formed and, due to the hydrogeology of the site, is transported by groundwater through

the aquifer to the Dee River, situated downstream of the mine site. This phenomenon is characterized by acid water rich in metals which polluted the ecosystem of the water systems present in the mine site.

Following this problem of contamination, the aim of this study was to establish a transport model of the contaminants: the copper (II); and to validate this model in order to be able to use it for the identification of unknown pollution sources present in the site. For that, a three-dimensional reactive transport simulation model PHT3D, along with the groundwater flow simulation model MODFLOW (also available within the processing software GMS) has been used. This reactive species transport simulation model allows numerical three-dimensional transient simulation of reactive chemical species.

Once the transport models for different transport process scenarios are implemented, one aim was to verify the validity of these models. For that, an unknown pollution sources characterization software is used. The dispersion and reactions models, which are the more representative of the phenomenon present on the site, are verified by testing the simulation model for a specified source: the Open Pit, and considering copper related reactions. Very limited evaluations show that the methodology can identify the source concentrations with the largest error of 16%. These errors are comparatively larger than those obtained when using MT3DMS with advection and dispersion only. However, those results do not represent realistic description of all the hydrogeochemical processes in this site. Including the reactive processes represents more realistic description of the actual transport processes in the site and these results are within acceptable range of accuracy. Therefore, the methodology using PHT3D as a simulation model linked to the optimization algorithm (SA) can be considered as potentially applicable for characterization of unknown contaminant sources in a complex contaminated aquifer with chemically reactive contaminant species. However, more rigorous evaluations are necessary to establish widespread applicability of the proposed computational code and the methodology. It is also noted that the SA optimization algorithm may have few inherent limitations in terms of efficiency in reaching an optimal solution. Application of Adoptive Simulated Annealing Algorithm (ASA) [22] could be a better choice to ensure more efficient convergence to a global optimal solution.

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