

## **Coupling and Testing the Fate and Transport of Heavy Metals and Other Ionic Species in a Groundwater Setting at Oak Ridge, TN – 13498**

Nantaporn Noosai\* and Hector R. Fuentes\*\*

\*CEE Florida International University, Miami, FL 33174, nnoos001@fiu.edu

\*\*CEE Florida International University, Miami, FL 33174, fuentes@fiu.edu

### **ABSTRACT**

Historical data show that heavy metals (including mercury) were released from Y -12 National Security Complex (NSC) at Oak Ridge, Tennessee, to the surrounding environments during its operation in 1950s. Studies have also shown that metals accumulated in the soil, rock, and groundwater, and are, at the present time, sources of contamination to nearby rivers and creeks (e.g., East Fork Poplar Creek, Bear Creek). For instance, mercury (Hg), zinc (Zn), cadmium (Cd) and lead (Pb) have been found and reported on the site groundwater. The groundwater type at the site is Ca-Mg-HCO<sub>3</sub>.

This paper presents a modeling application of PHREEQC, a model that simulates geochemical processes and couples them to flow and transport settings. The objective was to assess the capability of PHREEQC to simulate the transport of ionic species in groundwater at Oak Ridge, Tennessee; data were available from core holes and monitoring wells over a 736-m distance, within 60-300 m depths. First, predictions of the transport of major ionic species (i.e., Ca<sup>2+</sup> and Mg<sup>2+</sup>) in the water were made between monitoring wells and for GW-131. Second, the model was used to assess hypotheses under two scenarios of transport for Zn, Cd, Pb and Hg, in Ca-Mg-HCO<sub>3</sub> water, as influenced by the following solid-liquid interactions: a) the role of ion exchange and b) the role of both ion exchange and sorption, the latter via surface complexation with Fe(OH)<sub>3</sub>. The transport scenario with ion exchange suggests that significant ion exchange is expected to occur for Zn, Cd and Pb concentrations, with no significant impact on Hg, within the first 100 m. Predictions match the expected values of the exchange coefficients relative to Ca<sup>2+</sup> and Mg<sup>2+</sup> (e.g.,  $K_{Ca/Zn} = K_{Ca/Cd} > K_{Ca/Pb} > K_{Ca/Hg}$ ). The scenario with both ion exchange and sorption does affect the concentrations of Zn and Cd to a small extent within the first 100 m, but does more meaningfully reduce the concentration of Pb, within the same distance, and also decreases the concentration of Hg in between core holes.

Analysis of the above results, in the light of available literature on the ions of this study, does fundamentally support the capability of PHREEQC to predict the transport of major ions in a groundwater setting; it also generally supports the hypothesized role of ion exchange and sorption. The results indicate the potential of the model as a tool in the screening, selection and monitoring of remediation technologies for contaminated groundwater sites.

### **INTRODUCTION**

A diverse number of sources of contamination, for instance, wastewater discharges, accidental spills, and leaking storage and disposal facilities can contaminate groundwater by heavy metals. Once heavy metals access groundwater, they are most probably subject to both flow and transport, which depend on both the characteristics of the flow and transport in the groundwater environment of interest. In addition, any occurring fate reactions can affect the distribution and concentrations of metals; these reactions may

include precipitation, dissolution, oxidation and reduction, and sorption or ion exchange, which influence the speciation and mobility of metals. The reactions that take place may also depend on pH, complexation with other dissolved constituents, sorption and cation exchange capacity (CEC) of the geological materials, among other variables and processes.

Over the last decades, computational geochemical models (e.g., GEMS, Visual MINTEQ, PHREEQC) have been in development, assisting practitioners and researchers in the estimation and assessment of the fate reactions of metal contaminants in groundwater. Generally, these models calculate the complexation, ion exchange, and adsorption based on mass balance and assumptions of equilibrium. The current version of the model PHREEQC is able to couple detailed geochemical fate reactions to transport conditions, thus offering an opportunity to best simulate the effect of the changes in metal distribution and concentration as a result of reactions happening along transport pathways in groundwater [1].

The purpose of this paper was to explore the potential of the latest version of the model PHREEQC to assess the fate and transport of a group of heavy metals in a groundwater field site; the site is located at the Y-12 National Security Complex (NSC) in Oak Ridge, Tennessee. Historical data shows that more than 200 tons of Hg from this Y-12 atomic plant was released to the surrounding environment during operations in the 1950s [2]. Studies have also shown that metals accumulated in the soil, rock, and groundwater of the site consequentially became sources of contamination to nearby rivers and creeks (e.g., East Fork Poplar Creek, Bear Creek). For instance, mercury (Hg), zinc (Zn), cadmium (Cd) and lead (Pb) have been found and reported on the site groundwater [2, 3, 4, 5]. The site is reported to have a Ca-Mg-HCO<sub>3</sub> groundwater type.

In this study, ion exchange and surface complexation reactions were hypothesized to be the dominant reactions of the study metals in groundwater transport at this site. A previous study documented that the ion exchange and precipitation were the major reactions that affected the change of ionic species, along with rock weathering, for this site [6]. The approach uses the model PHREEQC to couple the geochemical and transport components to verify the possible role of ion exchange and surface complexation in the groundwater transport of the selected metals by comparison to observed concentrations.

### **Study Site**

The geology and hydrology as well as the groundwater quality data at Oak Ridge Y-12 plant were obtained from five existing core holes (GW 131 to GW 135). These core holes were instrumented with multiport monitoring systems at depths of 60–300 m below land surface within Bear Creek Valley [7]. Four of the core holes (GW-132 through GW-135) are along Bear Creek Valley and Chestnut Ridge on the western end of the Y-12 plant. The fifth core hole, GW-131, is located along the geologic strike with GW-135 on Chestnut Ridge near the eastern end of Y-12 plant (Fig. 1). The prevailing direction of the groundwater flow along the valley is from the west to the east (from GW-135 to GW-131) [7]. The distance between GW-135 and GW-131 is 2414 ft or 736 m.

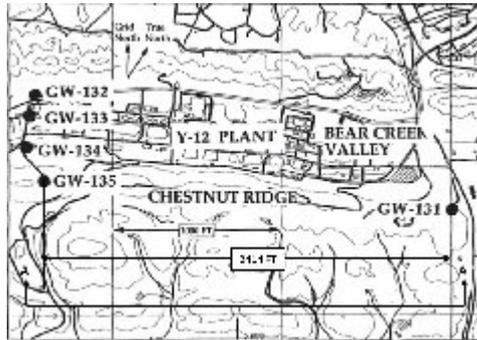


Fig. 1. Study area, location of the five core holes and of the section A-A between GW-131 and GW-135 of Fig. 2, at Y-12 plant, Oak Ridge, Tennessee [7].

Fig. 2. The A-A section profile (of Fig. 1) shows the general geology within core holes GW-131 and GW-135, where  $\epsilon_d$  is Copper Ridge Dolomite,  $\epsilon_m$  is Maynardville Limestone, and  $\epsilon_n$  is Nolichucky Shale [6, 7]. The study focuses on the flow in the saturated zone, between the water table and intermediate intervals level (depths of about 300 ft or 91.5 m.) [8]. At these depths, the groundwater lay on the Copper Ridge Dolomite where the background water is classified as Ca-Mg  $\text{HCO}_3$  water type [6, 7]. The water quality at GW-135 is shown in Table I and was input to define the groundwater quality background characteristics.

TABLE I. Analysis of groundwater at core hole GW-135, Oak Ridge, TN [7]

Parameters	Value	Units
pH	8.0 - 8.4	-
Temperature	20.2	°C
K	0.61 - 0.88	mg/L
Na	0.37 - 0.58	mg/L
Mg	17 - 22	mg/L
Ca	28 - 33	mg/L
Cl	1 - 2	mg/L
SO <sub>4</sub>	2 - 6	mg/L
NO <sub>3</sub>	0.5 - 1	mg/L
Fe	0.1 - 0.3	mg/L
Hg	0.00086 - 0.0066	mg/L
Pb	0.004 - 0.006	mg/L
Zn	0.013 - 0.022	mg/L
Cd	0.0031 - 0.059	mg/L

## METHODOLOGY

### Simulations in 1-D Transport

The geochemical one-dimensional (i.e., 1-D) transport model, PHREEQC, was used to assess the heavy metal contaminations fate and transport from a starting core hole (GW-135) to the destination point (GW-131) (Figures 1 and 2).

The 1-D transport calculation in PHREEQC model is governed by advection-reaction-dispersion equation (Eq. 1)

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D_L \frac{\partial^2 C}{\partial x^2} - \frac{\partial q}{\partial t} \quad (\text{Eq. 1})$$

where  $v$  is the average pore water flow velocity (m/s),  $x$  is distance (m),  $C$  is concentration in water (mol/L),  $D_L$  is the dispersion coefficient ( $\text{m}^2/\text{s}$ ), and  $q$  is the concentration in solid phase (mol/L pore water). The first term on the right hand side,  $-v \cdot \partial C / \partial x$  represents advective transport, the second term  $D_L \cdot \partial^2 C / \partial x^2$  represents dispersive transport, and  $\partial q / \partial t$  represents the change in concentration in solid phase due to a reaction (e.g., sorption, ion exchange, etc.).

The travel distance between GW-135 and GW-131 is 736 m (or 2414 ft). The average groundwater pore velocity was reported to be up to 0.66-1.00 m/day [8]. An average velocity of 0.66 m/day and a dispersion coefficient  $D_L$  of 0.066  $\text{m}^2/\text{d}$  were judged appropriate to be used in the transport simulations at the depths of interest [8].

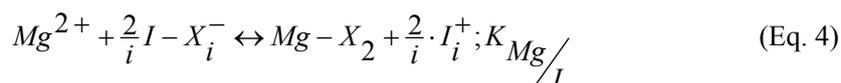
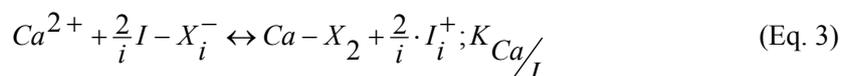
Initial conditions were defined by the water quality characteristics at core hole GW-135 for major ions, heavy metals of concern, pH and temperature (see Table I). A constant-flux type-three boundary condition was used to define as the boundary condition at GW-135 in the simulations. PHREEQC then calculated the change in aqueous chemistry (dissolution-precipitation, speciation, ion exchange, and sorption) along the travel distance based on an ion-association model for two scenarios: *a) ion-exchange only (with major cations) and b) ion-exchange with sorption reaction on  $\text{Fe}(\text{OH})_3$ .*

### Ion Exchange

At this site, the exchange capacity (CEC) of the dolomite and quartz rich sediment is about 39 meq/kg [9, 10], while the bulk density ( $\rho_b$ ) and the porosity ( $\theta$ ) of the used in this paper are, respectively, 1.67  $\text{g}/\text{cm}^3$  and 0.5 [7]. Converting CEC to a constant volume (meq/kg to meq/L) facilitates comparison with the quantities of elements in the pore solution and mass transfer associate with reaction and transport through the groundwater. The CEC of 39 meq/kg soil can be converted to 130 meq/L of pore water using Equation 2 [9]:

$$CEC \left( \frac{\text{meq}}{\text{kg}} \right) \times \frac{\rho_b}{\theta} \left( \frac{\text{g}}{\text{cm}^3} \right) = CEC \left( \frac{\text{meq}}{\text{L}} \right) \quad (\text{Eq. 2})$$

The exchange reaction equations used in this study included Ca and Mg, which assumed to occupy 100% of all exchanged sites. The exchange reactions for Ca-I and Mg-I, where I represents any cation with *i* valence state, are presented in Equations 3 and 4.



The exchange reactions and their exchange coefficients relative to  $Ca^{2+}$  and  $Mg^{2+}$  after the Gaines-Thomas convention [11] are shown in Table II.

TABLE II. Exchange reaction equations and coefficients for Ca and Mg [9, 11, 12]

Reaction	Coefficients (K)
$Ca^{2+} + Hg-X_2 \leftrightarrow Ca-X_2 + Hg^{2+}$	$K_{Ca/Hg} = 0.25$
$Ca^{2+} + Zn-X_2 \leftrightarrow Ca-X_2 + Zn^{2+}$	$K_{Ca/Zn} = 1.00$
$Ca^{2+} + Pb-X_2 \leftrightarrow Ca-X_2 + Pb^{2+}$	$K_{Ca/Pb} = 0.75$
$Ca^{2+} + Cd-X_2 \leftrightarrow Ca-X_2 + Cd^{2+}$	$K_{Ca/Cd} = 1.00$
$Ca^{2+} + Mg-X_2 \leftrightarrow Ca-X_2 + Mg^{2+}$	$K_{Ca/Mg} = 1.25$
$Mg^{2+} + Hg-X_2 \leftrightarrow Mg-X_2 + Hg^{2+}$	$K_{Mg/Hg} = 0.20$
$Mg^{2+} + Zn-X_2 \leftrightarrow Mg-X_2 + Zn^{2+}$	$K_{Mg/Zn} = 0.80$
$Mg^{2+} + Pb-X_2 \leftrightarrow Mg-X_2 + Pb^{2+}$	$K_{Mg/Pb} = 0.60$
$Mg^{2+} + Cd-X_2 \leftrightarrow Mg-X_2 + Cd^{2+}$	$K_{Mg/Cd} = 0.80$
$Mg^{2+} + Ca-X_2 \leftrightarrow Mg-X_2 + Ca^{2+}$	$K_{Mg/Ca} = 0.80$

## Sorption

PHREEQC offers a surface complexation model to calculate the sorption of heavy metals on a mineral, which can define the mineral (i.e., ferric oxide), the available sorption sites, and the sorption equilibrium constant (k). This study used the Linear Free Energy Relations (LFER) method to calculate the sorption reaction constant for each metal of interest [13] and used a complexation reaction on  $Fe(OH)_3$  for two types of sites, a strong site type (i.e., Hfo\_sOH) and a weak type site (i.e., Hfo\_wOH) [12,13]. Properties of hydrous ferric oxide and sorption reaction equations for major ions and metals of interest are presented in Tables III and IV.

TABLE III. Properties of hydrous ferric oxide [13]

Weak Sites (mol/mol Fe)	Strong Sites (mol/mol Fe)	Surface Area (m <sup>2</sup> /g)	Point of Zero Charge pH
0.2	0.005	600	8.11

TABLE IV. Equations and constants of sorption reactions of ions on Fe(OH)<sub>3</sub>

Reactions	Log K <sub>ads</sub> (LFER)
Hfo_sOH + Ca <sup>+2</sup> = Hfo_sOHCa <sup>+2</sup>	4.97
Hfo_wOH + Ca <sup>+2</sup> = Hfo_wOCa <sup>+</sup> + H <sup>+</sup>	-5.85
Hfo_wOH + Mg <sup>+2</sup> = Hfo_wOMg <sup>+</sup> + H <sup>+</sup>	-4.6
Hfo_sOH + Cd <sup>+2</sup> = Hfo_sOCd <sup>+</sup> + H <sup>+</sup>	0.47
Hfo_wOH + Cd <sup>+2</sup> = Hfo_wOCd <sup>+</sup> + H <sup>+</sup>	-2.9
Hfo_sOH + Zn <sup>+2</sup> = Hfo_sOZn <sup>+</sup> + H <sup>+</sup>	0.99
Hfo_wOH + Zn <sup>+2</sup> = Hfo_wOZn <sup>+</sup> + H <sup>+</sup>	-1.99
Hfo_sOH + Pb <sup>+2</sup> = Hfo_sOPb <sup>+</sup> + H <sup>+</sup>	4.65
Hfo_wOH + Pb <sup>+2</sup> = Hfo_wOPb <sup>+</sup> + H <sup>+</sup>	0.3
Hfo_sOH + Hg <sup>+2</sup> = Hfo_sOHg <sup>+</sup> + H <sup>+</sup>	7.98
Hfo_wOH + Hg <sup>+2</sup> = Hfo_wOHg <sup>+</sup> + H <sup>+</sup>	5.87

Under equilibrium conditions the mass law expression for a sorption reaction is defined by Equation 6:

$$K_{ads} = \frac{\{Hfo\_sOM^+\} \{H^+\}}{\{Hfo\_sOH\} \{M^{2+}\}} \quad (\text{Eq. 6})$$

where K<sub>ads</sub> is the sorption reaction constant at equilibrium and M<sup>2+</sup> is the dissolved metal cation [13, 14].

## RESULTS AND DISCUSSION

### Dissolved Metal Transport Prediction with Ion Exchange Occurrence

The concentrations of dissolved metals along the travel distance, when the effect of cation exchange capacity on the heavy metals retention is considered are shown in Fig. 3. The dissolved concentrations of Zn, Pb, and Cd are predicted to decrease sharply within the first 100 m, sorbing in trace amounts beyond 100 m, while the Hg concentration remains quite constant over most of the entire distance between core holes but showing a decreasing trend around GW-131. The pattern of transport and the differences among the metals of interest may be explained by the lower exchange coefficients of Hg to Ca and Mg (K<sub>CaHg</sub> = 0.25, and K<sub>MgHg</sub> = 0.20) than those of the other metals (i.e., Zn, Pb, and Cd) to Ca and Mg (see Table II).

Additional analyses also indicate that Ca and Mg occupy most of the exchanged sites in the rock matrix (~60% for Ca and ~40% for Mg), a dolomite bedrock [6], where dissolution should yield high concentrations of Ca and Mg in the groundwater (i.e., Ca-Mg-HCO<sub>3</sub> background water type).

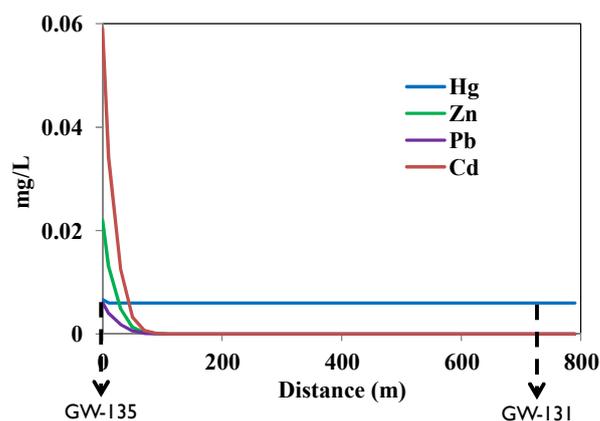


Fig. 3. Effect of ion exchange on metal concentration along the distance between core holes

#### Dissolved Metal Transport Prediction with Ion Exchange and Sorption Occurrence

Fig. 4 shows the concentration of heavy metal along the travel distance when ion exchange is simulated simultaneously with the sorption on the precipitated Fe(OH)<sub>3</sub>. The results show that the presence of precipitated Fe(OH)<sub>3</sub> may trigger more sorption on its surface of Hg and Pb than of Zn and Cd; Fig. 5 shows, with more detail, the comparison between the possible role of ion exchange only and that of simultaneous ion exchange and sorption for Hg and Pb along the distance between the core holes. The lower predicted concentrations of Zn and Cd may be explained by their much smaller sorption-reaction constants on Fe(OH)<sub>3</sub> (i.e., log K is 0.99 for Zn and 0.47 for Cd) than those of Hg (log K = 7.98) and Pb (log K = 4.65) [15, 16]. The latter difference is expected to specially occur when limited amounts of sorbent are available, which results in competition between metals with high sorption constants, such as those of Hg and Pb, and those with low constants such as Zn and Cd.

#### Field Verification of Simulation Scenarios

An attempt was made to verify the role of ion exchange and sorption, for the initial and boundary conditions of the simulations, using limited water quality data at GW-131 [7]. The estimated change in dissolved metal concentrations, with distance between GW-135 and GW-131 for the case of simultaneous ion exchange and sorption, and the available water quality measurements at GW-131 are tabulated in Table V.

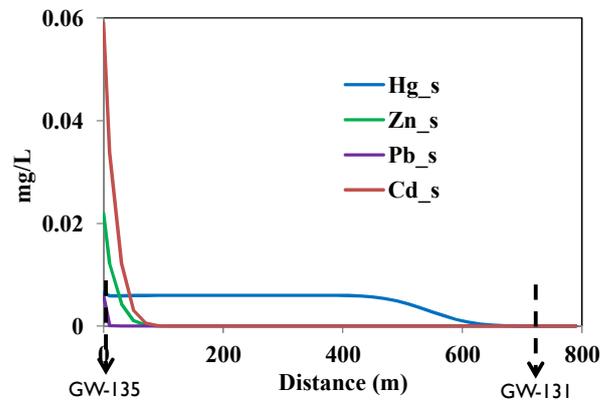


Fig. 4. Effect of ion exchange and sorption on dissolved metal concentration along the distance between core holes

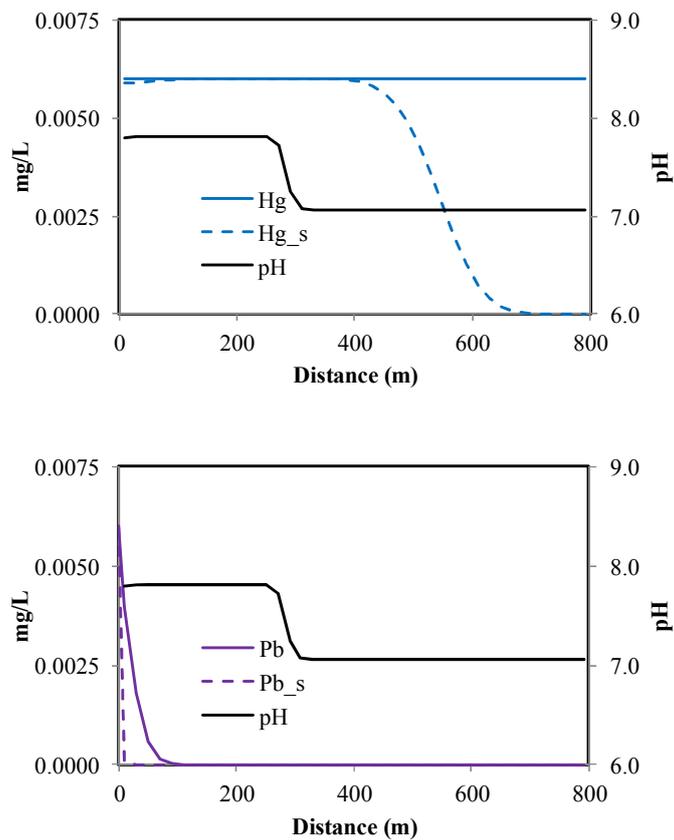


Fig. 5. Dissolved metal concentration and pH profile along the distance between core holes: only ion exchange model (dash line) and ion exchange with sorption on  $\text{Fe}(\text{OH})_3$  (solid line)

The predictions of dissolved concentrations at the location of core hole GW-131 are found to be, within

reported ranges, for all major ions, below limits of detection for the metals of interest, and for pH. Available measurements are however not sufficient to satisfactorily verify the hypothesized scenarios in the field setting, but they do provide an encouraging indication of the potential of the modeling approach to simulate field conditions. Clearly, an appropriate plan for measurements of both flow and transport parameters and water quality constituents is needed to enhance the opportunity for reasonable field verification. A reasonable verification should provide a tool that can be used for that site with a higher level of confidence.

TABLE V. Predicted and measured groundwater quality between core holes GW-135 and GW-131, Oak Ridge, TN (concentrations in mg/L)

Distance (m)	Observed data at GW 135	Calculated Data				Observed data at GW 131
	0 <sup>i</sup>	50	250	500	736	736 <sup>i</sup>
Parameters						
pH	8.0 - 8.4	7.54	7.4	7.3	7.1	7.0 - 7.9
K	0.61 - 0.88				0.82	0.73 - 9.9
Na	0.37 - 0.58	0.57	0.32	0.38	0.37	0.1 - 110
Mg	17 - 22	18.4	17.6	18.7	20	18 - 110
Ca	28 - 33	29.8	29	30.04	33	30 - 190
SO4	2-700	183	163	142	155	4 - 170
NO3	1-10	5.01	4.02	4.38	4.43	2-10
Hg	$8.6 \times 10^{-4}$ - $6.6 \times 10^{-3}$	0.0059	0.0059	0.0042	$1.3 \times 10^{-6}$	< 0.002 <sup>ii</sup>
Pb	0.004 - 0.006	$3.3 \times 10^{-10}$	$5.5 \times 10^{-19}$	$7.1 \times 10^{-23}$	~0.00	< 0.004 <sup>ii</sup>
Zn	0.013 - 0.022	0.001	$7.1 \times 10^{-19}$	$2.4 \times 10^{-22}$	~0.00	< 0.002 <sup>ii</sup>
Cd	0.0031- 0.059	0.003	$2.08 \times 10^{-15}$	$3.0 \times 10^{-21}$	~0.00	< 0.002 <sup>ii</sup>

<sup>i</sup>Data obtained from Dreier et al., 1991; <sup>ii</sup>the limited detection values

## CONCLUSIONS

The approach herein used couples geochemical and transport components in an attempt to verify the role of ion exchange and surface complexation in the transport of the selected metals in the groundwater setting at Oak Ridge, TN. Overall, the simulated dissolved concentrations fall within the ranges of the reported water quality measurements, supporting previous findings that concluded ion exchange to be an important fate process at this site [6]; however, a more comprehensive field monitoring of flow parameters and water quality should meaningfully enhance the effort of model verification.

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