

Investigating the Effect of Acidic Rain on Reactive Transport of Metal Contaminants in Groundwater

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Abstract

Multicomponent reactive transport in porous media is a complex process owing to a combination of variability in the processes involved and the inherent heterogeneity of nature. In recent years, various multicomponent reactive transport models have been developed to study the mobility of potentially toxic heavy metals in the subsurface. Heavy metals and other contaminants may be released from mining sites, especially from waste dumps and tailing ponds. Soil and groundwater contamination due to mining activities is an important environmental problem worldwide. Because of their abundance and potential toxicity, Pb^{2+} , Zn^{2+} , and Cd^{2+} figure prominently among inorganic contaminants of greatest concern in mine tailings. This study investigated the effect of pH on the transport of these metals through lead and zinc leaching plant tailings in Lakan, Iran. The HP1 model and PHREEQC database were used to simulate the transport of the metals through a saturated soil at the laboratory column scale during a 15-day time period. The simulations assumed local equilibrium. As expected, a lower pH increased metal transport. However, although the simulation results generally agreed well with results of the column study, they indicated that physical and chemical parameters must be carefully determined for use in the simulations. Improvements in the results are expected when using multi-dimensional models and a kinetic modeling approach for the reactions involved.

1. Introduction

Despite significant progress in science and technology, environmental problems are increasing at the national, regional, and international levels. Correlations between industrial activities and environmental contamination make it difficult to expect substantial industrial development without some impact on the environment. The production of inorganic wastes in mining operations has always been an important issue and a threat to the environment, especially the subsurface. These wastes often contain high levels of heavy metals, which constitute a major threat to human populations, aquatic species, plants, ecosystems, and groundwater quality in general because of their biological non-degradability and stability in the environment. Large-scale mining can especially adversely affect the environment. Iran, as a developing country, still needs to develop much of its mining activities. Unfortunately, a lack of necessary standards for proper processing and waste burial make environmental pollution more probable in Iran. Leaching of heavy metals from surface soils to deeper layers, and the risk of groundwater pollution, depend on the retention, mobilization, and transport of heavy metals in soils. Specific adsorption, ion exchange, and precipitation of various solid phases are the main processes responsible for the retention of heavy metals. Previous studies indicate that the pH is one of the most important factors affecting the transport and sorption of heavy metals (Chotpantararat et al.,

2011). Changes in the chemical composition or pH of the soil solution may impact the sorption of elements on organic matter or iron oxides.

Decision makers need predictions of the fate of heavy metals in soils to design management strategies that minimize adverse environmental impacts. Accurate simulations of pollutant transport require a coupled reactive transport code that integrates the physical processes of water flow and advective-dispersive solute transport with a range of biogeochemical processes. Many models have been developed to simulate and predict the fate and transport of pollutants in porous media (e.g., Šimůnek, 2007; Šimůnek et al., 2008b). The most commonly-used models are based on advection-dispersion equations and consider such mechanisms as advection, dispersion, sorption, and degradation.

Wu et al. (1998) showed that at lower pH levels, Cd and Pb precipitation will cause a sharp decrease in their external concentrations. Pang et al. (2002) showed that the breakthrough curves (BTCs) of Cd, Zn, and Pb in gravel columns with pore water velocities ranging from 3 to 60 m/day displayed long tailing, suggesting that non-equilibrium sorption conditions occurred in the gravel columns due to high pore water velocities. Using geochemical analyses and investigations of samples from mine tailings and water resources adjacent to the Piscinas River in Sardinia, Italy, Concas et al. (2005) concluded that a decrease in the pH level increased metal dissolution and transport from mine tailings. Pot et al. (2005) used different physical and chemical equilibrium and non-equilibrium transport models to simulate the impact of various rainfall intensities on herbicide transport. Their study showed that physical/chemical non-equilibrium conditions were dominant. Michel et al. (2007) used mathematical and empirical models to investigate nickel and cadmium transport in silty and sandy soils and concluded that a decrease in the pH will increase the transport of heavy metals in acidic soils. Using HP1 model, Jacques et al. (2008) further showed that reducing the inflow intensity will cause a decrease in the pH level, thereby promoting monovalent cations to sorb on the cation exchange complex, and bivalent cations to desorb into the soil solution. Simulating the effect of pH on Pb, Mn, Zn, and Ni transport using HYDRUS-1D, Chotpantararat et al. (2011) found that increasing the pH of the inflow solution will increase the retardation of heavy metals. They also showed that the use of a two-site model (TSM) for sorption produced a better match with measured heavy metal BTCs than linear or nonlinear Langmuir type equilibrium models.

The main objective of this research was to investigate the effect of aqueous pH conditions on the sorption and transport of three heavy metal ions, Cd^{2+} , Pb^{2+} , and Zn^{2+} , using the HP1 numerical model, to evaluate the model's utility in simulating the transport of heavy metals in soil columns, and to investigate the sorption behavior of heavy metals in soil columns.

2. Materials and Methods

2.1. General Features of Study Area

The Lakan lead and zinc processing plant is located 46 km Southwest of Arak City in the Markazi Province, Iran. The geographical location of this site is 33°42'5"N latitude and 49°43'26"E longitude. The Lakan plant is located in a temperate mountainous zone with hot

summers and cold winters. Annual variations in temperatures are very high, ranging from -20 °C in the winter to +35 °C in the summer.

2.2. Soil Physical and Chemical Properties

The deposited waste material had been studied previously by Marzban (2008) using X-ray fluorescence (XRF) tests. Table 1 shows the types and quantities of elements in a 100 g sample.

Table 1. Quantities of elements in a 100 g sample.

Compounds	Percentage	Compound/Element	Percentage
Na ₂ O	0.5	MnO	0.3
MgO	0.8	Ni	0.0146
Al ₂ O ₃	3.5	Zn	1.15
SiO ₂	66.6	Pb	1.5
SO ₃	4.5	Cd	0.005
K ₂ O	0.7	P ₂ O ₅	0.9
CaO	9.5	Fe ₂ O ₃	2.9
BaO	0.4	LOI	6.73

Using tailings from the same site, Marzban (2008) conducted 15-day leaching tests on 180 g samples in three 2.7-cm internal diameter columns in which the tailings occupied heights of 21 cm. The effluent from each column was analyzed after 3, 7, 10, and 15 days. Physical properties of the tailing dam soil as reported by Marzban (2008) are presented in Table 2.

Table 2. Physical properties of tailing dam soil.

Soil Property	Unit	Value
Bulk Volume	(mL)	150
Weight	(g)	221.77
Pore Volume	(mL)	40
Specific Volume	(mL)	110
Bulk density	(g/mL)	1.48
Specific density	(g/mL)	2.02
Solid fraction	-	0.73
Porosity	-	0.27

2.3. Transport Model

All calculations in this paper were carried out using version 2.2 of HP1 (Jacques et al., 2010). The HP1 reactive transport simulator, obtained by weak coupling of HYDRUS-1D and PHREEQC-2, was developed and designed to address multicomponent geochemical transport processes in the vadose zone. The software integrates a broad range of physical and biogeochemical processes, as described in the original manuals of HYDRUS-1D (Šimůnek et al., 2008ab), PHREEQC-2 (Parkhurst and Appelo, 1999), and HP1 (Jacques et al., 2010). HYDRUS-1D was originally designed mostly for simulating water flow, solute transport, and heat transport

in soils from the soil column scale to the field scale. The program can numerically solve the Richards equation for saturated-unsaturated water flow and the advection-dispersion equation for solute and heat transport. In this software, the solute transport module also considers equilibrium and non-equilibrium advection-dispersion in the liquid phase, and nonlinear equilibrium physical and chemical sorption. Important to note is that both the HYDRUS-1D and HP1 models account for soil heterogeneity at the macroscopic scale by using scaling factors (Vogel et al., 1991), and at the microscopic scale by using dual-porosity or mobile/immobile type flow models (Šimůnek et al., 2003). HP1 implements a weak coupling method in which the governing equations for water flow, heat transport, and solute transport are solved sequentially. The multicomponent reactive transport equations are solved using a non-iterative sequential approach, meaning that the physical part is solved first without any chemical interactions, while the chemical reactions that are uncoupled in space and coupled over the components are solved subsequently (Jacques et al., 2008). A flow chart of the operator-splitting approach used in HP1 was given in Jacques et al. (2006). Although operator-splitting errors may occur with this approach, Jacques et al., (2006, 2008) showed that very accurate results can be obtained by carefully selecting the spatial and temporal discretizations.

2.3.1. Soil Hydraulic Properties

Six analytical models are available in HP1 to describe the soil hydraulic properties, including the function of Brooks and Corey (1964), van Genuchten (1980), and Vogel and Cislérova (1988). In this study the van Genuchten-Mualem model (van Genuchten, 1980) was used to describe the water retention and hydraulic conductivity ($K(h)$) functions:

$$\theta(h) = \begin{cases} \theta_r + \frac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m} & h < 0 \\ \theta_s & h \geq 0 \end{cases} \quad (1)$$

$$K(h) = K_s S_e^l [1 - (1 - S_e^{1/m})^m]^2 \quad (2)$$

$$S_e(h) = \frac{1}{[1 + |\alpha h|^n]^m} \quad (3)$$

where $\theta(h)$ is the soil water content [-] as a function of the pressure head, h [L], θ_s is the saturated water content [-], θ_r is the residual water content [-], K_s is the saturated hydraulic conductivity [LT^{-1}], S_e is the effective water content [-], α , m , and n are empirical parameters of the retention curve ($m=1-1/n$ for $n>1$), and $K(h)$ is the unsaturated hydraulic conductivity [LT^{-1}]. The pore connectivity/tortuosity factor (l) used in the simulations was set to 0.5 for all simulation scenarios. This value was recommended by Mualem (1976) and is a default value used for soils in the HYDRUS software.

2.3.2. Water Flow Equation

A combination of the mass balance equation with the Darcy-Buckingham law results in the Richards equation describing water flow in variably-saturated porous media. The one-dimensional form of the Richards equation can be written as:

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} + \cos \alpha \right) \right] - S(h) \quad (4)$$

where h is the water pressure head [L], θ is the volumetric water content [-], t is time [T], z is the spatial coordinate [L] (positive upward), S is the sink term [$L^3L^{-3}T^{-1}$], α is the angle between the flow direction and the vertical axis, and K is the unsaturated hydraulic conductivity [LT^{-1}].

2.3.3. Solute Transport Equation

Solute transport in porous media can be described with the one-dimensional convective-dispersive equation (CDE):

$$\frac{\partial \theta C}{\partial t} + \frac{\partial \rho_b S}{\partial t} = \frac{\partial}{\partial z} \left(\theta D \frac{\partial C}{\partial z} \right) - \frac{\partial q_w C}{\partial z} \quad (5)$$

in which C is the solute concentration in solution [ML^{-3}], S is the sorbed solute concentration [MM^{-1}], ρ_b is the soil bulk density, q_w is the volumetric water flux [LT^{-1}], and D is the effective dispersion coefficient [L^2T^{-1}]. The effective dispersion is given by Bear (1972):

$$D\theta = \lambda_L |q_w| + \theta \tau D_0 \quad (6)$$

where λ_L is the longitudinal dispersivity [L], D_0 is the aqueous ionic or molecular diffusion coefficient of a solute in water [L^2T^{-1}], and τ is the tortuosity factor given by (Milington and Quirk, 1961):

$$\tau = \frac{\theta^{7/3}}{\theta_s^2} \quad (7)$$

By manipulating Equation (5), the modified convective-dispersive equation is obtained as follows:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (8)$$

where R is the retardation factor given by the following equation:

$$R = \frac{1 + \rho_b K_d}{\theta} \quad (9)$$

in which K_d is the partitioning coefficient of solute [L^3M^{-1}] and v the average pore water velocity [LT^{-1}].

2.3.4. Numerical Simulations

The water flow and solute transport equations were solved numerically using the HP1 code (Jacques et al., 2010). The upper and lower boundary conditions for water flow were assumed to

be a constant pressure head, and for solute transport to be a concentration flux BC (third type) and a zero concentration gradient (free drainage), respectively. In the HP1 model, the Galerkin finite element method with a space weighting scheme was selected, while the time derivatives for the solute transport solution were approximated using a Crank-Nicholson finite difference scheme. All simulations were conducted over a period of 15 days. The column height was 21 cm and the inflow rate 1 cc/min (cc stands for cubic centimeters), while acid concentrations were 0, 0.12, and 0.29 g/L. Selected parameter values (Levels 1, 2, and 3) used in the simulation scenarios are summarized in Table 3.

Table 3. Simulation parameters and levels.

Compounds	Level 1	Level 2	Level 3
pH	7	6	5
Time (day)	3	10	15

2.3.5. Modeling Efficiency

The modeling efficiency (EF) was calculated for the measured and modeled data using (Loague and Green, 1990)

$$EF = \frac{\sum_{i=1}^n (x_i - x_n)^2 - \sum_{i=1}^n (y_i - x_i)^2}{\sum_{i=1}^n (x_i - x_n)^2} \quad (10)$$

where x_i , y_i , x_n and n are measured values, model predictions, arithmetic means of the measured values, and the number of measured and modeled values, respectively. When model predictions perfectly match the measured data, EF is equal to 1. A negative value indicates that the predictions describe the data less than the mean of the observations.

3. Results and Discussion

The effects of pH on the transport of Cd, Zn, and Pb are shown in Figure 1. Taking into account the fact that the pH of rain in the Arak city is 5.5, three input solutions with pH values of 5, 6, and 7 were selected for the study, similarly as in the experiments carried out by Marzban (2008) and Darban et al. (2012). Maximum removal of Cd, Zn, and Pb was achieved after three days using the input solution with pH of 5. The removal concentrations of these three metals were 0.4, 16.38, and 1.21 mg/L, respectively. The lower removal concentrations of Cd and Pb, compared to Zn, is likely due to precipitation of Cd and Pb species, especially at lower pH levels. The higher removal of metals with decreasing pH is reasonable, since higher pH indicates lower quantities of H^+ ions and an increase in the retardation factor of heavy metals as shown by Chotpantararat et al. (2011), among many others. The removal concentrations of the three metals after 15 days are shown in Table 4.

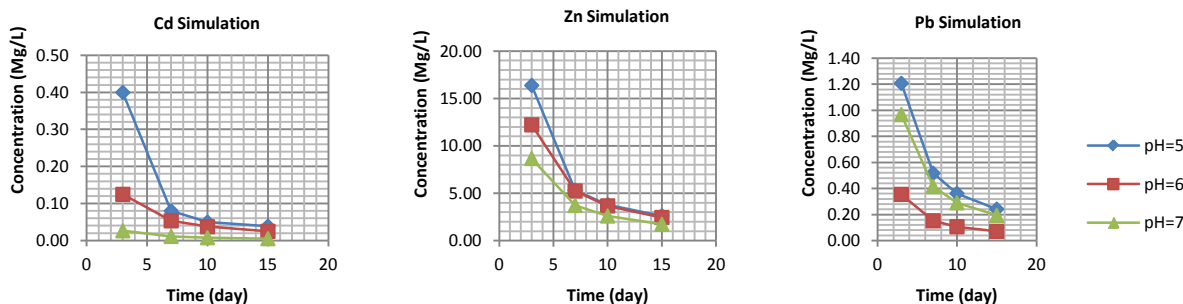


Figure 1. Effect of pH on Cd, Zn, and Pb transport and removal.

Table 4. Removal concentrations of heavy metals in mg/L after 15 days.

Element/pH	pH=5	pH=6
Cd	0.04	0.02
Zn	2.62	2.44
Pb	0.24	0.07

Allowable limits for concentrations of zinc, lead, and cadmium in groundwater according to the U.S. Environmental Protection Agency (US EPA, 1993) are 5, 0.005, and 0.01 ppm, respectively. The results in Table 4 indicate that the concentrations of Cd and Pb in solution exceeded the EPA limits. They also exceeded the Iranian standard for drinking water (Standard No. 1053). Similar findings were reported by Darban et al. (2012). Heavy metal mobility followed the order $Zn^{2+} > Pb^{2+} > Cd^{2+}$. The same results for similar conditions were reported by Wu et al. (1998), except for Pb. This difference can be attributed to the lower simulation efficiency for Pb in our study. As reported also by Wu et al. (1998), Darban et al. (2012), and Nguyen et al. (2010), the removal concentrations were lower for neutral solutions, as compared to more acidic solutions, because of precipitation of metals under neutral aquatic conditions.

Experimental and simulated concentrations for Cd, Zn, and Pb after 7 days are presented in Table 5, while the simulation efficiencies for different pH levels are listed in Table 6. Comparing the simulated and the experimental results, the highest efficiency was achieved for Cd removal concentrations, followed by Zn and Pb.

Table 5. Experimental and simulated removal concentrations of heavy metals (in mg/L).

Element	pH=6 (Experiment)	pH=6 (Simulation)	pH=5 (Experiment)	pH=5 (Simulation)
Cd	0.041	0.054	0.053	0.08
Zn	4.47	5.24	5.46	5.32
Pb	0.039	0.15	0.078	0.052

Table 6. Modeling efficiencies for the heavy metals removal concentrations at two pH values.

Element/pH	pH=6	pH=5	Average
Cd	0.80	0.69	0.75
Zn	0.77	0.5	0.63
Pb	0.79	0.29	0.54

Brown et al. (1998) attributed the differences in their observed and simulated results to the local equilibrium assumption. They indicated that due to the slow reaction kinetics and limited interactions of solid phase surfaces with solutes, the dominant process could not be effectively described using the assumption of local equilibrium in their simulation. Pot et al. (2005) concluded that the physical/chemical non-equilibrium models were also more effective in simulating herbicide transport. Michel et al. (2007) investigated the removal of Ni and Cd from acidic sandy and silty soils using empirical and mathematical modeling. They found the simulation efficiencies between 0.35 and 0.85 for different scenarios. The effects of different chemicals or other transport and reaction parameters were not considered.

Jacques et al. (2008) found that decreasing the pH level will increase bivalent cations removal concentrations. A comparison of our results with results reported by Motalebi et al. (2012) shows that the PHREEQC and HP1 models had approximately the same efficiency for Cd reactive transport, perhaps because of the saturated flow conditions in both studies.

Relatively good agreement between model predictions and experimental results was obtained in our study. Some small differences between the experimental and simulated results were observed only during the first few days of the simulations. The presence of dissolved organic matter (DOM) may have influenced the mobility and retention of heavy metals in soils. The formation of complexes with DOM can be especially important for Pb (Weng et al., 2002; Tipping et al., 2003). The lower simulated removal concentrations of metals may be attributed to the formation of complexes during the first few days of simulation.

Another possible reason for the differences may be the fact that the soil hydraulic conductivity was assumed to be constant during the simulations. In reality, the hydraulic conductivity changes with changes in pH, which should affect the heavy metal precipitation rate. In general, disagreement between the model and the data (lower modeling efficiencies) of some of the scenarios can be attributed also to uncertainty in the value of some parameters, simplification of the transport process to a one dimension, ignoring the effects of macropores and other transport processes in natural soil (such as bioturbation), and/or local physical or chemical non-equilibrium processes.

4. Conclusions

In this study, the effects of pH on reactive transport of Cd, Zn, and Pb from Lakan mine tailings were investigated using the HP1 model. Metal removal concentrations were predicted using the HP1 model. Simulation results were compared with previously published experimental results and the results of other researchers. Overall, the HP1 model successfully simulated water flow and solute transport in the columns, considering the limitations in the experimental data.

Using different pH levels for the inflow solution, the following conclusions were reached:

- The retardation of heavy metals followed the order $Zn^{2+} > Pb^{2+} > Cd^{2+}$
- Decreasing pH values produced higher metal removal concentrations
- The removal concentrations of Cd and Pb exceeded the allowable EPA and Iranian's 1053 standard thresholds
- The simulations for Cd had the highest modeling efficiency, followed by Zn and Pb

- Predicted early removal concentrations did not successfully match the observed data, likely due to the presence of sharp solute fronts, failure to establish local equilibrium, insufficient time for complete soil solid phase and soil solution reactions, or temporal variations in the physical properties. Some of the differences could be attributed also to the formation of complexes at the beginning of simulations.
- Differences between modeling and experimental results for some scenarios could also be attributed to uncertainty in the values of some parameters, simplification of the transport process to 1D, ignoring the effects of macropores and other transport mechanisms occurring in soils (such as bioturbation), local physical/chemical non-equilibrium, or uncertainty in the dominant chemical processes and their parameters.
- PHREEQC and HP1 models had approximately the same modeling efficiency for the Cd reactive transport simulations.

More research is needed to explore the various physico-chemical and biological processes that control the potential solubility of toxic metals from mine tailings. The use of two- and three-dimensional models, as well as kinetic modeling, is recommended to more accurately simulate reactive transport in actual field conditions.

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