

# MODELING OF HEAVY METAL MOVEMENT IN VEGETATED, UNSATURATED SOILS WITH EMPHASIS ON GEOCHEMISTRY

K.V. Nedunuri<sup>1</sup>, R.S. Govindaraju<sup>1</sup>, L.E. Erickson<sup>2</sup> and A.P. Schwab<sup>3</sup>, <sup>1</sup>Department of Civil Engineering, <sup>2</sup>Department of Chemical Engineering and <sup>3</sup>Department of Agronomy, Kansas State University, Manhattan, KS 66506

## ABSTRACT

In recent years, researchers have focused on modeling of multicomponent reactive transport and have developed models to study the mobility of potentially toxic heavy metals in the subsurface. In this study, a mathematical model for understanding the fate of a typical heavy metal (lead) in unsaturated soil is developed. The entire modeling activity comprises of three parts. During the first part, a geochemical model to describe the soil heavy metal interactions is developed. In the second part, a solute transport model is developed and linked with the unsaturated flow model which incorporates root water uptake. The final part involves the sequential solution of the transport and geochemical models, using the aquifer properties which are typical of contaminated sites in southeast Kansas. The local equilibrium assumption (LEA) is adopted, and the transport and geochemical models are decoupled while solving for the heavy metal transport. The model is used to simulate heavy metal movement through unsaturated soil at the laboratory column scale. The study provides insight on movement of heavy metals in chat-contaminated fields of Southeast Kansas.

## KEY WORDS

heavy metals, geochemistry, solute transport, mathematical model, unsaturated flow, remediation

## INTRODUCTION

The problem of contamination of groundwater by heavy metals has received much attention in recent years [1]. In particular, lead is a heavy metal of serious environmental concern. One of the physiological effects of lead is that it is detrimental to the neurological development of children. Reduction in IQ and other health effects are evident from several case studies [2]. Some of the sources of lead are gasoline, paints, antiknock additives in fuel, pigments and stack emissions from some metal industries. Major sources for lead in ground water are the smelter sites and areas where there has been significant mining activity. Drainage flowing from mine tailings can enter surface water, irrigated soils and groundwater, causing harm to human beings and animals. An understanding of the

movement of lead in soils, and its interaction with the soil minerals, is important. The impact of elevated concentrations of lead in human-plant-animal systems will be influenced by the dominant forms of the lead that are present in soil. The types of reactions that are likely to control the distribution of metals in soils are mineral precipitation and dissolution, ion exchange, adsorption and desorption, aqueous complexation, biological immobilization and mobilization, and plant uptake [1, 3].

In the past, several investigators studied the multicomponent transport of heavy metals in ground water [4, 5]. Earlier efforts on modeling metal transport have either not considered the chemically reactive nature of the soil, or have considered a simplistic linear retardation or a first order decay of the contaminant. However, it is essential to

consider the chemical reactions between the soil minerals and the heavy metals. The research in modeling contaminant transport with the inclusion of geochemical reactions has progressed in two directions, one in which all the chemical reactions are incorporated directly into the transport equations [6-8], and another in which the geochemical reactions are decoupled from the transport equations and solved separately [9-11]. The first approach has the advantage of high accuracy; however, it is computationally very intense. The second approach divides the solution into a physical step where the heavy metal and its associated aqueous components are transported individually by advection and dispersion, and a chemical step where the aqueous and solid phase components react with each other. Since the overall system is uncoupled this way, the solution to the transport problem is through an external coupling of the transport model and the geochemical model. The set of equations to be solved simultaneously has been reduced, and hence larger systems with more species and components can be considered [12].

Most of the previous work in heavy metal transport has concentrated on the groundwater regime of the soil. However, it is important to understand metal movement in the vadose zone of the soil, where there is a significant amount of organic matter in the form of root exudates in the rhizosphere. These exudates release organic acids, such as humic, fulvic and acetic acids, which further affect the geochemistry of lead dissolution. The objective of this study is to model the movement of lead through unsaturated soil in the presence of vegetation, with emphasis on the geochemistry. In order to achieve this objective, a hypothetical soil column is chosen where the movement of water and lead with its associated components is essentially in the vertical downward direction. The background ions chosen are sulfate and carbonate. The lead minerals are Cerussite (lead carbonate) and Anglesite (lead sulfate). The overall trans-

port model is solved using the second approach as described above.

## DYNAMIC MODELING

The objective of the model is to simulate the transient changes in the one-dimensional movement of heavy metals in a soil column under the influence of various geochemical interactions. The model also considers root uptake of water and the subsequent bulk movement of lead and associated components with water. Transport by diffusion, due to concentration gradients between the soil solution and root water, is neglected. The overall modeling effort involves establishing the flow field at various times within the column, computing the concentration field by convection and dispersion of the heavy metal under the influence of the imposed flow field, and equilibrating the system under the influence of various species and minerals.

### Equations for the flow model

The flow model is formulated using Richards equation for unsaturated movement of water in one dimension with the inclusion of root water uptake [13]. The equations governing vertical water movement are

$$q = -K \left( \frac{\partial \Psi}{\partial z} - 1 \right) \quad (1)$$

$$\frac{\partial \theta}{\partial t} = \frac{\partial q}{\partial z} - S \quad (2)$$

where  $\theta$  is water content by volume ( $\text{cm}^3/\text{cm}^3$ ),  $q$  is the water flux ( $\text{cm}/\text{h}$ ),  $S$  is the sink term for root water extraction ( $\text{cm}^{-1}$ ),  $K$  is the hydraulic conductivity ( $\text{cm}/\text{h}$ ),  $\Psi (< 0)$  is the soil matrix potential ( $\text{cm}$ ),  $z$  is the vertical coordinate direction taken positive downward, and  $t$  is time ( $\text{h}$ ). The two equations can be combined to yield the Richards equation in terms of  $\theta$  as

$$\frac{\partial \theta}{\partial t} = - \frac{\partial}{\partial z} \left[ K(\theta) \left( \frac{\partial \Psi}{\partial z} - 1 \right) \right] - S(\Psi) \quad (3)$$

where the sink term depends on  $\Psi$  which controls the water availability to roots. The  $K(\theta)$  and  $\Psi(\theta)$  are non-linear functions, and have been described by Brooks and Corey [14]. The pore water velocity at any depth is given by

$$v(z) = \frac{q(\theta)}{\theta} \quad (4)$$

The equation describing the root water uptake is expressed as

$$S(\psi) = \alpha(\psi)S_{\max} \quad (5)$$

where  $\alpha(\Psi)$  determines the proportion of the maximum possible root extraction rate  $S_{\max}$  for a particular value  $\Psi$ . The expression for  $\alpha(\Psi)$  is given as

$$\alpha(\psi) = \exp[-\delta|\psi - \psi_b|], \psi \leq \psi_b \quad (6)$$

where  $\Psi_b$  is the air entry pressure head. Equation 6 indicates an exponential reduction in rate of availability of water to the roots as the soil becomes drier.

### Equation for the transport model

The equation describing the movement of contaminants is

$$\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial z} \left[ D \frac{\partial C_k}{\partial z} \right] - \frac{\partial}{\partial z} (v(z)C_k) + R_k \quad (7)$$

$k = 1, 2, \dots, N_c$

where  $C_k$  is the concentration of the  $k$ -th component at any spatial location  $z$  at any time  $t$ ,  $D$  is the dispersion coefficient, and  $R_k$  is the chemical source/sink term representing the changes in aqueous component concentrations.

### Geochemistry

The interactions between heavy metals and various ions in both aqueous and solid phases are represented in the form of a set

of non-linear algebraic equations. The system of equilibrium equations relates the dependent variables (species) with independent variables (components). A species is defined as a chemical entity to be considered in the transport problem. The species are not limited to aqueous phase, but also include those that are in the solid phase. Associated with each species is a mass law equation and an equilibrium constant. A set of components is defined, so that for each species an equation can be written expressing it as the product of a reaction involving only components [9]. Thus, the set of components is defined as the minimum number of species that uniquely describe the chemical system [15]. In this paper, lead is chosen as the heavy metal of interest. The applicable geochemistry of lead in the presence of background ions and minerals is described in Table 1.

### SOLUTION STRATEGY

The solution space for the transport model described above consists of three domains: spatial, chemical and temporal [12]. The advection-dispersion terms describing aqueous phase transport are spanning over spatial and temporal domains only, and the geochemical equations describing the transformation of heavy metal into different species are spanning over the chemical domain only. In other words, the advection-dispersion equations and geochemical equations are decoupled and solved separately. The advantage of this method of solution is that the highly non-linear behavior of geochemical equilibrium is confined to the model describing the geochemistry. Thus, the overall solution system consists of two steps: a physical step in which the advective-dispersive terms of the transport equation are solved, keeping the reaction (sink/source) terms constant, and a chemical step in which the chemical equilibrium equations are solved for the aqueous and solid phase components, for each nodal point in the spatial domain.

A sequential coupling strategy of the physical and chemical steps has been adopted. The physical and chemical coupling is external. The disadvantage of this method is that chemical equilibrium is allowed to occur only at the end of a time step. This does not cause significant errors if small time steps are chosen.

## FLOW MODEL

The flow model consists of equations for

water content distribution, velocity field and root water uptake as described in the previous section. The partial differential equations are discretized in time and space using finite differences. At each time step, a set of non-linear algebraic equations are formulated. These equations are solved using Newton's method with tri-diagonal matrix representation to obtain the spatial distribution of the water content along the length of the column. Some of the input parameters to the model are saturated con-

### Terminology:

T indicates the total concentration of element in moles/L  
 C indicates the concentration of aqueous species in moles/L  
 S indicates the concentration of solid species in moles/L  
 $K_i^a$  equilibrium constant for species i in aqueous phase  
 $K_i^s$  equilibrium constant for species i in solid phase

### The aqueous species considered:

Pb=Pb<sup>2+</sup>, S=SO<sub>4</sub><sup>2-</sup>, C=CO<sub>3</sub><sup>2-</sup>, P= PO<sub>4</sub><sup>3-</sup>, pH  
 Cl=Cl<sup>-</sup>, PbS=PbSO<sub>4</sub><sup>0</sup>, PbC=PbCO<sub>3</sub><sup>0</sup>, PbOH=PbOH<sup>+</sup>

### The solid phase minerals considered:

Anglesite (PbSO<sub>4</sub>=PbS)  
 Cerusite (PbCO<sub>3</sub>=PbC)  
 Pyromorphite (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl=PbP)

### Elemental Mass Balances

Lead balance:

$$T_{Pb}=1.0 \cdot C_{Pb} + 1.0 \cdot C_{PbS} + 1.0 \cdot C_{PbC} + 1.0 \cdot S_{PbS} + 1.0 \cdot S_{PbC} + 5.0 \cdot S_{PbP}$$

Sulfate balance:

$$T_S=1.0 \cdot C_S + 1.0 \cdot C_{PbS} + 1.0 \cdot S_{PbS}$$

Carbonate balance:

$$T_C=1.0 \cdot C_C + 1.0 \cdot C_{PbC} + 1.0 \cdot S_{PbC}$$

Chloride balance:

$$T_{Cl}=1.0 \cdot C_{Cl} + 1.0 \cdot S_{PbP}$$

Phosphate balance:

$$T_P=1.0 \cdot C_P + 3.0 \cdot S_{PbP}$$

### Law of Mass Action Equations

Lead Sulfate in solution:

$$K_{PbS}^a=10^{2.75}=C_{Pb} \cdot C_S / C_{PbS}$$

Lead Carbonate in solution:

$$K_{PbC}^a=10^{7.24}=C_{Pb} \cdot C_C / C_{PbC}$$

Lead Hydroxide in solution:

$$K_{PbOH}^a=10^{-7.71}=C_{Pb} \cdot C_{OH} / C_{PbOH}$$

Lead Sulfate precipitation:

$$K_{PbS}^s=10^{-7.79}=C_{Pb} \cdot C_S$$

Lead Carbonate precipitation:

$$K_{PbC}^s=10^{-13.5}=C_{Pb} \cdot C_C$$

Lead Pyromorphite precipitation:

$$K_{PbP}^s=10^{-25.08}=(C_{Pb})^5 \cdot (C_P)^3 \cdot (C_{Cl})$$

Table 1. Applicable geochemistry of lead.

ductivity, water content at saturation and root water uptake parameters. The initial moisture content distribution and the water content at the top of the column (inlet) or the flux have to be provided at all times as boundary conditions. The model computes the transient water content distribution and flow field along the length of the column.

## TRANSPORT MODEL

The objective of the transport model is to compute concentrations of lead and background ions such as sulfate and carbonate as these undergo essentially vertical downward movement in the unsaturated soil. The heavy metal movement in the column is only due to the physical transport of the component. The mechanisms of transport considered are advection and dispersion. The retention of each component by the soil matrix is not explicitly considered in the transport step. Each component is transported independent of the other, i.e., the movement of one component has no influence on the other in the physical step. This is a reasonable assumption, when convection is larger compared to molecular diffusion. A finite difference method was used to discretize the equations. These equations usually have problems of numerical dispersion. In order to circumvent this problem, an Eulerian-Lagrangian approach was adopted [16]. The solution procedure for the transport component was split into two steps. During the first step, only pure convection is considered. Then, the convected concentrations obtained are solved for second-order dispersion using Eulerian approach. The system of algebraic equations resulting from discretization at each time step, are solved by formulating a tridiagonal system and invoking the Thomas algorithm.

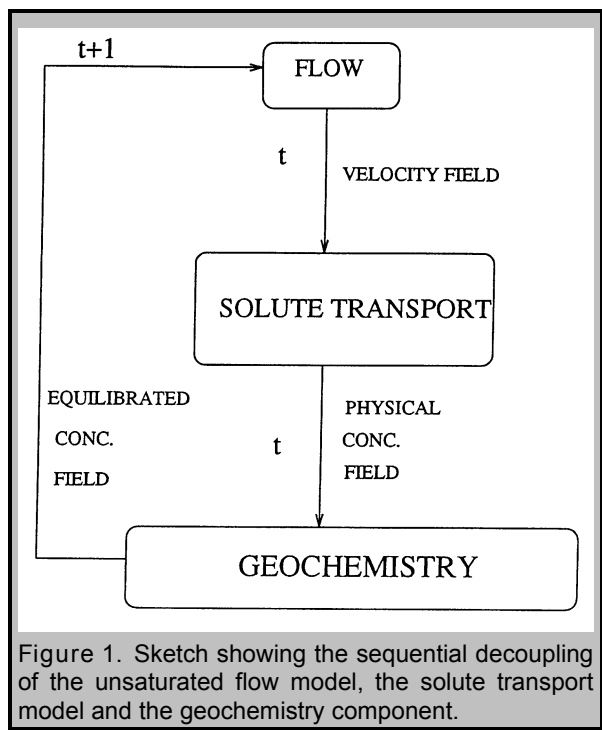
## GEOCHEMICAL MODEL

The heavy metals are reactive and undergo various chemical transformations in the contaminated soil. The concentration of

heavy metal depends on the various geochemical interactions between the metals and minerals. The geochem model attempts to solve the equilibrium chemistry of the heavy metal (lead, in this case) in the presence of various minerals. The retention mechanisms considered are aqueous complexation and mineral precipitation. The mineralogy and reactions chosen for a hypothetical lead-contaminated soil are depicted in Table 1. All the reactions are assumed to be taking place over a representative elementary volume (REV) and are instantaneous. The model receives advected component concentrations from the convective-dispersive transport model and equilibrates the system. The constants of equilibrium such as dissolution constants and solubility products were obtained from Lindsay [17]. The set of equilibrium reactions are solved simultaneously for concentrations of different aqueous and solid phase species. The equilibrated component concentrations are sent back to the transport model for the next time step. The set of equations are solved using a non-linear Newton-Raphson solution technique with Marquardt's modification (Source: IMSL library). The module checks for the precipitation and dissolution of solids. In case of precipitation of some of the solids, the module re-equilibrates the whole system. It determines the concentrations of all the species (solids as well as aqueous) and computes the modified total component concentrations in the aqueous phase. These modified component concentrations will be sent back to the transport model.

## IMPLEMENTATION OF THE DEVELOPED MODELS

A sequential coupling procedure is followed as described in the preceding section. At each time step, the master module first calls the flow model. This model computes the pore flow velocity at each spatial node. The other important process variables computed by the flow model are spatial distribution of water content and plant up-



take of lead. The master program then calls the transport model. This model furnishes the convected concentrations at each node for each component under consideration, for the given velocity distribution provided by the flow model. The convected concentrations of the components are taken as inputs by the geochemical model. This model equilibrates the chemical system using the appropriate reactions and returns the modified component concentrations which are further convected by the transport model at the next time step. The flow-chart depicting this methodology is shown in Figure 1.

## SIMULATION EXAMPLE

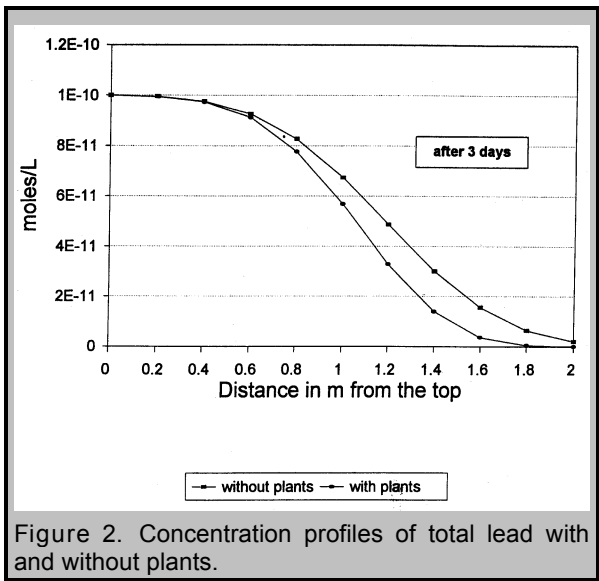
The system chosen in this study is a 2 m long one-dimensional soil column with a nodal spacing of 0.1 m, dispersion coefficient of 1.0 cm<sup>2</sup>/day, saturated hydraulic conductivity of 0.22 cm/day, and a flux of 0.11 cm/day at the soil surface. The soil was initially dry. A constant initial moisture content distribution of 0.1 is chosen within the column. The initial concentration distributions of all the components considered

are chosen as zero throughout the column. The boundary conditions at the top of the column are a constant water flux of 0.11 cm/day, lead concentration of 0.02 ppb, sulfate concentration of 9.6 ppm, and carbonate concentration of 6 ppm. In order to illustrate the influence of vegetation, a plant uptake parameter ( $S_{max}$ ) of 0.08 cm/day is chosen. While this parameter is a function of the rooting depth within the soil column, a constant value is used in this work. The pH of the soil solution was set to 8.5. The aqueous components considered are ionic lead, sulfate, carbonate, aqueous complexes such as lead sulfate and lead carbonate, and minerals such as cerusite (lead carbonate) and anglesite (lead sulfate).

## RESULTS AND DISCUSSION

Figure 2 shows the influence of plant uptake of the lead after three days. The concentration of lead in the soil solution is smaller with plant uptake than when plants are not present. Root uptake reduces the pore water velocity, and thus the movement of lead is also reduced. The model does not consider the diffusional driving forces between soil water and root water. These forces may be important when there is lot of resistance offered by the biofilms at the root vicinity [18].

Results in Figures 3a and 3b show concentrations after three days of simulation. A constant pH of 8.5 is used in the simulation. Figure 3a shows the concentration of the total lead component as a function of depth in the soil. Figure 3b shows the concentrations of the ionic lead and lead carbonate. In this scenario, precipitation of chemical species is not considered. The tailing of concentration observed in Figure 3a is expected due to the physical transport of lead under convective and dispersive concentration gradients in the vertically downward direction. Figure 3b shows the concentrations of ionic lead and lead carbonate. This figure clearly indicates that lead carbonate and ionic lead are the



dominant species at the specified conditions. The concentration of lead sulfate is negligible.

Figure 4 further demonstrates the influence of geochemistry on the movement of lead through the unsaturated soil column. The concentration of reactive lead in the column at any spatial location is smaller than that of nonreactive lead. At the prescribed pH of 8.5, lead forms soluble complexes such as lead sulfate, lead hydroxide and lead carbonate. The concentration of ionic lead has thus been reduced due to its geo-transformation in the presence of background anionic concentrations (sulfate, hydroxyl and carbonate ions).

Figure 5 shows the influence of precipitation on heavy metal transport. The solid phase controlling lead transport, in this case, is lead carbonate. The soil pH was reduced to 6.5, inlet lead concentration was 1.0 mg/L, and background carbonate concentration was 1.0 mmole/L. The difference in amount between the total lead without considering precipitation and total lead considering precipitation (Figure 5) indicates the extent of precipitation of lead carbonate. At locations where there is no lead precipitation, the profiles of lead are identical. After 2 days, for depths less than 0.4 m

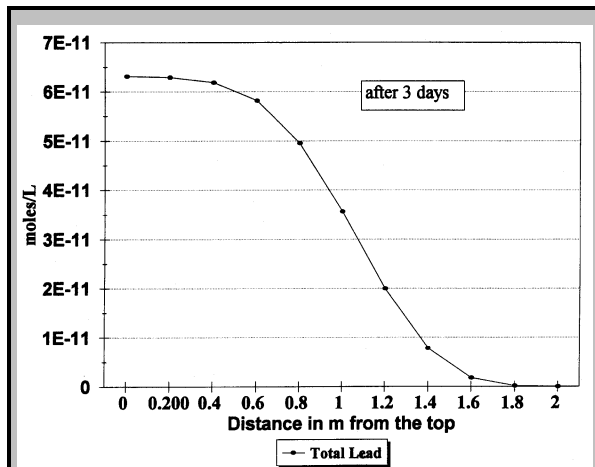


Figure 3a. Concentration of total lead as a function of position for slow flow through the column.

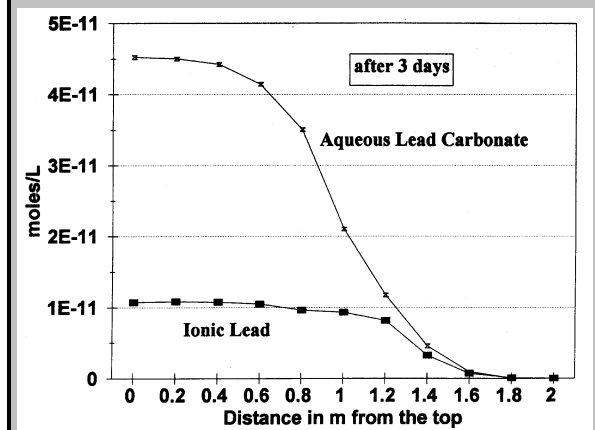


Figure 3b. Concentrations of ionic lead and lead carbonate in the aqueous phase after three days as a function of position.

in Figure 5, the lead and carbonate concentrations are high enough to cause precipitation.

Phosphorus may be added to soil to reduce the aqueous phase lead concentration as shown in Table 2. Lead is precipitated as lead pyromorphite. Lead concentrations can be reduced to values which are below the maximum allowable contamination level. Formation of insoluble and stable pyromorphites results in reduced bioavailability of lead [19].

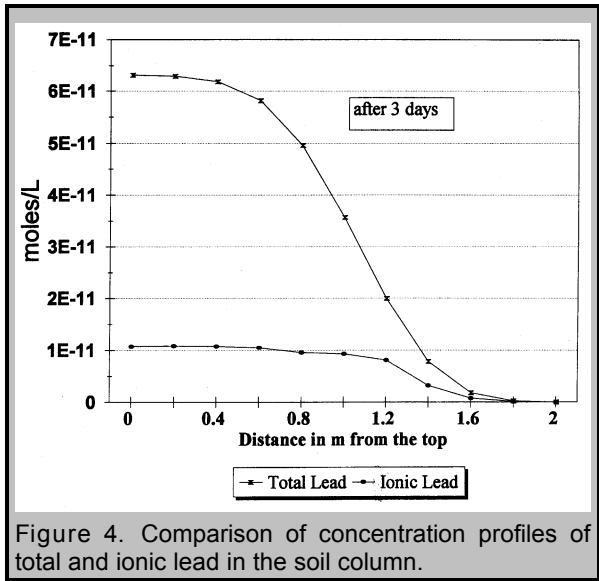


Figure 4. Comparison of concentration profiles of total and ionic lead in the soil column.

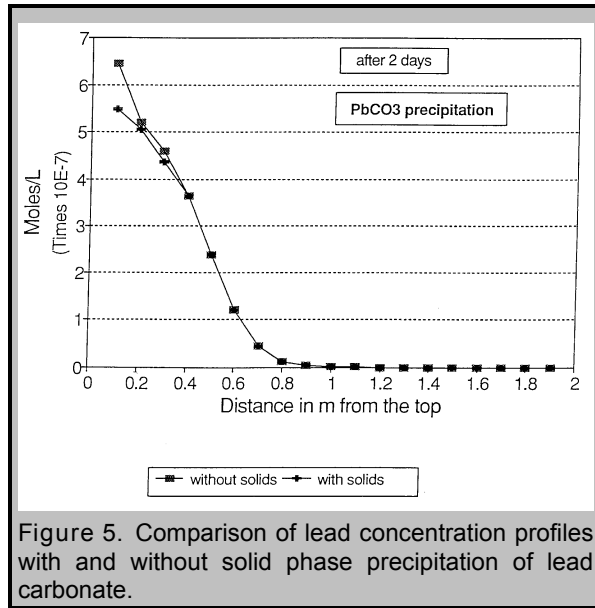


Figure 5. Comparison of lead concentration profiles with and without solid phase precipitation of lead carbonate.

### CONCLUSIONS

A unified solute transport model was developed to simulate the movement of lead, a heavy metal of environmental concern. The model integrates the unsaturated flow model with plant uptake, the physical transport model, and the geochemical model. The highly non-linear chemical equilibrium equations are separated from the overall system, thus allowing for ease in solving the transport problem. Preliminary results show plants do have significant influence on the transport of lead through the unsaturated soil. In this work, we have not incorporated the influence of speciation of heavy metals with organic ligands that are released by root exudates in the rhizosphere environment. An investigation

on the biochemical effects of lead geochemistry is underway. Lead is transported into the plants, not only by bulk water movement, but also by the concentration gradient between the soil-water and root-water.

This study has shown that the aqueous phase speciation of metals, with background ions and precipitation and dissolution of minerals, has a significant effect on the transport of heavy metals (lead) through unsaturated soils. The effect of unsaturation is reflected in the pore water velocities, which in turn affect the solute movement through the soil. Further study on the influence of geochemistry will be performed by considering physical and re-

Controlling solid phase of lead			
pH	Lead Sulfate	Lead Carbonate	Lead Pyromorphite
5	328	308,509	0.5
6.5	328	402	0.03
8	328	0.308	0.00013

Conditions for phosphate control:  $PO_4^{3-}=10^{-3}$  M,  $Cl^- = 10^{-4.5}$  M  
 Conditions for sulfate control:  $SO_4^{2-}=10^{-2}$  M  
 Conditions for carbonate control:  $CO_3^{2-}=10^{-4.5}$  M

Table 2. Soluble lead concentrations in ppb in soil for different chemical conditions.



active adsorption using empirical activity models such as Freundlich, Langmuir and BET models, molecular adsorption models such as diffuse layer models, and ion exchange adsorption reaction models.

Such modeling efforts provide insight into the geochemical effects of lead transport through vadose zone in a soil column, and may be used as a tool for understanding the geochemical transformations of heavy metals in the presence of various minerals existing in metal-contaminated sites.

## ACKNOWLEDGMENT

Although the research described in this article has been funded in part by the United States Environmental Protection Agency through the EPA EPSCoR program and under assistance agreement R-819653 through the Great Plains-Rocky Mountain Hazardous Substance Research Center headquartered at Kansas State University, it has not been subjected to the Agency's peer and administrative review and, therefore, may not necessarily reflect the views of the Agency. No official endorsement should be inferred. This research was partially supported by the state of Kansas through the EPSCoR program and the Kansas State University Center for Hazardous Substance Research.

## REFERENCES

1. G.M. Pierzynski, J.L. Schnoor, M.K. Banks, J.C. Tracy, L.A. Licht and L.E. Erickson, Vegetative Remediation at Superfund Sites, Mining and Its Environmental Impact, In: R.E. Hester and R.M. Harrison (Eds.), Issues in Environmental Science and Technology, Royal Society of Chemistry, 1 (1994) 49-69.
2. R.L. Chaney and J.A. Ryan, Risk Based Standards for As, Pb, and Cd in Urban Soils, DeChema 6, May 9, 1994.
3. D.B. Levy, K.A. Barbarick, E.G. Siemer and L.E. Sommers, Distribution and Partitioning of Trace Metals in Contaminated Soils Near Leadville, Colorado, J. Environmental. Qual., 21 (1992) 185-195.
4. J. Rubin and R.V. James, Dispersion-Affected Transport of Reacting Solutes in Saturated Porous Media: Galerkin Method Applied to Equilibrium Controlled Exchange in Unidirectional Steady Water Flow, Wat. Resour. Res., 9(5) (1973) 1332-1356.
5. D.J. Kirkner and H. Reeves, Multicomponent Mass Transport with Homogeneous and Heterogeneous Chemical Reactions: Effects of the Chemistry on the Choice of Numerical Algorithm, 1. Theory, Water Resour. Res., 24(10) (1988) 1719-1729.
6. A.J. Valocchi, R.L. Street and P.V. Roberts, Transport of Ion-Exchanging Solutes in Groundwater: Chromatographic Theory and Field Simulations, Water Resour. Res., 17(5) (1981) 1517-1527.
7. A.A. Jennings, D.J. Kirkner and T.L. Thies, Multicomponent Equilibrium Chemistry in Groundwater Quality Models, Water Resour. Res., 18(4) (1982) 1089-1096.
8. C.L. Carnahan, Coupling of Precipitation-Dissolution Reactions to Mass Diffusion via Porosity Changes, In: D.C. Melchior and R.L. Basset (Eds.), Chemical Modeling of Aqueous Systems 2, American Chemical Society, Washington, D.C., 1990, pp. 234-242.
9. G.A. Cederberg, R.L. Street and J.O. Leckie, A Ground Water Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems, Wat. Resour. Res., 21(8) (1985) 1095-1104.

10. T.N. Narasimhan, A.F. White and T. Tokunaga, Groundwater Contamination from an Inactive Uranium Mine Tailings Pile, 2, Application of a Dynamic Mixing Model, *Water Resour. Res.*, 22(3) (1986) 1820-1834.
11. H.J. Lensing, J.M. Vogt and B. Herrling, Modeling of Biologically Mediated Redox Processes in the Subsurface, *J. Hydrology.*, 159 (1994) 125-143.
12. A.L. Walter, E.O. Frind, D.W. Blowes, C.J. Ptacek and J.W. Molson, Modeling of Multicomponent Reactive Transport in Groundwater, 1. Model Development and Evaluation, *Wat. Resour. Res.*, 30(11) (1994) 3137-3148.
13. R.S. Govindaraju and M.L. Kavvas, Development of an Approximate Model for Unsaturated Flow with Root Water Uptake Under Rectangular Water Content Profiles Assumption, *Journal of Hydrology*, 146 (1993) 321-339.
14. R.H. Brooks and A.T. Corey, Hydraulic Properties of Porous Media, Hydrology Paper No. 3, Colorado State University, Fort Collins, 1964.
15. C.D. Mangold and C.F. Tsang, A Summary of Subsurface Hydrological and Hydrochemical Models, *Rev. Geophys.*, 29(1) (1991) 51-71.
16. N.R. Thomson, J.R. Sykes and W.C. Lennox, A Lagrangian Porous Media Mass Transport Model, *Wat. Resour. Res.*, 20(3) (1984) 391-399.
17. W.L. Lindsay, *Chemical Equilibria in Soils*, Wiley-Interscience, 1979.
18. M.Y. Corapcioglu, Modeling Plant Uptake and Biodegradation of Semi-Volatile Hydrocarbon Compounds, *Wat. Sci. Tech.*, 26(7-8) (1992) 1651-1658.
19. M.V. Ruby, A. Davis and A. Nicholson, In Situ Formation of Lead Phosphates in Soils as a Method to Immobilize Lead, *Environmental Science and Technology*, 28 (1994) 646-654.