

## Modeling Pb transport in soil column and ground water

S. A. Mirbagheri \*, N. Javadifar, A. H. Hasani

*Department of Environmental Engineering, Faculty of Environment and Energy, Tehran Science and Research Branch, Islamic Azad University, Tehran, Iran*

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A mathematical and computer model for the transport and transformation of Pb through a soil column from the surface to the groundwater is presented. The model simulates Pb species. This model is based on the mass balance equation including convective transport, dispersive transport, surface adsorption, oxidation and reduction, volatilization, chemical and biological transformation. The governing equations are solved numerically by the method of implicit finite difference. The simulation results are in good agreement with measured values. The major finding in the present study indicates that as the time of simulation increases, the concentration of different Pb species approaches the measured values.

**Key words:** Pb transport, mathematical, computer, model, Pb species

### INTRODUCTION

Mathematical modeling is an accepted scientific practice, providing the mechanism for comprehensively integrating basic processes and describing a system beyond what can be accomplished using subjective human judgements. It is possible to construct models that better represent the natural system and to use these models in an objective manner to guide both our future research efforts and current management practices.

Recent years have seen a variety of approaches to description of water and solute movement in soils field. A number of new models have been proposed in response to recently collected field data on solute leaching patterns. The contaminants are released from the refuse to the passing water by physical, chemical, and microbial processes and percolate through the unsaturated environment, polluting the groundwater with organic and inorganic matter.

The modeling of contaminant transport hinges on an understanding of the mechanisms of mass release from the solid to the liquid phase, and contaminant decay. These mechanisms are influenced by such factors as climatic conditions, type of waste, site geohydrologic conditions, and chemical reactions as well as microbial decomposition of organic matter.

Modeling of different kinds of contaminant was studied by several researchers [1-2-3-4-5]

The objective of this paper is to address the spatial and temporal distribution of contaminant

concentrations in soil column. The work has been done in Gorgan site, Golestan province, Iran in 2014.

### *Mathematical Model*

The flow and the corresponding moisture content and the concentration of a contaminant are considered here in as continuous functions of both space and time. This model considers a variety of processes that occur in the plant root zone as well as leaching to the ground water, including transient fluxes of water and contaminants, alternating periods of rainfall, irrigation and evapotranspiration, under variable soil conditions with depth.

### *Water flow model*

Water flow is calculated using a finite difference solution to the soil-water flow equation

$$\frac{\partial h}{\partial t} c(\theta) = \frac{\partial}{\partial z} \left[ K(\theta) \cdot \frac{\partial H}{\partial z} \right] \quad (1)$$

Where  $h$  is a soil water pressure head (mm),  $\theta$  is volumetric water content ( $\text{m}^3\text{m}^{-3}$ ),  $t$  is time (day),  $H$  is hydraulic head ( $h + z$ ),  $z$  is soil depth,  $K$  is hydraulic conductivity ( $\text{mm day}^{-1}$ ),  $c(\theta) = \partial\theta/\partial h$  is differential water capacity. Functions which characterized relationships between  $K - \theta - h$  described in LEACHM [6-7] are used. There is a two-part function that described the general shape of  $\theta(h)$  relationships [7-8].

\* To whom all correspondence should be sent:  
E-mail: cwl@ncepu.edu.cn

$$h = \frac{[1 - (\theta / \theta_s)]^{1/2} (\theta_i / \theta_s)^{-b}}{[1 - (\theta_i / \theta_s)]^{1/2}} \quad \text{for } 0 > h > h_i \quad (2a)$$

$$h = a(\theta / \theta_s)^{-b} \quad \text{for } h_i > h > -\infty \quad (2b)$$

Where  $h_i = a[2b / (1+2b)]^{-b}$  and  $\theta_i = 2b\theta_s / (1+2b)$  is the point  $h_i, q_i$  of intersection of the two curves,  $\theta_s$  is water content at saturation,  $a$  and  $b$  are constant. The two curves are exponential and parabolic for dry and saturated soil respectively. Similarly the equations for hydraulic conductivity can be derived as a function of soil water pressure head. When soil water pressure head is greater than  $h_i$  the following equation is used to calculate hydraulic conductivity:

$$K(\theta) = K_s (\theta / \theta_s)^{2b+2+p} \quad (3)$$

Where  $K_s$  is hydraulic conductivity at saturation water content ( $\theta_s$ ), and  $P$  is Pore water interaction parameter. When soil pressure head is less than  $h_i$  the equation for the calculation of hydraulic conductivity is:

$$K = K_s (a / h)^2 + (2+P) / b, \quad (4)$$

Solving equation (1) using finite difference techniques provides estimated values of  $h$  at each depth node used in the differencing equation. Water contents are calculated using equation (2). Water flux densities ( $q$ ) are calculated over each depth

$$\left( q = K(\theta) \frac{\Delta H}{\Delta Z} \right)$$

interval using Darcy's equation. Finally, the values of  $q$  are then used to estimate Pb transport in the soil profile. The finite difference solution of equation (1) described in detail can be found in LEACHM [9].

#### Pb transport model

The bulk motion of the fluid, and controls contaminant transport through the soil column by molecular diffusion and mechanical dispersion. Mixing due to molecular diffusion is negligible compared to that caused by dispersion. At the same time generation of loss of mass takes place due to adsorption and desorption, and the biokinetics of the mass dissolved or suspended in the moving water. In this study Pb was modeled. Figure 1 shows some of the Pb transport and transformation processes and the factors affecting each of the processes.

In general for steady-state water flow condition the transport terms for Pb are:

$$J_s = J_{DL} + J_{CL} \quad (5)$$

Where  $J_s$  is total Pb flux ( $\infty g m^{-2} day^{-1}$ ),  $J_{DL}$  is the diffusion flux in the liquid phase and  $J_{CL}$  is the convection flux in the liquid phase. In the case of diffusion in the liquid phase in a porous media, the equation represented by Fick's law as:

$$J_{DL} = D_M + (\theta) \frac{dC_L}{dz} \quad (6)$$

Where  $C_L$  is concentration in the liquid phase and  $D_M(\theta)$  is the molecular diffusion coefficient. The value of  $D_M(\theta)$  can be estimated (Kemper and Van Schaik, 1966) as:

$$D_M(\theta) = D_{OL} a \exp(b\theta) \quad (7)$$

Where  $D_{OL}$  is the diffusion coefficient in a pure liquid phase and  $a$  and  $b$  are empirical constants reported by Olsen and Kemper (1981) to be approximately  $b = 10$  and  $0.005 < a < 0.01$  the convective flux of Pb can be represented as:

$$J_{CL} = -\theta D_h(q) \frac{dC_1}{dz} + q C_1 \quad (8)$$

Where  $q$  is the water flux, and  $D_h(q)$  is the hydrodynamic dispersion coefficient that describes mixing between large and small pore as the result of local variations in mean water flow velocity. Combining the molecular diffusion coefficient and hydrodynamic dispersion coefficient as:

$$D(\theta, q) = D_M(\theta) + q D_h(q), \quad (9)$$

Where  $D(\theta, q)$  is the apparent diffusion coefficient ( $cm^2 day^{-1}$ ). Substituting equations 6, 8 and 9 into equation 5 the overall Pb flux is given as:

$$J_s = -\theta D(\theta, q) \frac{\partial C_L}{\partial Z} + q C_1 \quad (10)$$

Partitioning Pb between sorbed and solution phases, according to Alemi [2], adsorption of Pb are assumed taken to be nonlinear equilibrium process described by:

$$C_s = C_s K^n \quad (11)$$

Where  $C_s$  is the concentration of Pb adsorbed on the soil ( $\alpha$  mole  $K^{-1}$ ),  $K_s$  is the adsorption coefficient for Pb ( $L Kg^{-1}$ ),  $C$  is the concentration of Pb in the soil solution ( $\alpha$  mole  $L^{-1}$ ),  $n$  is the nonlinear equilibrium adsorption reaction exponent for Pb.

The total amount of Pb ( $C_T$ ) contained in the solution and adsorbed phases in a soil volume of one liter are:

$$C_T = \rho C_s + \theta C_1 \quad (12)$$

Where  $\rho$  is the soil bulk density ( $g cm^{-3}$ ). Substituting equation (11) for  $C_s$  in equation (12) one can get the convection-dispersion equation:

$$C_T = C_T + (\theta + \rho K_s), \quad (13)$$

Pb transports in soil system occur under non-steady (transient) water flow condition. The water content ( $\theta$ ) and water flux ( $q$ ) both vary with depth

and time. Using continuity relationships of mass over space and time gives:

$$\frac{\partial C_T}{\partial t} = -\frac{\partial J_s}{\partial z} \pm \Phi \quad (14)$$

Where  $C_T$  the total Pb concentration in sorbed and solution is phases and  $\phi$  represents all sources or sinks of Pb. Substituting equation (8) and (13) into (14) gives general one-dimensional transport equations for Pb transport:

$$\frac{\partial C}{\partial t}(\theta + \rho K_s) = \frac{\partial}{\partial z} \left[ \theta D(\theta, q) \frac{\partial C}{\partial z} - qC \right] \pm \Phi \quad (15)$$

Where C is concentration of all Pb species in soil solution, and  $\phi$  indicates all possible sources or sinks term.

*Solution procedure*

Prediction of the concentration of Pb in all phases (liquid, sorbed, gas) as well as leaching losses at any depth for all time levels requires simultaneous solution of equations for all Pb species.

The equations are solved numerically using an implicitly finite difference scheme and Crank-Nicholson approximation.

Using Figure 2 for the nodes and segments as well as time interval; the first term in equation (15)

is evaluated at node i and time  $t^{j+1/2}$  and is differenced as:  $C = C_1$

$$R_1 \frac{\partial C}{\partial t} = (C_i^{j+1} - C_i^j) / \Delta t \quad (16)$$

$$R_1 = 1 + \frac{\rho}{\theta} \cdot N \cdot K S_1 \cdot C_1^{N-1}$$

The second term in equation (15) is a diffusion and dispersion term. D (q) for the interval between nodes i-1 and i is differenced as:

$$D_{i-1/2}^{j+1/2} = \lambda q_{i-1/2}^{j+1/2} / \theta_{i-1/2}^{j+1/2} + D_{OL} a [\exp(-b \theta_{i-1/2}^{j+1/2})] / \theta_{i-1/2}^{j+1/2} \quad (17)$$

Where

$$\theta_{i-1/2}^{j+1/2} = (\theta_{i-1}^{j+1} + \theta_{i-1}^j - \theta_i^{j+1} - \theta_i^j) / 2 \quad (18)$$

$$\frac{\partial}{\partial z} (D(\theta, q) \frac{\partial C}{\partial z}) =$$

$$[D_{i-1/2}^{j+1/2} (C_{i-1/2}^{j+1/2} + C_{i-1}^j - C_i^{j+1} - C_i^j) / \Delta z_1 - D_{i+1/2}^{j+1/2} (C_i^{j+1} + C_i^j - C_{i+1}^{j+1} - C_{i+1}^j) / \Delta z_2] \Delta z_3 \quad (19)$$

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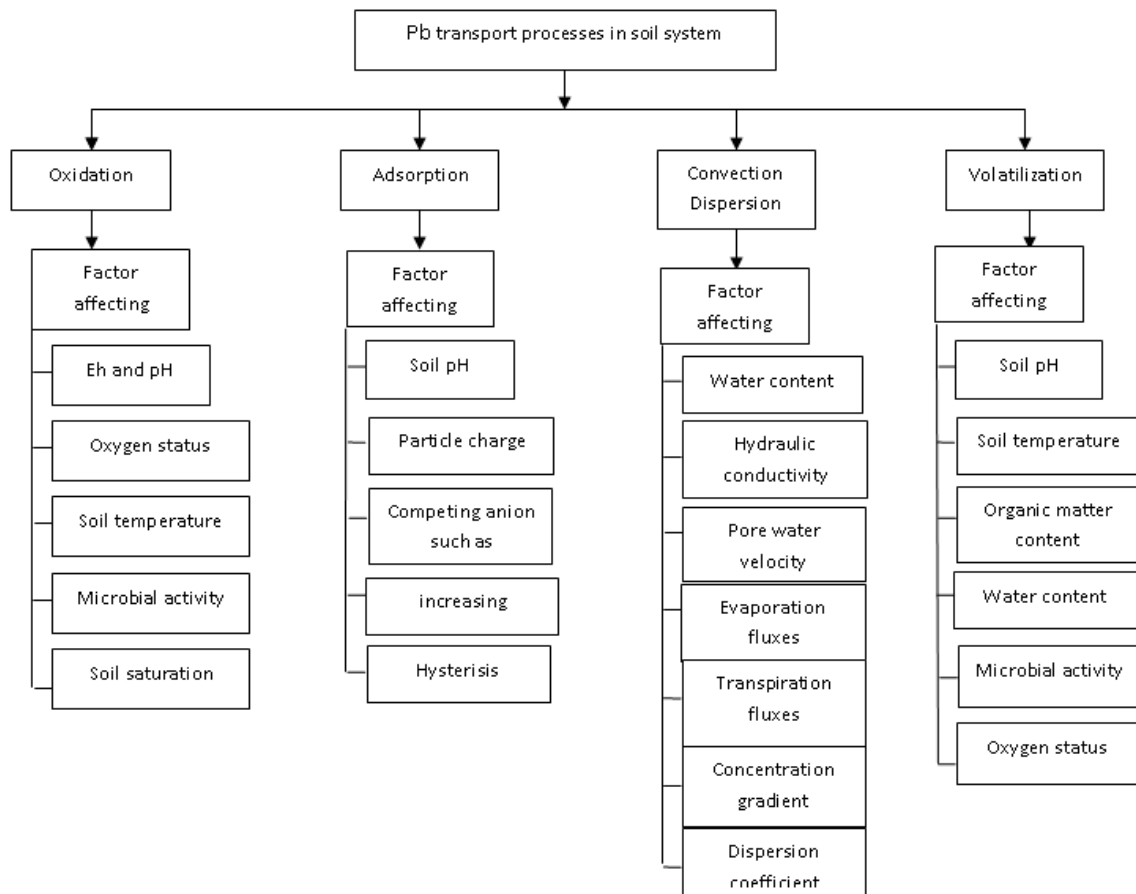


Fig.1. The transport processes and the related factors.

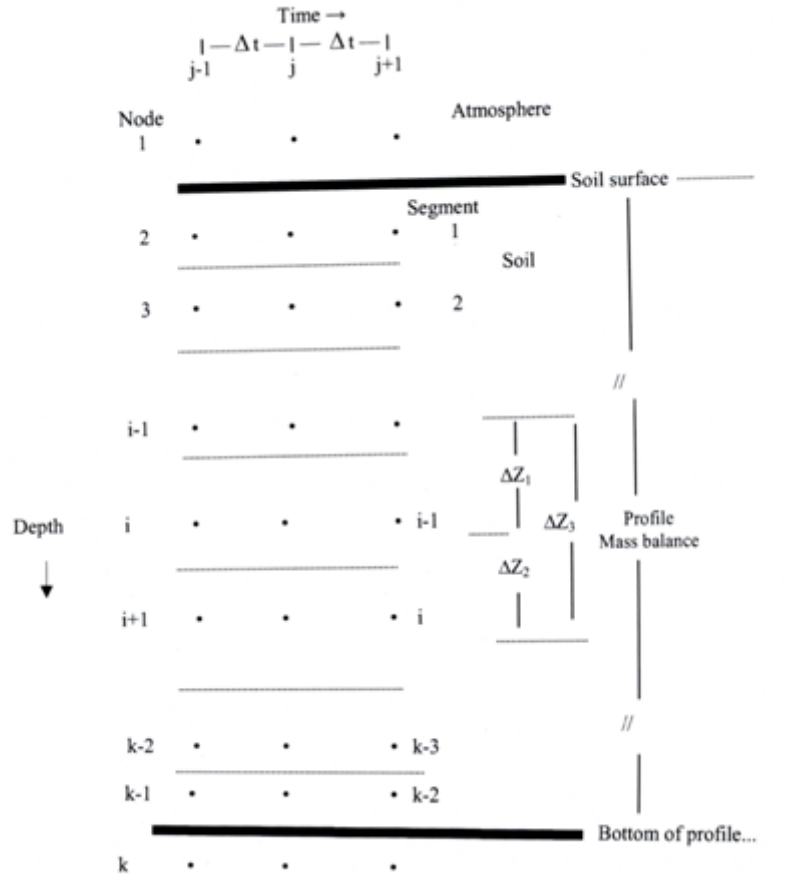


Fig. 2. Definition of nodes and segments.

The convection term in equation (15) is differenced as:

$$v \frac{\partial C}{\partial z} = v_i - 1/2 (C_{i-1}^J + C_{i-1}^{J+1}) / \Delta z_3 - v_i + 1/2 (C_i^J + C_i^{J+1}) / \Delta z_3 - v_i + 1/2 (C_{i+1}^J + C_{i+1}^{J+1}) / \Delta z_3 \pm \Phi \quad (20)$$

Multiplying out and collecting the unknown  $C_i^{J+1}$  terms on the left-hand side and the known  $C^J$  terms on the right-hand side, the general form of equation as:

$$A_i C_{i-1}^{J+1} + B_i C_i^{J+1} + C_i C_{i+1}^{J+1} = D_i$$

Where  $D_i$  considers all the sources and sinks in equation (16). For example the sources and sinks term for equation (16) are:

$$\Phi = \frac{\alpha_1 C_1 U(z,t)}{\theta} - [K_1 + K_1 v_1 + K_3] C_1 + \frac{\rho}{\theta} K_5 S_0 \quad (21)$$

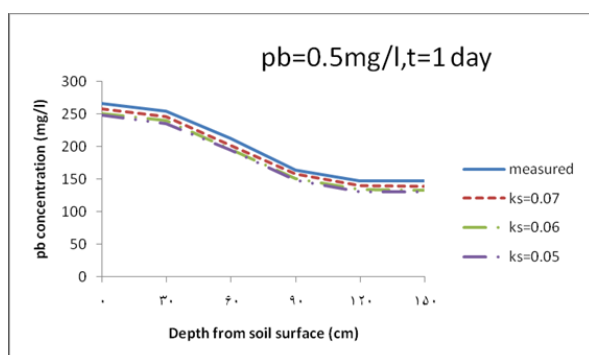
The finite difference forms are written similarly for all other equations for each node from 2 to K-1 where K is the lowest node in the profile. This set of equations, then is solved for defined boundary

conditions using the Thomas tridiagonal matrix algorithm.

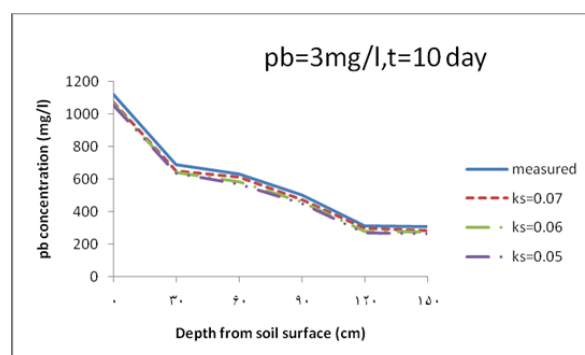
#### Upper and lower boundary conditions

The upper boundary condition for Pb needs to be defined to represent zero flux, infiltration the value of  $C_1^J = C_w$  and  $D_{1+1/2}^{J+1/2} = 0$  Where  $C_w$  is concentration of Pb in applied water and Pb enter the profile is equal to  $q_{1+1/2}^{J+1/2} (\Delta t) (C_w)$ . during surface evaporation  $C_1^J = 0$ ,  $q_{1+1/2}^{J+1/2} = 0$  and  $D_{1+1/2}^{J+1/2} = 0$ .

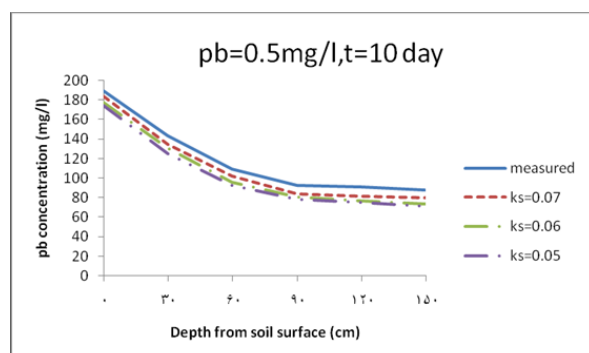
The lower boundary condition for Pb needs to be defined for zero flux, water table and unit hydraulic gradient. For zero flux  $q_{K-1}^{J+1/2} = 0$ ,  $D_{K-1/2}^{J+1} = 0$  and  $CK = 0$ . If water table is present, the value of  $C_k = C_{gw}$  and  $D_{K-1/2}^{J+1} = 0$ . Finally, for unit hydraulic gradient  $C_K = \text{constant}$  and  $D_{K-1/2}^{J+1} = 0$  where  $C_{gw}$  is concentration of Pb in groundwater.



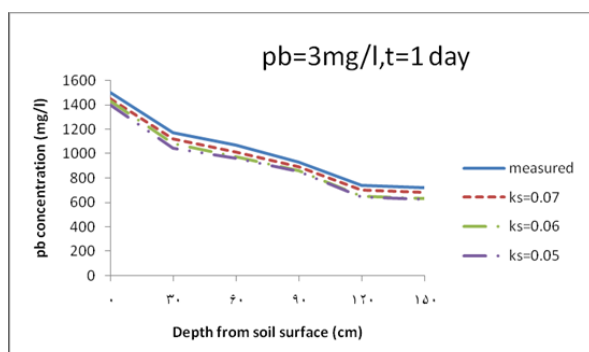
**Fig. 3.** Comparison of simulated and measured concentration of Pb for different depths ( $t=1$  day,  $Pb = 0.5 \text{ mg.L}^{-1}$ )



**Fig. 6.** Comparison of simulated and measured concentration of Pb for different depths ( $t=10$  day,  $Pb = 3 \text{ mg.L}^{-1}$ )



**Fig. 4.** Comparison of simulated and measured concentration of Pb for different depths ( $t=10$  day,  $Pb = 0.5 \text{ mg.L}^{-1}$ )



**Fig. 5.** Comparison of simulated and measured concentration of Pb for different depths ( $t=1$  day,  $Pb = 3 \text{ mg.L}^{-1}$ )

## RESULTS

The model was applied to simulate Pb in soil column under steady state and transient water flow conditions. The soil column was assumed to be unsaturated under both conditions. The model was applied to simulate the transport and transformation of Pb in soil column under steady – state and transient water flow conditions , The soil column was assumed to be unsaturated under both conditions for the validation of model under transient state , the data sets collected by Javadifar, et al from Gorgan site, Golestan province, Iran 2014, was used. In this experiment, Vertical soil columns were in uniformly layered in 30 cm thick with 150 cm long.

In this Table 1 shows the soil texture details and properties. Study under transient water flow conditions, 240 liters of influent solution containing 0.5 and 3  $\text{mg.L}^{-1}$  of Pb in the form  $\text{Pb}(\text{NO}_3)_2$ .

In this study under steady – state water flow conditions, 240 liters of influent solution containing 0.5  $\text{mg.L}^{-1}$  of Pb in the form of  $\text{Pb}(\text{NO}_3)_2$  were applied to the soil Also in the same time 240 liters of influent solution containing 3  $\text{mg.L}^{-1}$  of Pb were applied to the another pilot in this site . The experiment was run for 10 days. At the end of each run the concentration of Pb was measured in soil and ground water table. The data from the results of Pb transport and transformation modeling in experiment was used to run model. The time and distance interval in vertical direction for running the model were 0.25 day and 30 cm respectively.

**Table 1.** The soil texture details

Sand%	Silt%	Clay%	Organic Carbon %	Total saturated acidity	Electric Conductivity $\text{EC} \cdot 10^3$
39	41	20	1.5	6.9	8.1

The results indicate that transport and transformation model adequately simulates the measured quantities at time = 1 day, t= 10 days as shown in Figures 4 to 7. The simulation results for total time from 0.25 day to 10 days indicate that as the time increases the influent concentration approaches the inflow, which is comparable with measured values.

The sensitivity analysis of the model to some parameter at steady state water flow condition shows that the model is very sensitive to the adsorption coefficient,  $K_s$ , such that when  $K_s$  is equal to 0.07 liter  $\text{kg}^{-1}$ , the simulation results get closer to measured values. The computed results for measures Pb concentration in  $K_s = 0.07$  have mean relative error =4.36. These results imply that the model can produce a less than 5% error in predicting measured Pb concentration in the soil zone and groundwater. Mirbagheri model was used for the simulation of water content and water flux.

#### DISCUSSION AND CONCLUSION

One-dimensional water flow and contaminant transport model was applied to simulate Pb in soil column. The model predicts the concentration of different contaminant in ground water. The simulation results indicate as the total time from the beginning to the end of simulation increases, the concentration of Pb approaches the measured values, as indicated in the results section the model is sensitive to adsorption coefficient,  $K_s$ . The results also shows the variation of water flux with times steps in soil column, as the time increases from 1 days to about 10 days the water flow approaches the steady state.

LEACHM, which is the Leaching Estimation and Chemical Model, was used for the simulation of water flux and hydraulic conductivity of soil used in the study area. The model was very useful tool for the estimation of water content. The model can be used for the prediction of water pollution in groundwater systems.

#### NOTATION

$\theta$  = Volumetric water content  
t = time  
h = soil water pressure head  
H = hydraulic head  
K = hydraulic conductivity  
 $\theta_s$  = Water content at saturation  
a = constant  
b = constant  
 $K_s$  = hydraulic conductivity at saturation  
P = pore water interaction parameter  
q = water flux  
z = soil depth  
J<sub>t</sub> = total lead flux  
J<sub>OL</sub> = diffusion flux in liquid phase  
J<sub>CL</sub> = convection flux in liquid phase  
C<sub>l</sub> = concentration in liquid phase  
C<sub>s</sub> = concentration of adsorbed lead  
 $\rho$  = Soil bulk density

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