

Modeling arsenic transport in soil column and ground water

S. A. Mirbagheri*, F. G. Avili, A. H. Javid

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 arsenic through a soil column from the surface to the groundwater is presented. The model simulates arsenic 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 arsenic species approaches the measured values.

Key words: arsenic transport, mathematical, computer, model, arsenic 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, e.g. [1-9]. 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), θ is volumetric water content (m^3m^{-3}), t is time (day), H is hydraulic head ($h + z$), z is soil depth, K is

hydraulic conductivity (mm day^{-1}), $c(\theta) = \frac{\partial \theta}{\partial h}$ is differential water capacity. Functions which characterized relationships between $K - \theta - h$ described in LEACHM [7] are used. There is a two-part function that described the general shape of θ (h) relationships [6],

* To whom all correspondence should be sent:
E-mail: seyedahmad_mirbagheri@yahoo.com

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

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

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, θ_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 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 interval using Darcy's equation:

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

Finally, the values of q are then used to estimate arsenic transport in the soil profile. The finite difference solution of equation (1) described in detail can be found in LEACHM (Hutson & Wagenet [7]).

Arsenic 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 arsenic was modeled. Figure 1 shows some of the arsenic transport and transformation processes and the factors affecting each of the processes.

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

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

Where J_s is total arsenic 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.

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 (θ_s), and P is Pore water interaction parameter. When soil pressure head is less than h_i the

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 arsenic can be represented as:

$$J_{cl} = -\theta D_h(q) \frac{dC_1}{dz} + qC_1 \quad (8)$$

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:

$$J_{cl} = -\theta D(\theta, q) \frac{dC_1}{dz} + qC_1 \quad (9)$$

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

$$J_s = -\theta D(\theta, q) \frac{\partial C_L}{\partial Z} + qC_1 \quad (10)$$

Partitioning arsenic between sorbed and solution phases, according to Alemi [2], adsorption of arsenic 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 arsenic absorbed on the soil (α mole K^{-1}), K_s is the adsorption coefficient for arsenic ($L Kg^{-1}$), C is the concentration of arsenic in the soil solution (α mole L^{-1}), n is the exponent in the nonlinear equation for equilibrium adsorption reaction for arsenic.

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

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

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

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

Arsenic transports in soil system occur under unsteady (transient) water flow condition. The water content (θ) 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 arsenic concentration in sorbed and solution is phases and ϕ represents all sources or sinks of arsenic. Substituting equation (8) and (13) into (14) gives general one-dimensional transport equations for arsenic 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 arsenic species in soil solution, and ϕ indicates all possible sources or sinks term.

Solution procedure

Prediction of the concentration of As in all phases (liquid, adsorbed, gas) as well as leaching losses at any depth for all time levels requires simultaneous solution of equations for all arsenic 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:

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

Where

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

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

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

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

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

Multiplying out and collecting the unknown C_i^{j+1} terms on the left-hand side and the know 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:

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

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 arsenic 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 arsenic in applied water and arsenic 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 arsenic 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 arsenic in groundwater.

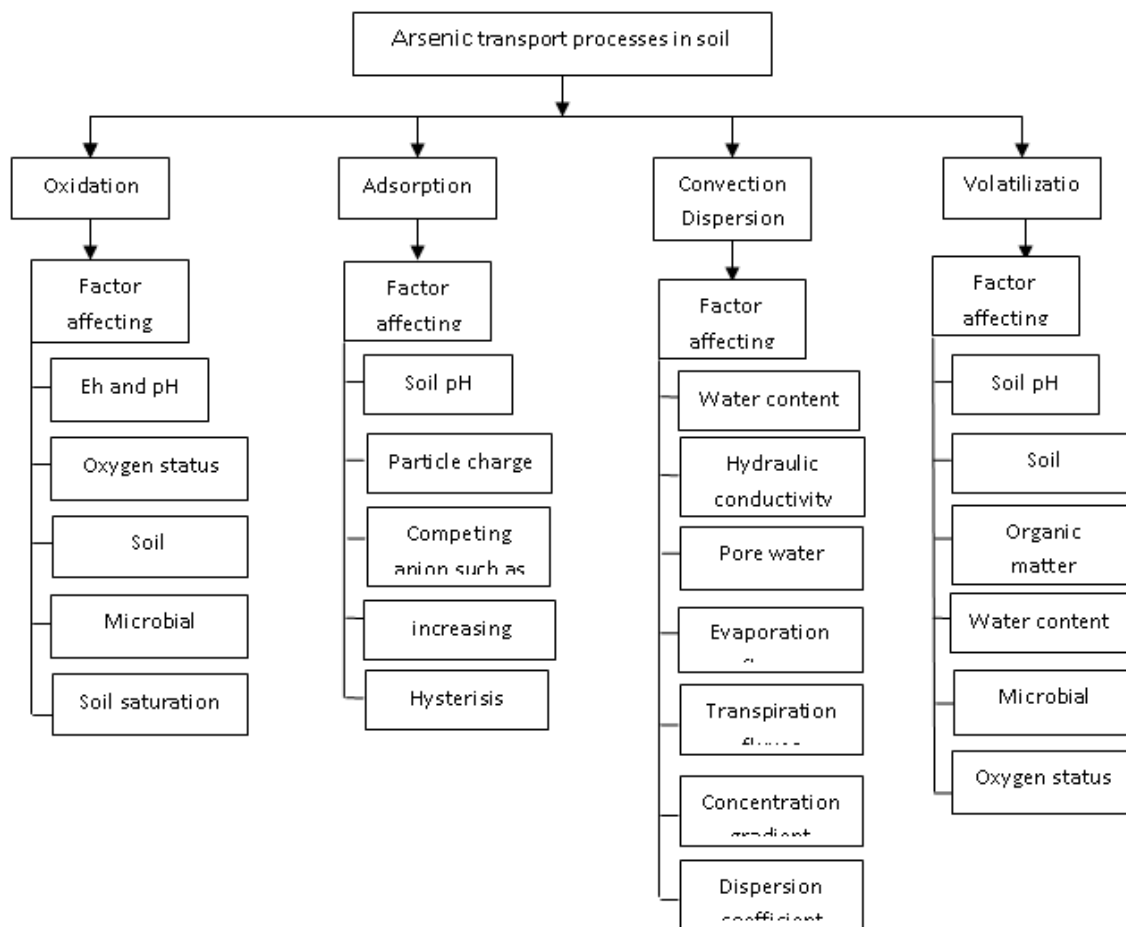


Fig.1. The transport processes and the related factors.

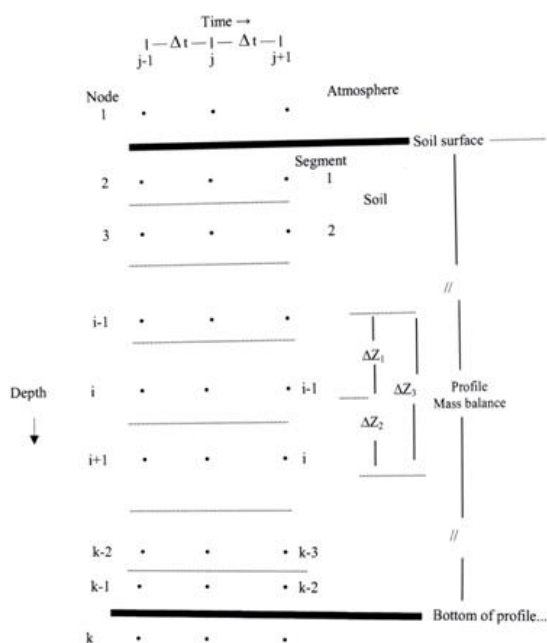


Fig. 2 Definition of nodes and segments.

RESULTS

The model was applied to simulate arsenic 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 As 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 [8, 10] 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 0.2 and 0.4 mg.L⁻¹ of As in the form As₂O₃.

In this study under steady – state water flow conditions , 240 liters of influent solution containing 0.2 mg.L⁻¹ of As in the form of As₂O₃ were applied to the soil Also in the same time 240 liters of influent solution containing 0.4 mg.L⁻¹ of As were applied to the another pilot in this site . The experiment was run for 10 days.

Table 1. The soil texture details

Sand%	Silt%	Clay%	Organic Carbon %	Total saturated acidity	Electric Conductivity EC*10 ³
39	41	20	1.5	6.9	8.1

At the end of each run the concentration of As was measured in soil and ground water table .The data from the results of As 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 .The results indicate that transport and transformation model adequately simulates the measured quantities at time =1 (day) , t= 10(day) as shown in Figures 3 to 6.

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 the measured values.

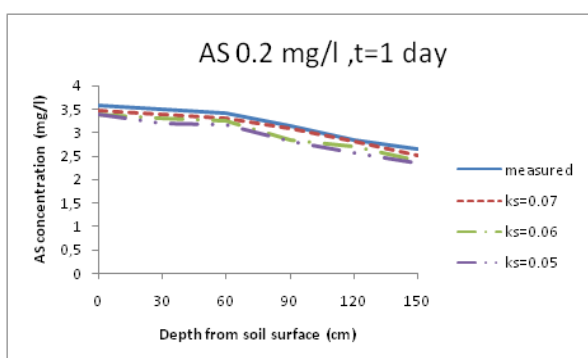


Fig. 3. Comparison of simulated and measured concentration of arsenic for different depths (t = 1 day, As = 0.2 mg.L⁻¹)

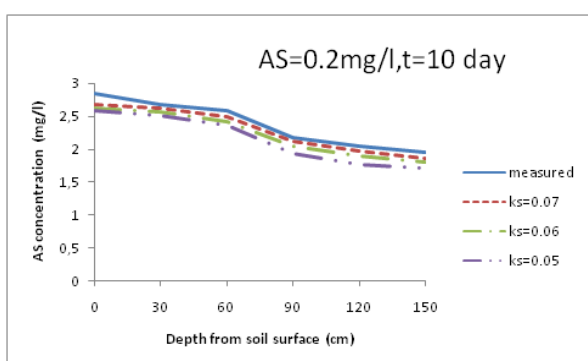


Fig. 4. Comparison of simulated and measured concentration of arsenic for different depths (t = 10days, As = 0.2 mg.L⁻¹).

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 kg⁻¹ , the simulation results get closer to measured values. The computed results for

measures As concentration in $K_s = 0.07$ have mean relative error =4.43 These results imply that the model can produce a less than 5% error in predicting measured arsenic concentration in the soil zone and groundwater .LEACHM model was used for the simulation of water content and water flux .

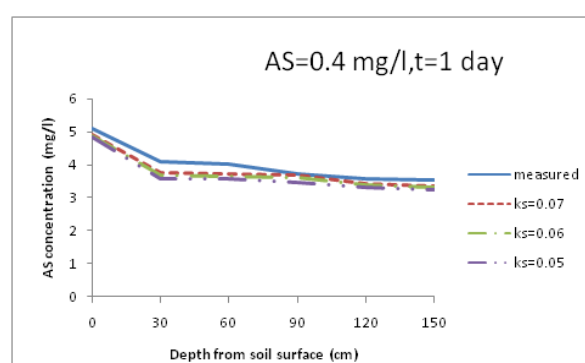


Fig. 5. Comparison of simulated and measured concentration of arsenic for different depths (t = 1 day, As = 0.4 mg.L⁻¹).

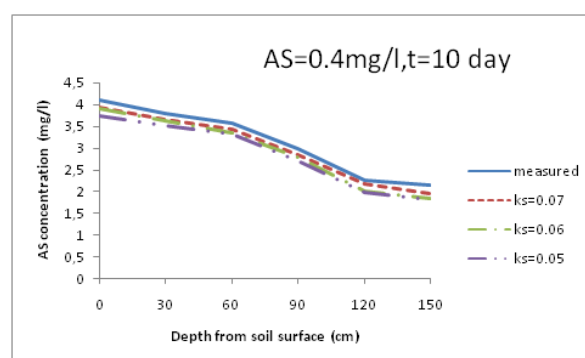


Fig. 6. Comparison of simulated and measured concentration of arsenic for different depths (t = 10days, As = 0.4mg.L⁻¹)

DISCUSSION AND CONCLUSION

One-dimensional water flow and contaminant transport model was applied to simulate arsenic 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 arsenic 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

θ = Volumetric water content
t = time
h = soil water pressure head
H = hydraulic head
K = hydraulic conductivity
 θ_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_t = total arsenic flux
J_{OL} = diffusion flux in liquid phase
J_{CL} = convection flux in liquid phase
C_l = concentration in liquid phase
C_s = concentration of adsorbed arsenic
 ρ = Soil bulk density

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