Predicting Model of Arsenic Transport and Transformation in Soil Columns and Ground Water Contamination (Case study: Gorgan Plain, Iran)

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Abstract: Soil and water resources quality is affected by various pollutants because of human direct interventions in recent decades. Arsenic is recognized as one of the toxic heavy metals in environment. Arsenic is a metalloid whose unauthorized amounts in soil and ground water tables is a serious threat to human life. Soil and ground water of Golestan Province, Iran is contaminated with Arsenic in some areas such as Gorgan plain area. In this study Arsenic transport in soil columns and ground water tables of Gorgan is investigated. A mathematical computer model, LEACHM is applied which is based on mass balance equation, including dispersive and convective transport, surface adsorption, oxidation and reduction, and also volatilization, chemical and biological transformation. This model simulates different species of arsenic such as arsenite, arsenate, and organic arsenic. Validation of model is by comparison of simulation results to sampling data under transient states. The simulation results by LEACHM model are in good agreement with measured values. Variation between measured data and the simulation results is highly affected by the absorption coefficient with a coefficient of 0.07 with a mean error of 4.43%. Results of this study indicate that the distribution of arsenic in soil column to the ground water table is predictable. The simulation results represents that by increase of total time from beginning to end of the simulation, the concentration of Arsenic compounds approaches the measured values.

Keywords: Leachm model, Transport and transformation, Arsenic, Finite differential method

1. Introduction

Arsenic is a toxic element existing in water, soil, earth's crust, and air which can be mobilized in the environment through natural process of weathering, waste disposal, emission of the volcanic ashes and fossil fuel burning (Morita and Edmonds 1992). Arsenic in the environment exists in the following inorganic forms: zero (or metalloid), +3 or arsenite (ASIII), +5 or arsenate (ASV), and as organic compounds such as mono methyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA), trimethyl arsenic acid (TMAA), etc. Inorganic As generally is more mobile and toxic than organoarsenic species, while trivalent arsenite is considered to be more toxicant, soluble, and mobile than pentavalent arsenate, while arsenic is mostly found as ASIII in ground water, and rarely in the form of ASV. Many geophysical-chemical processes such as absorption process cause arsenic releasing from soil and precipitate in underground water. Also many natural inorganic elements such as (NOM) increase arsenic absorption in ground water. Existence of unauthorized amount of this element causes skin, lung, and kidney cancer as well as many other problems (Wang and Mulligan 2006). Also, heavy metal and toxic compounds soil contamination could effect on agricultural crops (Seyed Mousavi and Saeb 2019).

Uncontrolled exploitation of groundwater in many parts of the world has led to a sharp drop in groundwater levels (Zare Aghbolagh and Fataei 2016). The contaminant transport modeling is based on an understanding of mechanisms of mass release from solid phase to liquid phase, and contaminant decay process. The mechanisms above are influenced by environmental factors such as climatic conditions, site geohydrologic conditions, waste type, chemical reactions and the microbial decomposition of organic matter. The objective of this study is to address the temporal and spatial distribution of contaminant concentration in soil column.

LEACHM (leaching estimation and chemistry model) refers to set of simulation models describing the water and chemical regime in partially saturated and unsaturated soil profiles. This model utilize similar mathematical and numerical solution schemes to simulate vertical water and chemical movement (Ramos 1991, Hutson and Wagenet 1995). Contaminated soil and ground water of Golestan province to the

Arsenic as a toxic element, the temporal and spatial distribution of arsenic is estimated in soil column of Gorgan plain area. Also, to develop one-dimensional dynamic simulation model, t approximates arsenic concentration in soil column and the groundwater system by finite differential method (FDM) under unsteady state of water flow that microbial activities and plant growth were present.

2. Materials and methods

Arsenic heavy metal Simulation of the transport and transformation of soil column in steady-state and transient water flow condition, is based on the data sets from Gorgan plain, Golestan Province, Iran. The soil column assumed to be unsaturated under several conditions to validate the model under transient state, which the vertical soil columns were in uniformly layers in 30 centimeters thick and 150 centimeters length (Javadifar et al. 2016). Soil texture details and properties are represented in Table 1.

Table 1. Gorgan plain soil texture details

Compound	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	Total acidity (saturated)	Electric Conductivity
amount	39	41	20	1.50	6.90	8.10

In order to simulate Arsenic flow field in soil to the ground water plant, LEACHM model is applied. In every material transfer in porous media, there is a water flow model which pore water velocity as well as spatial and temporal variations of the field are calculated to estimate concentrations of filed material. Practical equations consist of Richard's equation, Campbell's equation, and soil hydraulic pressure equation which the saturated soil moisture percentage and flow flux calculated. Afterward, the transfer-diffusion equation id the mail equation in which other reducing and increasing sources, including evaporation, absorption and excretion, and biological experimentation are considered (Mirbagheri 2004; 2006; 2008).

2.1. Water flow model

Water flow is computed using a finite difference solution of the soil Water flow equation as Eq. 1:

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

where:
h is the soil water pressure head (mm);
θ is the volumetric water content (m3/m3);
t is time (days);
H is the hydraulic head, h-z (mm);
z is the soil depth (mm);
K is the hydraulic conductivity (mm/day);
And c(θ) is the differential water capacity.

Functions describing the relationship between K, θ and h are used in LEACHM model. Solving Equation (1) by finite difference techniques provides estimated values at each depth node in the differencing equations. Also, Water contents are calculated as well as Water flux densities over each depth interval using Darcy's equation. Finally, the values are used for estimation of Arsenic element transport in the soil profile. The detailed description solution of finite difference model of Eq.1 can be found in LEACHM (Hutson and Wagenet 1989).

2.2. Arsenic transport model

The Arsenic transport and transformation process in the soil column under transient flow condition is complex. Several complicating factors such as pore Water velocity gradient, hydraulic conductivity, evaporation flux, transpiration flux, concentration gradient, and also seasonal rise and fall of the water table, control the transportation of the different Arsenic compounds in soil. Generally, Arsenic is transported in soil by dispersion and convection which is the result of concentration gradient and mass flow. The Arsenic transformation processes in soil systems are adsorption and desorption, oxidation and reduction, mineralization and immobilization, and volatilization. The steady-state water flow condition transport terms of Arsenic are as Eq. 2 (Mirbagheri 2008):

$$\frac{\partial C}{\partial t}(\theta + \rho K_s) = \frac{\partial}{\partial z}\left[\theta D(\theta,q)\frac{\partial C}{\partial z} - qC\right] \pm \Phi \quad (2)$$

Where C parameter is concentration of all Arsenic species and compounds in soil solution, and Φ indicates all possible sources and sinks term.

2.3. Solution procedure

The equations are solved numerically by use of a finite difference scheme and Crank-Nicolson approximation. In order to solve the equation, nodes and segments as well as time interval are used which represented in figure 1.
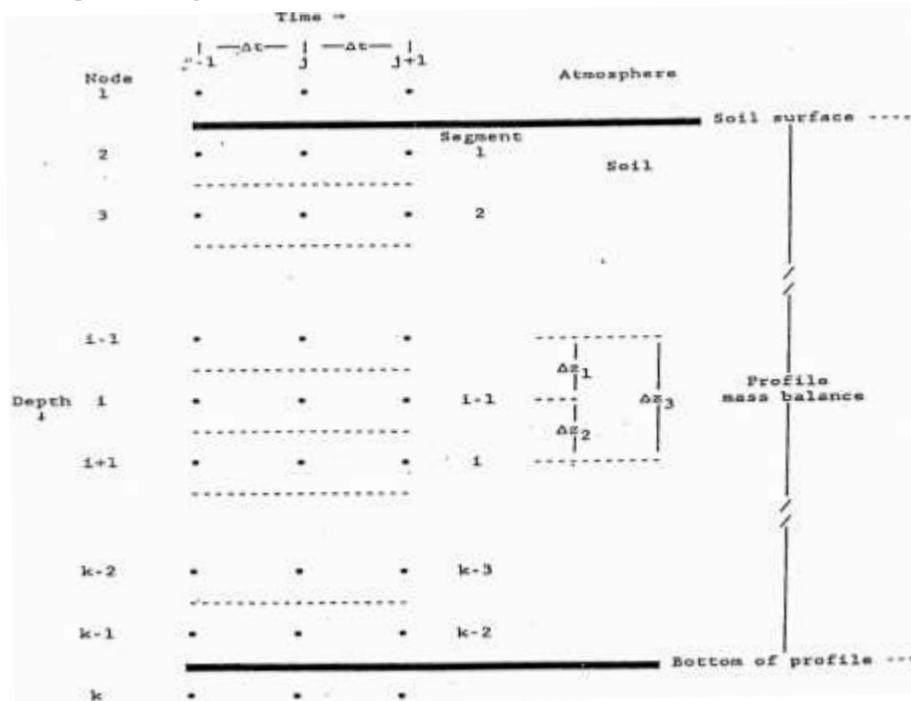
Figure 1. Definition of nodes and segments

The first term in Eq. 2 is evaluated at node i and time l j+1/2. The second term in equation is a dispersion and diffusion term. $D(\theta,q)$ is the interval between nodes i-1 and i. The finite difference forms are similar for all other equations in each node from 2 to K-1 and K is the lowest node in the profile above. This set of equations are solved for defined boundary conditions by using the method of Thomas tridiagonal matrix algorithm.

2.4. Required parameters of Arsenic movement in soil

In order to bring the model closer to the natural conditions, the volumetric moisture content θ and flow flux q are considered in the variable soil column. Therefore, to estimate θ in each layer of soil column, water pressure applied to the soil in the region and accordingly, the θ value of each layer was obtained, and the continuance estimations are based on θ calculation.

The simulation time period is considered 10 days. Total precipitation is considered zero to the Iran Meteorological Organization data in limited time. In this section, the percentages of volumetric moisture, water pressure in soil, water flux at each cross section of soil profile is obtained, and these values are used in second part of the model, which relates to pollutant movement in soil.

The second part of model input parameters are as:

C_0 is Arsenic input concentration (µg/lit) where in this study input concentrations are 200 µg/lit and 400 µg/lit;

C_{gw} is underground water pollution (µg/lit);

K_S is absorption coefficient (lit/kg);

K_v is evaporation constant rate (1/day).

The above parameters as primary modeling input data are presented in Table 2.

Table 2. LEACHM Modeling equations input parameters

Parameter	Amount (unit)
Z	30 to 150 (cm)
T	10 (day)
Q	30 (mm/day)
θ_s	0.6
P	3 to 7
θ	Water flow model output
C_0	0 (µg/l)
C_{gw}	0 (µg/l)
K_v	0.02 (1/day)
K_s	10.4 (m/day)

By the results of the first part calculations and above parameters, the second part of model is calculated. The other determinative parameter modeling is upper and lower boundary condition. The boundary conditions for the solute and water flux are not always same algebraic sign within each time interval as water evaporation occurs, causes salt accumulation on soil surface. The upper boundary condition for Arsenic needs to be specified as zero flux, infiltration and evaporation. Also, lower boundary condition of Arsenic has to be defined as zero flux, water table and unit hydraulic gradient.

2.5. Sampling and field measurement

Gorgan city treatment plant in Golestan Province is considered as sampling area. Two plots of land in dimensions of 200 centimeters length and 150 centimeters width of wastewater treatment plant site was specified. The sampling hole drilled of 100 centimeters diameter and 160 centimeters depth to perform measurement which marked various depths of 30, 60, 90, 120 and 150 centimeters on the side of the hole. Two solution samples containing distilled water of 250 liters volume and Arsenic as AS_2O_3 with concentrations of 0.2 mg/l and 0.4 mg/l was prepared. These solutions were poured on the sampling areas and after several hours of solution infiltration into the soil, it was reached deep down. Soil samples of different specified levels were transferred to the soil lab by the labels including time and local information. Soil samples were prepared in lab to determine the relative humidity of samples and extraction of dissolved compounds by drying, grinding and sieving the soil. Afterward in Water and Wastewater lab, 20 grams of prepared soil from each sample was mixed with 40 milliliters of DTPA solution to measure Arsenic Concentrations by atomic absorption method. All the sampling periods within the time interval of three days on the day four, seven and ten after infusion of the solution, were repeated for both solution samples with different Arsenic concentrations (Nasiri Rajabli et al. 2013; Javadifar et al. 2016).

3. Results

In this study under steady–state water flow conditions, two samples of 250 lit of influent solution containing 0.2 mg/l of Arsenic in the form of AS_2O_3 were infused to the soil, resulting 250 liters of solution containing 0.4 mg/l of Arsenic, were applied to the another area in the site. The experiment continued in 10 days. At the end of each experiment time period, the Arsenic concentrations were measured in soil and ground water table. Arsenic measurement data is presented in Table 3 and Table 4.

Table 3. Arsenic concentrations measurement at different soil depths and time (C0 =0.2 mg/l)

Soil Depth (cm)	Measured Arsenic Concentration (µg/l)				
	background concentration	Day 1	Day 4	Day 7	Day 10
0	0	57.3	49.3	97.2	84.2
30	0	5.3	4.3	82.2	68.2
60	0	4.3	98.2	65.2	59.2
90	0	14.3	94.2	51.2	18.2
120	0	84.2	72.2	43.2	5.2
150	0	64.2	38.2	35.2	96.1

Table 4. Arsenic concentrations measurement at different soil depths and time (C0 =0.4 mg/l)

Soil Depth (cm)	Measured Arsenic Concentration (µg/l)				
	background concentration	Day 1	Day 4	Day 7	Day 10
0	0	11.5	31.4	19.4	9.4
30	0	1.4	96.3	92.3	77.3
60	0	4.4	8.3	62.3	57.3
90	0	74.3	16.3	8.3	97.2
120	0	6.3	53.2	51.2	24.2
150	0	55.3	45.2	37.2	14.2

In order to run simulation model, the measurement data of Arsenic transport and transformation applied. Distance and time period interval in vertical direction to run the model was 30 centimeters and 0.25 day respectively. Output results data declare that the transport and transformation model adequately simulates the measured quantities at the time period of day 1 to the day 10 as shown in Fig. 2 to Figure 5.
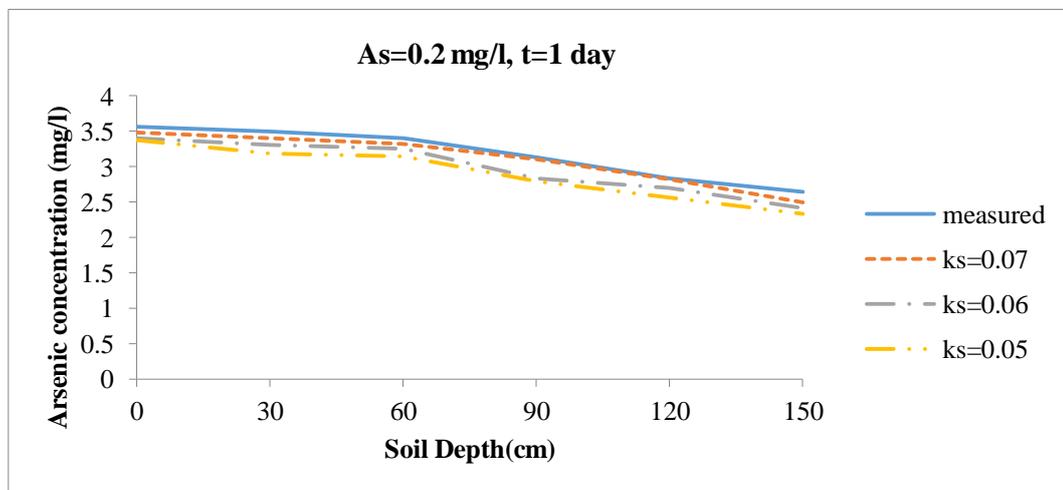
Figure 2. Soil Arsenic simulation and measurement concentration (t=1 day, As=0.2 mg/l)
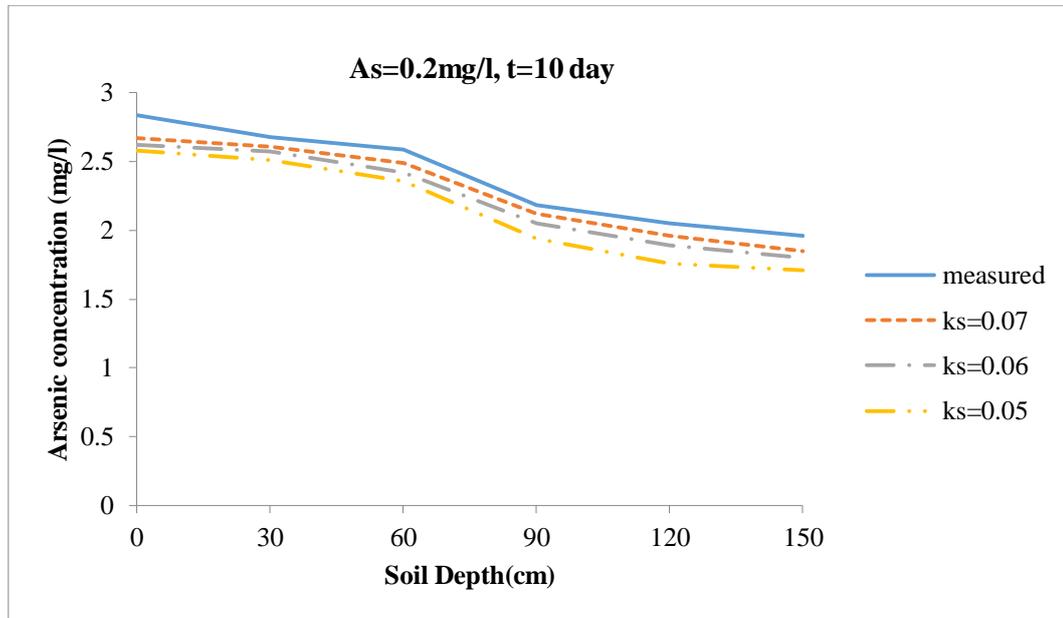
Figure 3. Soil Arsenic simulation and measurement concentration (t=10 day, As=0.2 mg/l)
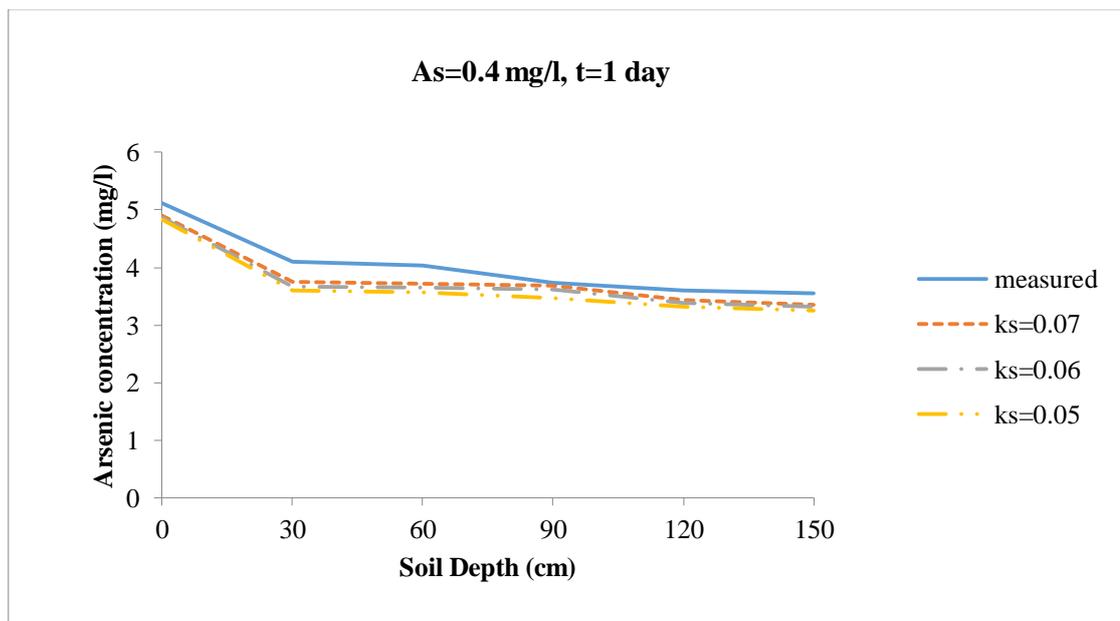
Figure 4. Soil Arsenic simulation and measurement concentration (t=1 day, As=0.4 mg/l)
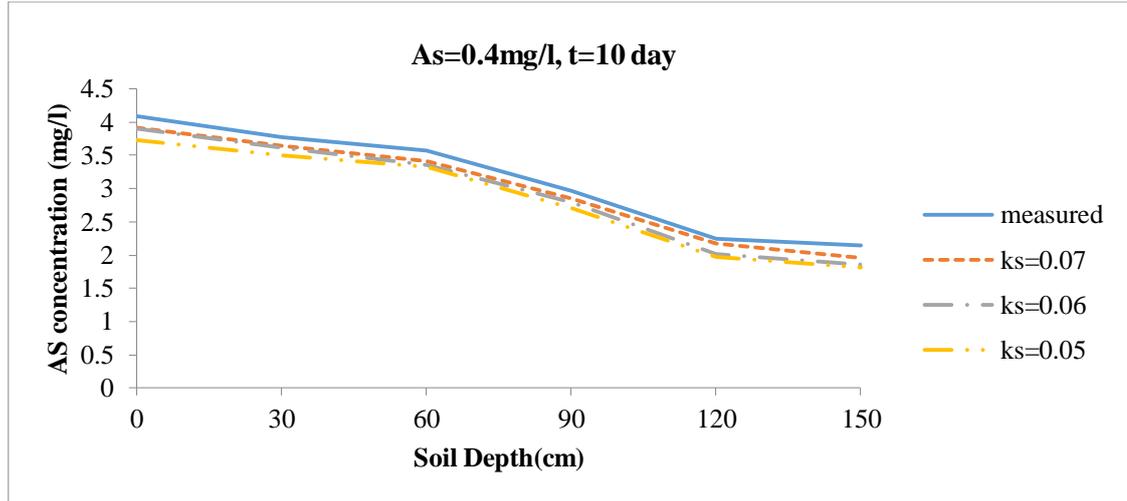
Figure 5. Soil Arsenic simulation and measurement concentration (t=10 day, As=0.4 mg/l)

4. Discussion

The simulation results for the total time from the day 0.25 to the day 10 indicate that as the time increases, the influent concentration decreases, which could be compared to measured values. The sensitivity analysis of the model to some parameters at steady state condition of water flow shows that this model is very sensitive to the K_S parameter which is adsorption coefficient. For instance when adsorption coefficient is equal to 0.07 l/kg, the simulation results get closer to the measured samples values. The calculated results for Arsenic measurement concentration in K_S of 0.07 have mean relative error of 4.43. These results declare that the model can produce less than 5% of errors in Arsenic concentration prediction in the soil and groundwater. According to output results of this study, measured Arsenic concentrations in surface water around sampling area, in about 40 meters in different temporal measurement are likely to be 0. Also, the sampling of horizontal direction dispersion in several depths measurement represent the 0 concentration.

5. Conclusion

In this study, the one-dimensional FDM was used to simulate Arsenic transport and transformation in unsaturated and saturated soil. Also, the model is to predict the concentration of Arsenic in ground water. The model is sensitive to absorption coefficient, K_s. By the increase of K_s the relative concentration of Arsenic increases accordingly. Simulation results indicate that by increase of the total time from beginning to the end of simulation, the concentration of Arsenic compound approaches the measured concentration. When adsorption coefficient, K_S is equal to 0.07 l/kg, the model simulation results get closer to the measured samples values. The computed results for Arsenic measurement concentration in K_S of 0.07 have mean relative error of 4.43. These results declare that the model can produce less than 5% of errors in Arsenic concentration prediction in the soil and groundwater. The results represent that LEACHM model can be used either in prediction of water pollution in soil and ground water.

Marzieh Makaremi: analyzed the data, authored and revised drafts of the paper.
Data Availability
All the data are shown in the tables of this article .
Ethics Statement
This study was conducted by national and international guidelines. The methods and scientific papers of similar studies were conducted which are listed in references.
Supplemental Information
There is no supplementary. Any questions and request of more information could be addressed on correspondence author.

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