A blueprint for simulating heavy metal transport in soil under dynamic acidic conditions

R.W. Al-Soufi

Laboratory of Hydrology & Water Resources Management, Helsinki University of Technology, Konemiehentie 2, SF-02150 Espoo, Finland

ABSTRACT

A blueprint is presented for simulating long-term heavy metals transport through clay barriers. The calculation methodology is based on 3-dimensional advection-dispersion model. Modelling the adsorption-desorption process is based on the fact that more ions are retained by soil matrix during the adsorption phase than the amount released during the desorption phase. The model calculates the amount of ions remains in soil solution under dynamic acidic conditions. Among several applications, the model can be used to determine the optimum thickness of clay liner which ensures a secured place for the soluble heavy metals over a long period of time.

INTRODUCTION

Industry serves as an originator of chemicals for groundwater pollution. Most of these sources are point sources. Very often, pollution occurs due to leaks from buried wastes, deep well waste disposal activities and landfills. Soil liners have widely been used in hazardous waste landfills. Clay is the most important component of soil liners because the clay fraction of the soil ensures low hydraulic conductivity and retains the heavy metals as well. Therefore, it is becoming increasingly apparent that the depth below which contaminant concentration is reduced to a harmless level, must be accurately determined. In order to achieve this goal, it is crucial to have a reliable design tool capable to accurately calculate the water balance components and reasonably predicts pollutants attenuation through soil medium.

TRANSPORT OF HEAVY METALS IN CLAY LINERS

In waste disposal areas, heavy metal can be adsorbed by soil and organic substances and therefore, its movement becomes substantially slow. In the long term and after the remediation of waste site, this zone may become a source of heavy metal to the lower saturated soil strata.
Water may be considered as the main vehicle for the heavy metal transport in soil continuum. Water flow is modelled by combining the well known equation of Darcy and the continuity equation. The result is a differential equation which in three dimensional form it reads:

$$\frac{\partial C}{\partial x} \frac{\partial C}{\partial y} \frac{\partial C}{\partial z} + \frac{\partial C}{\partial y} \frac{\partial C}{\partial x} \frac{\partial C}{\partial z} + \frac{\partial C}{\partial z} \frac{\partial C}{\partial x} \frac{\partial C}{\partial y} - R \frac{\partial C}{\partial x} - F \frac{\partial C}{\partial y} \left( \frac{\partial C}{\partial T} \right)$$

where, $\Phi$ is the hydraulic head (L), $q$ is the flux (L/T), $R$ is the recharge rate (L/T), $A$ is the flow cross sectional area (L$^2$), $F$ is the storage coefficient (L$^3$/L$^3$) and $T$ is the time (T).

This equation can be solved numerically by using the integration finite difference method which combines the simplicity of the finite difference method and the accuracy of the finite elements method. Details of the calculation scheme is described elsewhere (Al-soufi [1,2]).

The general form of the dispersion-advection equation, including the effects of molecular diffusion and a source-sink term describing sorption, for dissolved constituents being transported in a porous media, can be written in the following one dimensional form:

$$\frac{\partial C}{\partial x} \left[ D \frac{\partial C}{\partial x} - \nu C \right] = \frac{\partial C}{\partial t} + \rho \frac{\partial S_c}{\partial t}$$

where, $C$ is the solute concentration (M/L$^3$), $D$ is the dispersion-diffusion coefficient (L$^2$/T), $\rho$ is the soil bulk density (M/L$^3$), $\theta$ is the soil moisture content on volume basis (L$^3$/L$^3$), $S_c$ is the adsorbed solute concentration (M solute/M soil) and $\nu$ is the pore water velocity (L/T).

The dispersion-diffusion coefficient is calculated by the following equation:

$$D = q DM + D_0 \left( \text{EXP}(b\theta) \right)$$

where DM is the medium’s dispersivity (L), $D_0$ is the molecular diffusivity in free water system (L$^2$/T) and $a,b$ are constants.

In solving Equation (2) numerically by the integration finite difference method, the whole soil continuum is divided into a matrix of elemental cubic nodes and Equation (2) is integrated over the whole cubic node. In three dimensional form, Equation (2) becomes as follows:

$$\sum_{i=1}^{6} \left( Q_{i,b} C_{i} \right) + \sum_{i=1}^{6} \left( \left( C_{i} - C_{b} \right) \frac{A}{L} \right) + \frac{\partial S_c}{\partial T} A \Delta z \rho$$

where $\left( C_{b} \right)$ is the adsorbed solute concentration (M solute/M soil) and $\Delta z$ is the thickness of the cubic node.
where, $Q_{ib}$ is the lateral flow between node i and node b ($L^3/T$), $C_w$ is the solute concentration in migrated water between two nodes ($M/L^3$) and $C_b$ is the solute concentration at node b ($M/L^3$).

The calculation scheme is essentially a mass balance equation which computes changes in concentration within each cubic node. The mass of solute flowing into a cubic node is first added to the mass already exist, thereafter, the total mass of the solute is adjusted by considering the influence of the other processes, namely, the adsorption and desorption. After chemical reaction have been taken in consideration, a new concentration is computed and the procedure is repeated for the next cubic node in the numerical scheme.

Generally speaking, the outcome of any contaminant introduced into the groundwater system is largely dependent on the capacity of the solid matrix material to adsorb substances. This is because the surface areas exposed to ion reactions differ in physico-chemical behavior as represented by cation and anion exchange properties. Changes in soluble solute concentrations, organic matters and pH level in soil solution, are all have a significant effects on the extent of adsorption process (Al-Soufi, [3]).

The computational scheme of ion adsorption begins first by estimating or calculating the leachate production term by Equation (1). Very often clay barrier situated below landfill site is considered saturated where water regime follows the concept of steady state flow. In this case, leachate rate can be estimated according to the precipitation rate and infiltration rate of water through the cover soil layer.

In the second step, soil water pH is calculated as a function of the acidity of the recharge water. The changes in soil solution pH is a process described here by the general type of time dependent equation. Based upon laboratory investigations, it was possible to establish norms of predicting soil solution pH at any depth and at any time with respect to the pH of input solution. The equation reads:

$$pH_z = \Pi_s \left( 100.0 \times Z \right)^{\alpha T - \beta}$$

where, $pH_z$ is soil solution pH, $\Pi_s$ is a constant depends mainly on leachate water pH, $Z$ is the depth (m), $\alpha$ (1/day), $\beta$ are lumped constants and $T$ is the elapsed time (days).

Thereafter, ion-concentration of the imported water ($C_i$) is checked against the concentration in the nodal water in order to choose between the adsorption or the desorption function. This is a necessary step because laboratory investigations have shown that adsorption and desorption of heavy metals can not be represented by a single valued function (Al-Soufi, [4]). At equilibrium state and at a specific level of acidity, it was found that during adsorption, less cadmium was retained on the soil at a given concentration, than during desorption. Adsorption and desorption of heavy metal are both simulated by an equation that contains some lumped coefficients reflect the physical and chemical characteristics of the soil and the pH magnitude of soil solution. The process is described by the following equations:

$$C_z = \eta_1 \left( pH_z \right)^{-\gamma_1} \cdot C_i^{\eta_2 \left( pH_z \right)^{\gamma_2}}$$
\[ C_d = \frac{(\zeta - \rho H_z)}{\omega} \quad (\zeta = 4.2, \omega = 20) \quad 1.5 \leq \rho H_z \leq 4.0 \quad (7) \]

\[ (\zeta = 10.0, \omega = 600) \quad 4.0 \leq \rho H_z \leq 6.5 \]

\[ C_d = 0.0009 \quad 6.5 \leq \rho H_z \]

where, \( C_r \) is the ions remains in solution represented as a fraction of the ions in input solution, \( C_i \) is the ion concentration of the input solution (mg/l), \( \eta_1 \) (l/mg,pH), \( \eta_2 \) (1/pH), \( \gamma_1, \gamma_2 \) are constants, \( C_d \) is the ions desorbed into soil solution represented as a fraction of the ions adsorbed by soil solid surface and \( \zeta \), \( \omega \) are constants.

In the next step, ion concentration is computed by solving the dispersion-advection equation. Since the sorption rate is a function of ion concentration and pH of soil solution, performance of the numerical scheme depends mainly on how rapidly the concentration and the acidity change during a specific time step. For small changes, few iterations for the numerical scheme may be enough for a given time step and relatively long time increments can be used.

RESULTS AND DISCUSSION

The model presented here was constructed on the basis of batch test data. Data were processed by regression analysis in such a way that the results provided equations that describe simple relationships which could be used to predict heavy metals movement in soil strata. The model was then tested by using data from soil column experiment which was carried out for a period of about 400 days. Admittedly, direct application of batch test data or soil column data to real field cases, is often not a realistic practice, particularly, because not all the other constraints have been taken in consideration. Moreover, under field conditions, soil does not make a complete contact with a specific metal solution as it happens in batch test or soil column profiles. However, the author anticipates that the general trend of ion sorption by soil in the field should follow the same trend as it has been found in the laboratory. Certainly, all the lumped constants have to be determined through field investigations or by modifying constants values determined in the laboratory. The judgment of modifying the value of a certain empirical constant should be made upon physical basis taken in considerations the extent to which the parameter value can be varied over the tolerance level.

Since the results of the tests applied to soil column experimental data had established a reasonable degree of confidence in the ability of the model to simulate solute transport in soil, it was applied to the movement of heavy metals through clay barriers. The case study is a hypothetical one, but, the physical characteristics of soil are taken from local investigations. The general hydrologic features of the aquifer are presented in Figure 1. The whole aquifer is considered saturated. Soil under landfill site is considered clayey soil to a depth of 21 m. Afterward, comes sandy soil in which the sorption process is rather low and can be neglected. The same applies to the other
part of the aquifer. Water flow direction in the aquifer, is mainly horizontal from left to right. Input contaminant concentration history follows a step function which is normally envisaged in waste disposal sites (Pohland, [6]). The concentration began at a low value of 30.0 mg/l, increased to a peak value of 100.0 mg/l in five years and diminished slowly in 10 years. Water in the rest of the system had a relative concentration of 0 at to and a condition of $C=0$ was assumed on the other boundaries. Leachate pH was assumed to begin with a value of 6.5 and drops gradually to 3.0 in a period of 20 year.

![Schematic representation for the hydrologic features of the aquifer.](image)

In the numerical scheme, nodal spacing of 3 m in the vertical direction and 200 m in horizontal direction with a time step of one week, were chosen as adequate for simulation of the transport case. During application of the model to the hypothetical case, various limitations of this model became evident. Small element size and relatively small time step were required to accommodate the strong dependence of the desorption on the changes in soil solution pH.

A simple and brief sensitivity analysis for some of the parameters, is presented here to visualize which parameters need to be well defined and what are the likely effects of change in the value of a parameter. This analysis also provides much insight for interpreting and explaining the verification results. Results of the sensitivity analysis were made by varying the input parameter's value while all the other parameters were held constant.

The value of Medium’s Dispersivity $D_M$ is rather difficult to obtain and in many cases it is estimated by the method of trial and error. Its value depends on the transport distance or in other words, depends on the scale at which the velocity and the concentration are defined. $D_M$'s values are as much as five orders of magnitude greater...
than values obtained from laboratory experiments. Robson [7] has found that the value of dispersivity depends upon the nodal spacing and he concluded that as the nodal spacing increases to a higher value say 1600 m, the solution becomes less sensitive to changes in dispersivity. Similar conclusion was also obtained by Konikow and Bredehoeft [5] who found that the larger the grid spacing, the less sensitive the model is to dispersivity. For medium texture soils and a nodal spacing of 250 m, DM values could be in the range of 10 m to 70 m. In this study, three values of DM were chosen and the results are shown in Figure 2. As the DM value is increased, heavy metal moves faster and further through the soil continuum indicating the importance of this parameter in the system. Soil moisture content may show similar sensitivity because the propagation of the plume is directly proportional to the porosity. The general plume movement corresponds very closely to the water flow pattern. Ion concentration below the clay liner decreases as water and contaminant move out of the liner and mix with the dilute water outside the liner. In about 22 years, most part of the plume is already being moved out of the system through the right side (Figure 2a).

The constants $\alpha, \beta$ of Equation (5) were examined by selecting three values for $\alpha$; 0.1, 0.5, 0.05 and for $\beta$; 0.1, 0.03, 0.003. The general influence of $\alpha$ on the concentration distribution is rather slight in comparison with $\beta$ which shows a greater influence on the final concentration profile (Figures 3,4). Since these parameters are function of the flow rate in soil, their values are expected to be alike for a wide range of flow regime in clayey soils. However one can easily determine their values in the laboratory by applying acidic water to soil column and recording the changes in soil water pH as a function of time. These data can then be regressed on log-log paper to determine the empirical constants.

![Simulated areal distribution of contamination shows the effect of varying the value of the diffusivity DM (time: 22 yr).](image)

a. DM = 55.0 m.  
b. DM = 5.5 m.
Fig. 3 Simulated areal distribution of contamination shows the effect of varying the value of $\beta$ of Equation 5 (time: 18 yr)

a. $\beta = 0.1$

b. $\beta = 0.003$

Fig. 4 Simulated areal distribution of contamination shows the effect of varying the value of $\alpha$ of Equation 5 (time: 18 yr)

a. $\alpha = 0.5$

b. $\alpha = 0.05$
Figure 5 shows clearly the high sensitivity of the model to $\eta_1$ and $\gamma_1$ of Equation (6). Their values are therefore, should be determined in the laboratory from analyzing the batch test data or by using the soil column technique where the transport process of the contaminant is simulated under a predetermined hydro-chemical conditions.

The overall sensitivity of the model to $\eta_2$ and $\gamma_2$ of Equation (6) is rather low (Figure 6). This can be explained by the fact that, the effects caused by lowering the value of $\gamma_2$ was neutralized by lowering the value of $\eta_2$.

CONCLUSIONS AND SUMMARY

In this study a method is presented with sensitivity analysis, for solving the transient movement of heavy metals in soil continuum under dynamic acidic conditions. The method of calculation presented here is based mainly on batch tests data and soil column tests data in association with the concept of an appropriate mathematical model for prediction purposes. Bearing in mind that, this blueprint does not rule out the use of data gathered for the natural geochemical processes, in fact, field investigations are eventually of absolute necessity. In addition, this method evaluates only the soil’s capacity to retain heavy metals and may not, in some cases, reflect actual field conditions where the many natural soil variations cannot be identified. The model was applied to a hypothetical case of simulating heavy metal movement nearby a landfill site. The general trend of the results were qualitatively reasonable. Difficulties and shortcomings of the model include; lack of data required for calibration and uncertainty over the nature and occurrence of chemical reaction within the subsurface system.

Changes in soil solution pH may result in a sudden increase or decrease of ion concentration and therefore, this requires some times small element size and short time step which impose some limitations on the applicability of the model for large scale systems. However, these limitations could be eliminated in the future as the computer technology offers us fast PCs particularly the expected clones of '586 microprocessors.

Model simulation indicates that areas adjacent to landfill site will not be suffering from pollution as it might be expected. Therefore, in monitoring groundwater quality, sampling from areas around landfill site would underestimate the pollution problem. However, this conclusion cannot be generalized over all the cases simply because groundwater streamlines, barrier thickness and boundary conditions are all determine the configuration of the contamination plume.

The overall performance of the model suggests that this computational tool could be useful in the study of variety of problems involving flow and solute transport in soil continuum such as the selection of best soil materials and barrier thickness that retains contaminant which are generated in landfill sites. In addition, the model should be equally useful in the study of other solute migration problems. Some of these could include pesticides and nutrient movement in arable lands.

The successful application of this blueprint will depend a great deal on our ability to describe the field system. Incorrect results can be expected when there is an incorrect definition for the properties of the medium.
Fig. 5 Simulated areal distribution of contamination shows the effect of varying the value of the parameters $\eta_1$ and $\gamma_1$ of Equation 6 (time: 15 yr).

a. $\eta_1 = 384.0$, $\gamma_1 = 8.0$

b. $\eta_1 = 180.0$, $\gamma_1 = 4.0$

Fig. 6 Simulated areal distribution of contamination shows the effect of varying the value of the parameters $\eta_2$ and $\gamma_2$ of Equation 6 (time: 18 yr).

a. $\eta_2 = 0.009$, $\gamma_2 = 2.5$

b. $\eta_2 = 0.00075$, $\gamma_2 = 0.02$
REFERENCES


