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Media: Diffusion and Infiltration Coupling of  
Thermodynamically and Kinetically Controlled  
Radionuclide Water—Mineral Interactions**

M. Yu. Spasennykh and J.A. Apps

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AND KINETICALLY CONTROLLED RADIONUCLIDE WATER – MINERAL  
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**MASTER**

# **Radionuclide Behavior in Water Saturated Porous Media: Diffusion and Infiltration Coupling of Thermodynamically and Kinetically Controlled Radionuclide Water—Mineral Interactions**

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## **Abstract**

A model is developed describing one dimensional radionuclide transport in porous media coupled with locally reversible radionuclide water-mineral exchange reactions and radioactive decay. Problems are considered in which radionuclide transport by diffusion and infiltration processes occur in cases where radionuclide water-solid interaction are kinetically and thermodynamically controlled. The limits of Sr-90 and Cs-137 migration are calculated over a wide range of the problem variables (infiltration velocity, distribution coefficients, and rate constants of water-mineral radionuclide exchange reactions).

## **Introduction**

The mathematical modeling of radionuclide transport by groundwater flow is a commonly used tool in environmental investigations of contaminated areas [Wang et al., 1983; Loucks and Fedra, 1987; Mangold and Tsang, 1991; Yeh and Tripathi, 1989; Parker et al., 1989]. However many problems arise in developing and applying models describing contaminant transport when coupled chemical reactions between water and rock forming minerals are taken into account. Whereas models combining one, two and three-dimensional aspects of contaminant transport by groundwater, and incorporating a thermodynamic description of the water and soil chemistry, have been previously developed and are currently being applied [Gröve and Wood, 1979; Shulz and Reardon, 1983; Mangold and Tsang, 1983], several problems of contaminant transport modeling remain to be addressed. Difficulties are associated with finding an adequate description of dispersion [Neuman,

1990], solute transport in fractured media [Wels and Smith, 1994], changes in rock permeability due to water-mineral interactions [Camahan, 1990], the incorporation of kinetics, redox ratios, and partial equilibrium models [Rubin, 1983; Noorishad, 1989; McNab and Narasimhan, 1994; Valocchi et al., 1989; Apps, 1992; Kravynov and Ryzhenko, 1994], and also in model validation [Tsang, 1987].

Furthermore, many questions relating the effects of transport and water-rock interaction regimes on radionuclide migration still remain unresolved. Radionuclide migration is an important problem concerning many environmental processes where infiltration velocities and radionuclide water-mineral reaction rates can vary over a wide range. Therefore, not only advective transport but also fluid phase radionuclide diffusion and the kinetics of heterogeneous reactions should be taken into account in addition to the decay of radionuclides in both fluid and solid phases. But, for the most part, hydrochemical models do not describe decay, diffusion and kinetics of chemical interactions [Mangold and Tsang, 1991], because these aspects are very difficult to program for multicomponent systems. In general, however, radionuclide migration is a simple process, which is either not coupled with multicomponent water-rock interactions, or occurs under conditions where multicomponent water-rock interactions have an insignificant effect on radionuclide water-mineral exchange reactions. In these cases, multicomponent water-rock interaction can be ignored and some of the above mentioned restrictions of hydrochemical models may be overcome using models describing water-rock interaction with one or few components. Such an approach is used in a variety of models describing the reactive transport of elements or isotopes at high-temperatures in geologic systems [e.g., Lichtner, 1985; Blattner 1989; Spasennykh, 1991; Johnson and DePaolo, 1994], although, these models can not be used directly for radionuclide transport modeling. The same approach is also used in the so-called solute transport models [Narasimhan and Alavii, 1986; Yeh, 1989; Kipp, 1987], which describe the multicomponent transport of aqueous solutions coupled with sorption or ion-exchange. Whereas most solute transport models take into account decay and diffusion,

they do not describe the kinetic aspects of these interactions. Furthermore, all such codes provide numerical solutions, which have led to well-known difficulties during use. In this report we consider some aspects of radionuclide migration in terms of a simple transport model describing kinetically controlled water-soil interactions and radioactive decay. All conclusions are based on analytical solutions of governing reactive transport equations. The principal question to be answered is how water-soil interaction affects the spatial limits of radionuclide migration over a wide range of problem variables.

### **Basic Model Assumptions and Formulations**

The following principal processes controlling radionuclide behavior in water saturated porous media, e.g., rocks, soils or bottom sediments, are taken into account by the model developed: fluid phase transport, multiminerall radionuclide solution-soil interaction and radioactive decay. One dimensional radionuclide diffusion and infiltration along a fluid flow stream line are considered. The rock composition is defined by the volumetric proportions of the minerals. The equilibrium concentration state description is based on the distribution coefficient approach. In spite of well-known difficulties in the general case [Reardon, 1981; Miller and Benson, 1983], this approach is often the most convenient or possibly the only way for treating radionuclides. First order kinetic equations are used for modeling radionuclide water-mineral reaction kinetics. The following symbols are used in the model:

$\alpha$	–	radionuclide activity in fluid phase ( $\{activity\}/L^3$ )
$c_i$	–	radionuclide activity of the $i$ -th mineral ( $\{activity\}/M$ )
$v_i$	–	volume content of $i$ -th mineral (dimensionless)
$\phi$	–	porosity (dimensionless)
$V$	–	filtration velocity ( $L/T$ )
$D$	–	diffusion coefficient of radionuclide in the fluid phase ( $L^2/T$ )
$n$	–	number of minerals in the rock (dimensionless)
$k_{di}$	–	distribution coefficient of the $i$ -th mineral ( $L^3/M$ )

$\rho_i$	–	mass density of the $i$ -th mineral ( $M/L^3$ )
$J_i$	–	kinetic function of $i$ -th mineral–fluid reaction ( $([activity])/(L^3T)$ )
$r_i$	–	kinetic constant of $i$ -th mineral–fluid reaction ( $L/T$ )
$S_i$	–	specific area of $i$ -th mineral ( $1/L$ )
$L$	–	the characteristic length of radionuclide migration ( $L$ )
$\Psi$	–	integral interaction coefficient (dimensionless)
$\lambda$	–	decay constant ( $1/T$ )
$x, t$	–	spatial and temporal coordinates ( $L/T$ )
$\tau^{dif}$	–	characteristic period of radionuclide transport by diffusion ( $T$ )
$\tau^{inf}$	–	characteristic period of radionuclide transport by infiltration ( $T$ )
$\tau_i^r$	–	characteristic period of reaction between water and $i$ -th mineral ( $T$ )
$\tau^d$	–	characteristic period of decay ( $T$ )

### The Transport Equations

Let us consider a contaminated solution infiltrating a porous medium accompanied by radionuclide interactions between solution and rock (soil) minerals. To describe the process of radionuclide transport, consider a column coincident with one of the stream lines. Let the infiltration velocity be a constant, and the mineral composition of the rock remain unchanged with time. The transport equations describing one-dimensional infiltration and diffusional transport of radionuclides coupled with radionuclide water–mineral interaction and radioactive decay in this case are:

$$\frac{\partial \phi a}{\partial t} + V \frac{\partial \phi a}{\partial x} = D \frac{\partial^2 \phi a}{\partial x^2} - \sum_i J_i - \lambda \phi a \quad (1)$$

$$\frac{\partial \rho_i v_i c_i}{\partial t} = J_i - \lambda \rho_i v_i c_i \quad i = 1, n$$

The expression for the kinetic function  $J_i$  is determined by the mechanism of the heterogeneous water-  $i$ -th mineral reaction. The flux from fluid to one of the minerals is determined by the specific area of that mineral and the flux density at the phase boundary.

Here we define the radionuclide flux density at the phase boundary to be proportional both to the deviation from the equilibrium concentration, as determined by the radionuclide concentration in the fluid and a distribution coefficient, and also to a kinetic rate constant,  $r$ :

$$J_i = -s_i r_i \rho_i (c_i - k_{di} a) \quad (2)$$

The equations should also include the initial and boundary conditions describing the initial distributions of radionuclides in the solids and the radionuclide concentrations in the source water penetrating the porous medium.

Equations (1) and (2) describe radionuclide transport coupled with kinetically controlled water-mineral interactions. These equations can be simplified for the case when heterogeneous reactions are fast and radionuclide concentrations are close to local equilibrium concentrations. Local equilibrium implies the following relationships between radionuclide concentration in fluid and solid phases:  $c_i = k_{di} a$ . The system considered is close to local equilibrium if the characteristic times of reaction between the fluid and each of the minerals,  $\tau_i^r$ , are less than the characteristic period of diffusion,  $\tau^{dif}$ , and less than the characteristic period of infiltration  $\tau^{inf}$ . The equations describing radionuclide transport with the local equilibrium approximation are:

$$\frac{\partial a}{\partial t} + \frac{V}{R} \frac{\partial a}{\partial x} = \frac{D}{R} \frac{\partial^2 a}{\partial x^2} - \lambda a \quad (3)$$

$$c_i = k_{di} a \quad i = 1, n$$

where

$$R = 1 + \sum_i \frac{\rho_i v_i k_{di}}{\phi} \quad (4)$$

Parameter  $R$  is the so-called retardation factor [Bear et al., 1967; Wels and Smith, 1994]. Equations (3) show that local equilibrium interaction between water and the rock minerals leads to an  $R$ -fold decrease of radionuclide migration rate.



## Characteristic Length of a Radionuclide Migration

Let us consider a typical contamination scenario in which contaminated solutions of a steady state source with radionuclide activity,  $a(a,t) = a_0$ , penetrates into initially uncontaminated porous media,  $c_i(x,0) = 0$ . The stationary solutions are radionuclide concentration distributions along a fluid flow line obtained after an infinite time period. Radionuclides cannot penetrate infinitely into porous media because of radioactive decay. These distributions show the limit of radionuclide migration and can be useful in the study of the influence of water-solid interactions on radionuclide transport. The stationary solutions are :

$$a(x) = a^0 \exp\left\{-\frac{x}{L}\right\}$$

$$c_i(x) = a^0 \frac{k_{di}}{1 + \lambda_{vi} / r_i s_i} \exp\left\{-\frac{x}{L}\right\}$$
(5)

where a characteristic length of radionuclide migration,  $L$  (the distance of e-fold decrease of radionuclide activity influx) is:

$$L = \frac{2}{\sqrt{\left(\frac{V}{D}\right)^2 + \frac{4\lambda}{D}(1 + \Psi) - \frac{V}{D}}}$$
(6)

where parameter,  $\Psi$ , which characterizes the combined effect of water-rock interactions, is:

$$\Psi = \sum_i \frac{k_{di} \rho_i v_i / \phi}{1 + \lambda_{vi} / r_i s_i}$$
(7)

Equations (5) show the decrease of radionuclide concentrations in fluid and rock with distance along a stream line. It means that certain concentrations of radionuclides cannot penetrate beyond a certain depth. Equations (5) permit an expression to be derived for the porous medium thickness required to decrease the fluid radionuclide activity from its initial value,  $a_0$ , to a safe level,  $a_s$ :

$$X_{safe} = -L \ln \frac{a_s}{a_0}$$
(8)

## The Effect of Water-Mineral Interaction on the Characteristic Length of Radionuclide Migration

The effect of the parameters characterizing the water-mineral interaction on the characteristic length of radionuclide migration is provided by expressions (6) and (7). Generally, the radionuclide water-mineral interaction decreases the characteristic length,  $L$ , compared with the case where fluid does not interact with the solid. This effect is due to the decay of radionuclides in the solid phases, which results in a steady state radionuclide flux from the fluid into the minerals. It follows from (6) and (7) that the parameter,  $\Psi$ , characterizing the combined effect of interaction, varies from zero for the case of no reaction between minerals and fluid to a value equal to  $\sum v_i \rho_i k_{di} / \phi$  for local equilibrium, when  $1 + \Psi$  becomes equal to the retardation factor,  $R$ , in (3) and (4).

It is interesting to note that for the kinetically controlled interactions, the value of  $\Psi$  depends not only on parameters characterizing the rates of reaction, but also on the decay constant. In this connection, let us rewrite parameter  $\Psi$  in another form using the characteristic periods of decay and water-mineral interaction instead the decay and kinetic constants. The characteristic period of decay,  $\tau^d$  (the period of for an e-fold decrease of radionuclide activity due to decay) and the period of chemical relaxation,  $\tau_i^r$  (the period of e-fold approach to equilibrium of the  $i$ -th mineral concentration due to reaction with fluid in a closed system) could be defined as:

$$\tau^d = \frac{1}{\lambda}$$

$$\tau_i^r = \frac{1}{r_i s_i (1 / v_i + k_{di} \rho_i / \phi)}$$
(9)

In this case the parameter  $\Psi$  is:

$$\Psi = \sum_i \frac{k_{di} \rho_i v_i / \phi}{1 + (\tau_i^r / \tau^d)(1 + k_{di} \rho_i v_i / \phi)}$$
(10)

Expression (7) shows that  $\Psi$  and the characteristic migration length,  $L$ , are determined by the ratio of reaction rates to the decay rate, but not by absolute rates of chemical

processes. It follows from (10), that the value of  $L$  depends on the ratios of characteristic periods of exchange reactions to the characteristic period of decay.

### Diffusion and Infiltration Transport

Expression (7) permits comparison of the roles of diffusion and infiltration processes in radionuclide migration. It follows from (7), in the case when infiltration transport can be neglected by comparison with diffusion transport, that is when  $\tau^{dif} \gg \tau^{inf}$ , the expression for  $L$  can be simplified, thus:

$$L_{dif} = \sqrt{\frac{D}{(1 + \Psi)\lambda}} \quad (11)$$

In the opposite case when  $\tau^{dif} \ll \tau^{inf}$ , the expression for  $L$  is:

$$L_{inf} = \frac{V}{(1 + \Psi)\lambda} \quad (12)$$

Diffusion and infiltration transport result in equivalent infinite time distributions of radionuclides in porous media in the case when  $L_{dif} = L_{inf}$ . In this case, the infiltration velocity,  $V_{eq}$ , is defined by the following expression:

$$V_{eq} = \sqrt{D\lambda(1 + \Psi)} \quad (13)$$

Equation (13) shows that in the case when an infiltrating solution interacts with minerals of the rock, the parameter,  $V_{eq}$ , depends not only on the infiltration velocity and the diffusion coefficient, but also on the parameters characterizing the water-mineral interactions and on the decay constant. In the case when the infiltration velocity is considerably less than  $V_{eq}$ , *the role of infiltration is negligible when compared with diffusion and  $L$  increases in proportion to the square root of the diffusion coefficient of a radionuclide in fluid phase. If the role of diffusion is negligible by comparison with infiltration ( $\tau^{dif} \gg \tau^{inf}$ , or  $V \gg V_{eq}$ ) the characteristic length of radionuclide migration is proportional to the infiltration velocity.*

### **Transport of Sr-90 and Cs-137**

The derived equations allow us to determine the spatial limits of radionuclide migration by diffusion and infiltration transport coupled with thermodynamically and kinetically controlled radionuclide fluid-solid interaction. In this paper we apply the approach to Sr-90 and Cs-137 transport in water saturated porous media. The contamination of soils, rocks and bottom sediments of reservoirs by fission products Sr-90 and Cs-137 commonly occurs at sites where radionuclides have been released to the environment, e.g., at Chernobyl, Ukraine; Mayak, Chelyabinsk region, Russia; and at Hanford, Washington State, USA [Routson 1981; Serne and Wood, 1990; Bradley, 1992; Fauer, 1993]. Because of this fact, Sr-90 and Cs-137 behavior in water - rock systems have been considered in many studies, and parameters characterizing their contamination, transport and radionuclide solution-solid interactions are available in the literature [Ames et al., 1982; Brouwer et al., 1983; Delagard et al., 1984; Serne and Wood, 1990; Zachara, 1991].

Let us consider a typical scenario in which water contaminated by radionuclides infiltrates a porous medium, for example, water from a contaminated reservoir penetrates into bottom sediments and bed rock. The following assumption and parameters are used in the calculations. The porosity of the porous medium is arbitrarily set equal to the value 5%. The infiltration velocity during radionuclide migration is assumed to range between  $0 - 10^4$  m/year. The value of the diffusion coefficients for strontium and cesium are taken to be equal  $10^{-9}$  m<sup>2</sup>/sec. Data available in the literature for  $k_d$  have been determined in most cases for interaction in the system water—whole rock [e.g., Serne and Wood, 1990; Fayer et al., 1993], but not for  $k_d$  values for interactions between water and individual minerals, [Brouwer et al., 1983; Zachara, 1991]. For this reason, whole rock  $k_d$  values have been used. According to the cited studies, the  $k_d$  values vary from 1 to 200 for strontium, and from 1 to 10000 for cesium, so a  $k_d$  range from 1 to 10000 has been used in the calculations. The decay constant has been set equal to  $0.76 \cdot 10^{-9}$  sec<sup>-1</sup>, this value is close to the decay

constants of both Sr-90 and Cs-137 and corresponds to the half-life period,  $T_{1/2} = 29$  years. The range of the kinetic constants is over 5 orders of magnitude. For convenience in comparing the results corresponding to different  $k_d$  values, the variation in the kinetic constant has been provided for by the variation of the  $\tau^r/\tau^d$  ratio in Equation (10).

The results of calculations of the characteristic length of a migrating radionuclide are shown on Figures 1–5. The calculations show how  $L$  depends on parameters characterizing transport and radionuclide water-mineral interaction processes. Figures 1, 2, 3, 4, 5 corresponds to the different values of 1, 10, 100, 1000, 10000 respectively of  $k_d$  in porous media. The Curves 1–6 in each figure show how the value of the characteristic length,  $L$ , depend on the infiltration velocity at different values of reaction rates. Curve 1 corresponds to the local equilibrium case  $\tau^r/\tau^d \ll 1$ , whereas curve 6 corresponds to the case when fluid does not interact with minerals, i.e.,  $\tau^r/\tau^d \gg 1$ . Curves 2–6 have been calculated respectively for the following values of the  $\tau^r/\tau^d$  ratio: 0.001, 0.01, 0.1, and 1.0.

The comparison of Curves 1 on Figures 1–5 shows how the increase in  $k_d$  influences the characteristic length of migration. This effect is very weak for the case of low reaction rates when  $\tau^r/\tau^d > 0.1$  (the Curves 4, 5, 6 in Figure 1 are close to Curves 4, 5, 6 in Figure 5). It follows from (10) that in this case  $\Psi$  is close to

$$\sum_i (\tau^d / \tau_i^r)$$

and does not depend explicitly on  $k_d$ .

In the case of high reaction rates, the effect of  $k_d$  on  $L$  depends on the regime of radionuclide transport. As follows from a comparison of Figures 1 and 3 in the local equilibrium range (Curve 1) for diffusion controlled transport, a 100-fold increase of  $k_d$  leads to a 10-fold decrease of  $L$ , whereas in the infiltration controlled case, a 100-fold increase of  $k_d$  results in a 100-fold decrease of  $L$ .

A comparison of Curves 1–6 on Figures 1–5 elucidates the effect of water-mineral reactions rates on radionuclide migration. Generally a decrease in reaction rate increases the

value of  $L$ . However this effect depends on the infiltration velocity and also on the  $k_d$  value. For the diffusion transport of radionuclides at the lower distribution coefficient ( $k_d = 1$ , Figure 1), the change of a thermodynamically controlled regime (Curve 1) to the case of no reaction (Curve 6) results in 10-fold increase of  $L$ . Whereas for a high infiltration velocity range ( $V > 10$  m/year) at  $k_d$  equal to 10000 (Figure 5) the difference in values of  $L$  between local equilibrium and the case of no reaction is about 5 orders of magnitude.

## Conclusions

The results obtained in this work elucidate the effects of water-soil exchange reactions on radionuclide migration in water saturated porous media under different conditions. In some cases, the expressions derived and the calculated data provide an easy way to estimate the limits of radionuclide migration and to evaluate the decrease of fluid activity during transport in ground waters. However, the limitations of the model should be taken into consideration. One of the most important limitations is the neglect of hydrodynamic dispersion. Other limitations follow from neglect of solution and rock composition changes, and also from the use of the  $k_d$  approach in describing radionuclide water-rock interactions. Because of these limitations, the best results in applying the model can be obtained in situations where dispersion and chemical changes do not significantly affect radionuclide migration. The penetration of radionuclides into bottom sediments and bed rock of contaminated reservoirs is, in some cases, an example of such a situation. However in many other cases, even when model limitations should be taken into account, the model can be used to obtain approximate estimates of the penetration depth.

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## FIGURE CAPTIONS

- Figure 1. Calculated values of the characteristic length of radionuclide migration versus infiltration velocity, for different radionuclide water-rock exchange rates. Curves 1, 3, 4, 5, 6 correspond to values of  $\tau'/\tau^d$  ratio 0, 0.01, 0.1, 1, and unlimited, respectively,  $T_{1/2} = 29$  years,  $D = 10^{-9}$  m<sup>2</sup>/sec,  $k_d = 1$ .
- Figure 2. Calculated values of the characteristic length of radionuclide migration versus infiltration velocity, for different radionuclide water-rock exchange rates. Curves 1, 3, 4, 5, 6 correspond to values of  $\tau'/\tau^d$  ratio 0, 0.01, 0.1, 1, and unlimited, respectively,  $T_{1/2} = 29$  years,  $D = 10^{-9}$  m<sup>2</sup>/sec,  $k_d = 10$ .
- Figure 3. Calculated values of the characteristic length of radionuclide migration versus infiltration velocity, for different radionuclide water-rock exchange rates. Curves 1, 2, 3, 4, 5, 6 correspond to values of  $\tau'/\tau^d$  ratio 0, 0.001, 0.01, 0.1, 1, and unlimited, respectively,  $T_{1/2} = 29$  years,  $D = 10^{-9}$  m<sup>2</sup>/sec,  $k_d \approx 100$ .
- Figure 4. Calculated values of the characteristic length of radionuclide migration versus infiltration velocity, for different radionuclide water-rock exchange rates. Curves 1, 2, 3, 4, 5, 6 correspond to values of  $\tau'/\tau^d$  ratio 0, 0.001, 0.01, 0.1, 1, and unlimited, respectively,  $T_{1/2} = 29$  years,  $D = 10^{-9}$  m<sup>2</sup>/sec,  $k_d \approx 1000$ .
- Figure 5. Calculated values of the characteristic length of radionuclide migration versus infiltration velocity, for different radionuclide water-rock exchange rates. Curves 1, 2, 3, 4, 5, 6 correspond to values of  $\tau'/\tau^d$  ratio 0, 0.001, 0.01, 0.1, 1, and unlimited, respectively,  $T_{1/2} = 29$  years,  $D = 10^{-9}$  m<sup>2</sup>/sec,  $k_d \approx 10000$ .

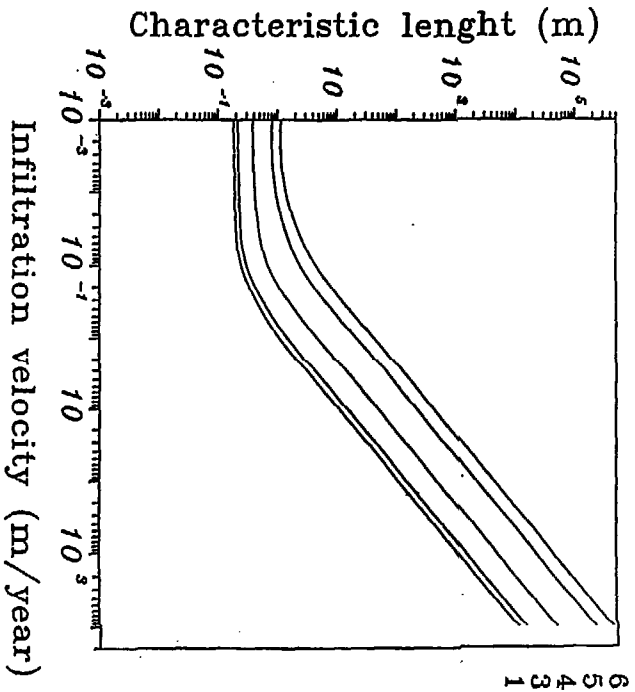


Figure 1.

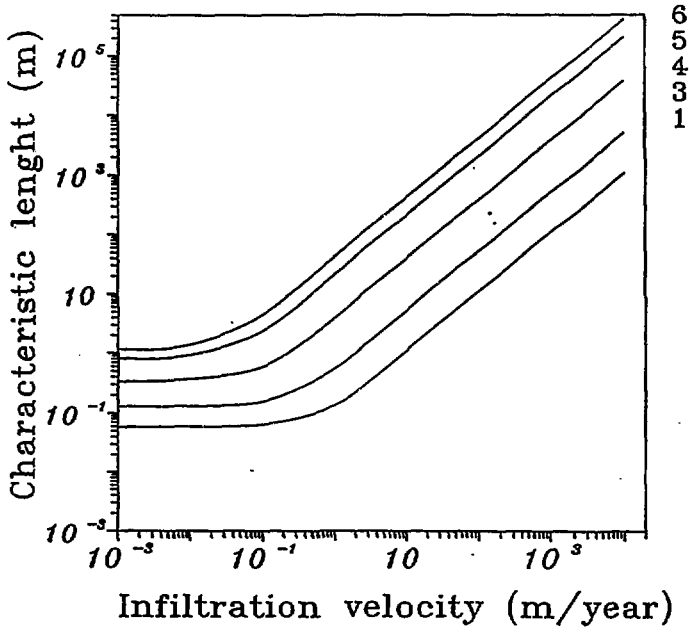


Figure 2.

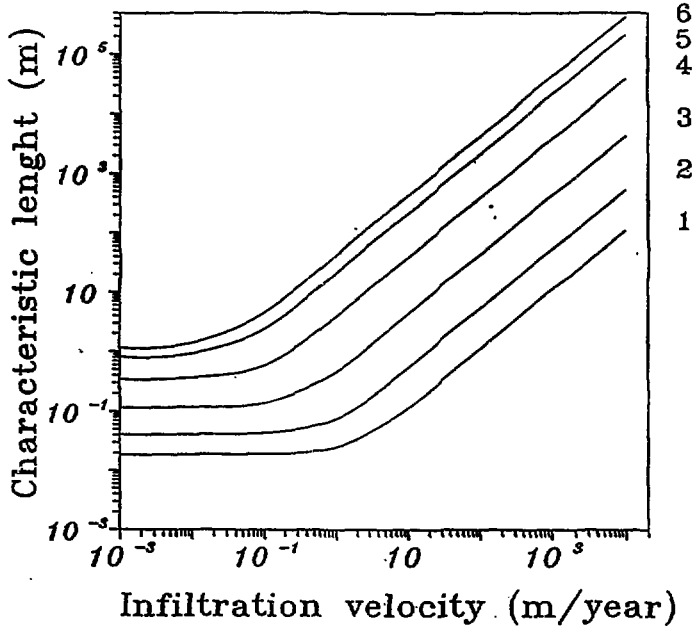


Figure 3.

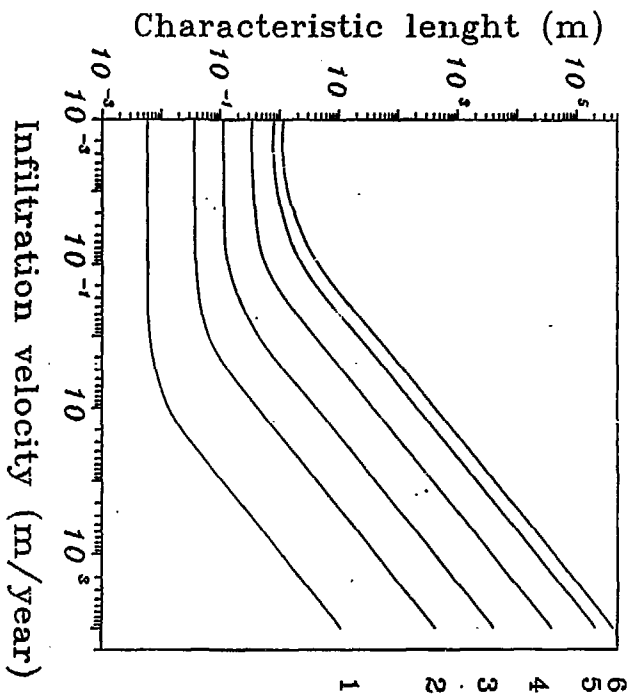


Figure 4.



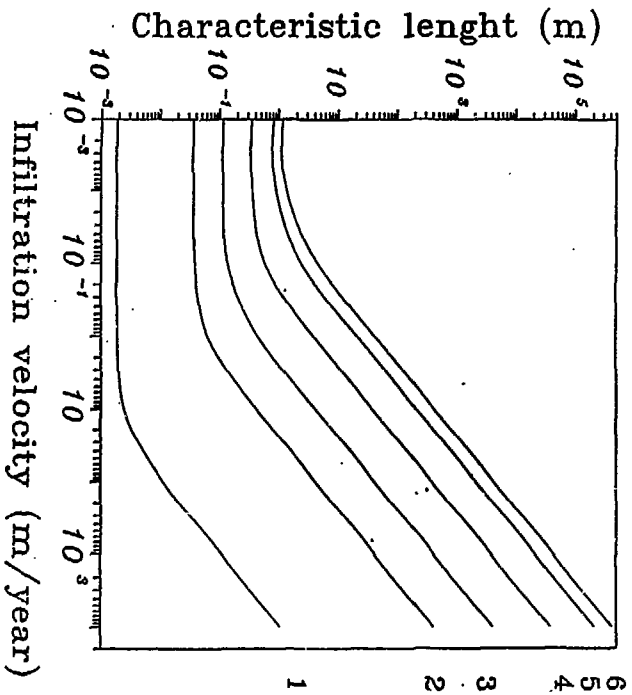


Figure 5.