SIMPLIFIED ESTIMATION TECHNIQUE FOR ORGANIC CONTAMINANT TRANSPORT IN GROUNDWATER

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Summary

The analytical solution for one-dimensional dispersive—advective transport of a single solute in a saturated soil accompanied by adsorption onto soil surfaces and first-order reaction rate kinetics for degradation can be used to evaluate the suitability of potential sites for burial of organic chemicals. The technique can be used to the greatest advantage with organic chemicals that are present in groundwaters in small amounts. The steady-state solution provides a rapid method for chemical landfill site evaluation because it contains the important variables that describe interactions between hydrodynamics and chemical transformation. With this solution, solute concentration, at a specified distance from the landfill site, is a function of the initial concentration and two dimensionless groups. In the first group, the relative weights of advective and dispersive variables are compared, and in the second group the relative weights of hydrodynamic and degradation variables are compared. The ratio of hydrodynamic to degradation variables can be re-arranged and written as $(a_L \cdot \lambda)/(q/\epsilon)$, where a_L is the dispersivity of the soil, λ is the reaction rate constant, q is groundwater flow velocity, and ϵ is the soil porosity. When this term has a value less than 0.01, the degradation process is occurring at such a slow rate relative to the hydrodynamics that it can be neglected. Under these conditions the site is unsuitable because the chemicals are unreactive, and concentrations in groundwaters will change very slowly with distance away from the landfill site.

Introduction

The recent discoveries that synthetic organic chemicals migrate from subsurface burial sites through the unsaturated zone of the soil into groundwaters has brought the practice of disposal of chemicals in subsurface burial sites into question. Migration of solubilized organic chemicals into groundwaters is not a rapid process, but requires many months or years before chemicals or their degradation products enter and contaminate an aquifer. Even though solubilized chemicals pass through aerobic and anaerobic zones of the soil on their way to the saturated soil zone, many of them are not

completely degraded or chemically bound to soil surfaces. The chemicals that are not degraded or bound to soil surfaces or are only partially degraded can persist as constituents of the groundwater flow and be transported great distances away from the burial site.

Once a confined or unconfined aquifer has become contaminated, it is very difficult to return it to an uncontaminated state. As a result, there are two fundamental problems that must be addressed in determining if a proposed site is suitable and if subsurface burial is a feasible method of disposal of waste organic chemicals. The first problem is the collection of appropriate field and chemical data on transport and transformation of solutes in groundwaters. The second is to develop a procedure for interpreting these data to determine if the burial of organic chemicals in certain types of hydrogeological environments will produce significant contamination of groundwaters at a future time. In this report a method is presented to interpret field and laboratory data for this purpose. Previously derived models for solute transport in saturated soils have been adapted to examine the interactions among the governing transport processes that determine if a proposed burial site is or is not suitable. The proposed technique is an outgrowth of previous efforts directed towards the simulation of toxic chemical movement in soils [1, 2]. In developing this estimation technique, criteria for evaluating site suitability are suggested and important transport variables are identified for which values need to be determined by laboratory and field studies.

Transport model descriptions

The principal events that must be accounted for during the migration of chemicals from submerged burial sites into an unconfined aquifer are shown in Fig. 1. The phenomena and interactions that determine solute movement in soils include dispersion, advection, sorption, and chemical degradation mediated by microbial activities or free enzymes attached to soil surfaces. The proposed method for interpreting field data considers solute transport only in the saturated zone of the soil, even though it is recognized that a more realistic analysis should include migration in the unsaturated soil zone as well. The literature on the topic of flow of groundwater in unsaturated soils is extensive, but several investigators who have focused on the special problems of simulation of solute flow in this type of environment are Bear [3, 4], Freeze [5], Bresler [6, 7], Duguid and Reeves [8], and Pinder and Gray [9].

It will be assumed that the soil is saturated and isotropic, and that all of the transport properties (e.g., dispersion coefficients, velocities, adsorption coefficients, and reaction rate coefficients) have constant values and are not functions of solute concentration, moisture content, or spatial variations. Migration of chemical mixtures from submerged burial sites is simulated with a single-solute model because concentrations of the solubilized constituents of the mixture are low and the degree of interaction among individual mem-

bers is low. These assumptions greatly simplify the mathematical analysis and make it possible to use analytical methods. Without these simplifications, the equations describing transport and transformation are coupled non-linear partial differential equations requiring numerical methods for solution.

Chemicals that migrate from submerged burial sites located above the water table will pass through unsaturated soil zones where they can be degraded by microbial processes or very strongly bound to soil surfaces. The net effect of either one or both of these processes is to lower solute concentration. Once the chemical enters the groundwater, however, degradation will occur almost exclusively by anaerobic bacteria. Most of these bacteria can be characterized as being at survival levels of existence, which usually means that extra enzyme systems have been eliminated and only those metabolic pathways have been retained that are the most efficient and essential for viability [10—12]. As a result, chemicals that are not easily metabolized are degraded very slowly in the aqueous phase, and the rate of degradation can be represented by a first-order reaction rate mechanism.
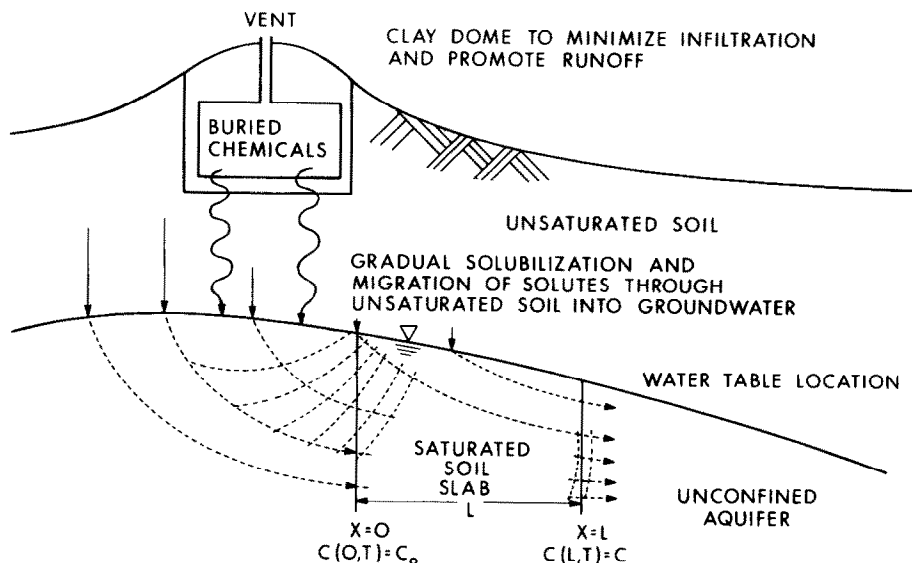

Fig. 1. Physical representation of the burial site.

One-dimensional subsurface transport of a single solute in saturated soils with constant transport properties

The simplest model containing all of the significant variables needed to define the migration of organic chemicals from submerged burial sites is a one-dimensional single-solute model. In this model interphase mass transfer is represented by a Freundlich-type adsorption process, and the disappearance of the solute by the combined biochemical activity of microorganisms and soil enzyme follows a first-order reaction rate mechanism. When all of these

simplifications are incorporated into the equation of continuity for transport of a single chemical, where moisture content is equal to the soil porosity, the model is:

$$\frac{\partial}{\partial t} \left(1 + \frac{\rho_b \gamma}{\epsilon} \right) C = D_h \frac{\partial^2 C}{\partial X^2} - \frac{q}{\epsilon} \frac{\partial C}{\partial X} - \lambda C, \tag{1}$$

where ρ_b is the bulk density of the soil, ML^{-3}; γ is the adsorption coefficient, $L^3 M^{-1}$; ϵ is soil porosity, L^0; D_h is the horizontal dispersion coefficient, $L^2 T^{-1}$; q is the groundwater velocity, LT^{-1}; and, λ is the first-order reaction rate constant, T^{-1}. A more rigorous derivation of the general equation of continuity of which this is a simplified expression was derived by Bear [3, 4].

The groundwater velocity is related to the average interstitial flow velocity through the soil by:

$$\bar{V} = q/\epsilon, \tag{2}$$

and the horizontal dispersion coefficient is related to the average interstitial flow velocity by [4]:

$$D_h = a_L \bar{V} + D_d^*, \tag{3}$$

where D_d^* is the molecular diffusion coefficient defined by Fick's law of diffusion, $L^2 T^{-1}$; and a_L is the longitudinal dispersivity of the porous medium, L^1, a quantity that is a function of the properties of the porous medium. Dispersivity, a_L, has dimensions of length and is often referred to as the mixing length for dispersion of solutes in soils and porous media [13]. For this model, $D_h = a_L \cdot (q/\epsilon)$, and the contribution of molecular diffusion is considered to be negligible.

With the initial solute concentration entering the saturated soil given as C_0, the initial and boundary conditions are:

$$C(X, 0) = 0, \qquad X \geqslant 0 \tag{4a}$$

$$C(0, t) = C_0, \qquad t \geqslant 0 \tag{4b}$$

$$\lim_{X \to \infty} C(X, t) = 0. \tag{4c}$$

The model can be simplified more by defining the following modified transport properties:

$$D_h^* = \frac{D_h}{1 + \rho_b \gamma/\epsilon}; \qquad Q^* = \frac{q}{1 + \rho_b \gamma/\epsilon}; \qquad \lambda^* = \frac{\lambda}{1 + \rho_b \gamma/\epsilon}. \tag{5}$$

The denominator of each of these modified transport properties is the retardation factor or time delay for solute holdup on soil surfaces due to adsorption. In saturated soils with high organic carbon content, adsorption is more irreversible and the analysis of solute behavior is better simulated by the model developed by Ogata [14]. For our model, Freundlich-type adsorption is used. When the new modified transport properties are substituted, the

model is given as:

$$\frac{\partial C}{\partial t} = D_h * \frac{\partial^2 C}{\partial X^2} - \frac{Q^*}{\epsilon}\frac{\partial C}{\partial X} - \lambda^* C. \tag{6}$$

This equation can be solved by LaPlace transforms directly or by referring to the solutions provided by other authors [3, 4, 14—18]. For the boundary conditions of this problem, the solution is given as:

$$C(X, t) = \frac{C_0}{2}\left\{ \exp\left[\frac{XQ^*}{2D_h^*\epsilon} + X\left(\frac{\lambda^*}{D_h^*} + \frac{Q^{*2}}{4D_h^{*2}\epsilon^2} \right)^{1/2} \right] \cdot \mathrm{erfc}\left[\frac{X}{\sqrt{4D_h^*t}} + \right.\right.$$

$$\left(\lambda^*t + \frac{Q^{*2}t}{4D_h^*\epsilon^2} \right)^{1/2} \right] + \exp\left[\frac{XQ^*}{2D_h^*\epsilon} - X\left(\frac{\lambda^*}{D_h^*} + \frac{Q^{*2}}{4D_h^{*2}\epsilon^2} \right)^{1/2} \right] \cdot$$

$$\cdot \mathrm{erfc}\left[\frac{X}{\sqrt{4D_h^*t}} - \left(\lambda^*t + \frac{Q^{*2}t}{4D_h^*\epsilon^2} \right)^{1/2} \right]\right\} \tag{7}$$

With the transient solution, arrival times for a pollutant plume at an observation well can be calculated for a specified set of hydrodynamic and reaction kinetic properties. An example of this type of behavior is plotted in Fig. 2.

For site evaluation purposes, however, the long-term or steady-state solution provides a means of evaluating the concentration of the solute at a specified or predetermined distance away from the burial site. This solution can be obtained by allowing the time variable to become very large. When this is done, the steady-state solution gives the solute concentration at a specified distance, $X = L$, away from the burial site as:

$$\frac{C(L, \infty)}{C_0} = \exp\left\{ \left(\frac{Lq}{2D_h\epsilon} \right) \cdot \left[1 - \sqrt{ 1 + \frac{4D_h\lambda\epsilon^2}{q^2} } \right] \right\} \tag{8}$$

The distance $X = L$ is the thickness of the soil slab or distance away from the burial site at which a particular level of reduction in solute concentration will occur for the boundary conditions of this model. This distance, L, is not to be confused with the dispersivity, a_L. The reduction in solute concentration is a function of two dimensionless groups that contain the important transport properties that define the migration and degradation of a single chemical species. Note that the properties used in this equation are not the modified properties that included the influence of adsorption. Because we are interested in the relative amount of degradation occurring at a particular distance away from the burial site, eqn. (8) can be rearranged and solved for distance in terms of the reduction in concentration and the transport properties to give the following:

$$L = \left[\frac{2a_L}{1 - \sqrt{1 + 4\lambda a_L \epsilon/q}} \right]\left(\ln\frac{C(L, \infty)}{C_0} \right). \tag{9}$$

A plot of this equation for different values of λ, q/ϵ, and a_L is given in Fig. 3.

Discussion

Figure 2 provides an example of the transient behavior of a migrating solute in an unconfined aquifer. Values of the constants in this example are: q = 2.0 cm/d, a_L = 100 cm, γ = 0.5 cm³/g, λ = 0.001 d⁻¹, ϵ = 0.5, and ρ_b = 1.5 g/cm³. In this example, the rate constant for degradation has a low value and the soil has a dispersivity characteristic of a coarse-grained, well-drained soil. Because there is degradation and the product of hydrodynamic properties and reaction rate properties, $(a_L \cdot \lambda)/(q/\epsilon)$, is greater than 0.01, eqn. (7) is required to determine the concentration profile. However, if this term has a value less than 0.01, degradation processes can be neglected and transport approaches the dispersive—advective situation for non-reactive solutes given by Brenner [19].
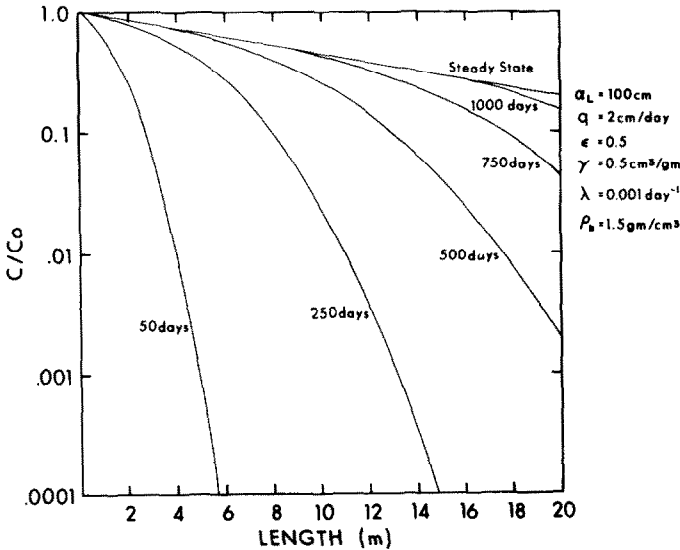

Fig. 2. Transient response of transport model.

Figure 3 is a plot of eqn. (9) for different values of hydrodynamic and reaction rate constants. With the steady-state solution, the thickness of a soil slab can be calculated in which a definite level of reduction in solute concentration for a particular set of the hydrodynamic and chemical kinetic properties will be achieved. When the chemical is moderately unreactive (λ equal to 0.001 d⁻¹), solute concentration as a function of distance is only very slightly attenuated from its original concentration. For very unreactive chemicals (λ less than 0.0001 d⁻¹), the level of reduction in solute concentration is very insensitive to variations in dispersivity and groundwater-flow velocity. The net result is that the solute concentrations of very unreactive chemicals will remain relatively constant as a function of increasing distance

away from the burial site. As with the transient solution, the interactions between hydrodynamic and reaction rate processes are summarized in the dimensionless group, $(a_L \cdot \lambda)/(q/\epsilon)$.

Chemicals with reaction rate constant between 0.0025 and 0.001 d^{-1} are regarded as moderately reactive, and chemicals with reaction rate constants greater than 0.0025 d^{-1} are regarded as very reactive. With moderately reactive chemicals, however, hydrodynamic properties begin to have a greater influence on solute concentration as a function of distance away from the burial site. Both the magnitudes of the dispersivity and the ratios of dispersivity to the groundwater flow velocity begin to have a greater effect on solute concentration for a fixed value of the reaction rate constant. In Fig. 3, groundwater flow velocity has been held constant at 1.0 cm/d and a_L has values of 10, 50, and 100 cm. In this example, the reduction in solute concentration at a fixed distance away from the burial site is much less at $a_L = 100$ cm than at $a_L = 10$ cm. Because of this, the attenuation in the solute concentration for a moderately reactive chemical will be much less in a soil with a high dispersivity than in a soil with a low dispersivity, for the same value of the groundwater flow velocity.
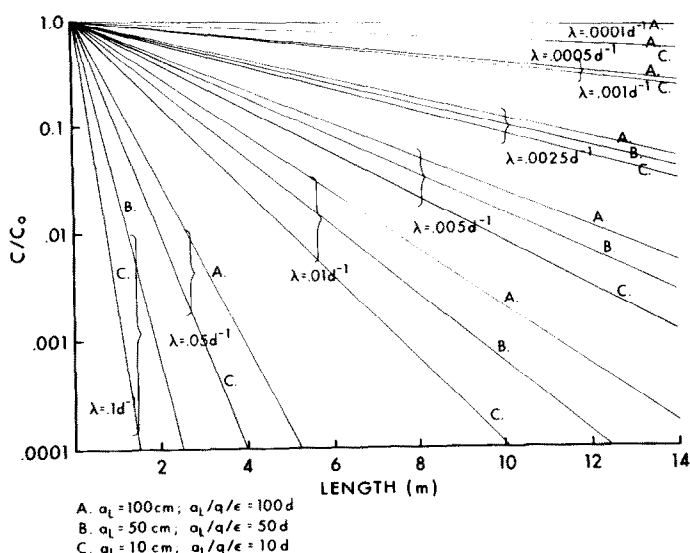

A. $a_L = 100$ cm; $a_L/q/\epsilon = 100$ d
B. $a_L = 50$ cm; $a_L/q/\epsilon = 50$ d
C. $a_L = 10$ cm; $a_L/q/\epsilon = 10$ d

Fig. 3. Effect of variable reaction rates, dispersivites and groundwater flow velocities on solute reduction.

Conclusions

A pseudo first-order kinetic mechanism has been used throughout this discussion to describe chemical degradation. Clearly, for molecules with very complicated structures and with degradation processes occurring with mixed cultures of microorganisms that may degrade the material completely,

partially, or not at all, this type of one-step degradation process is difficult to defend without experimental verification. However, in a sequential or parallel reaction rate scheme, one step will usually be rate controlling. Because of this situation, the overall rate of reaction will be dominated by this one process if sufficient biomass is available. In situations when sufficient biomass is available, the degradation process can be approximated by a first-order mechanism, even though it is recognized that this is a surrogate for what may be a very complicated degradation process, carried out by a number of different microbes acting either independently, symbiotically, synergistically, or antagonistically.

With the experience of degradation of DDT by soil microbes, one must also be aware that degradation can produce very stable intermediate products that are more toxic than the original starting materials. DDT, however, is a very unreactive chemical to begin with, and it would appear prudent as a general rule not to use subsurface burial as a method of disposal for unreactive chemicals. This is not to say that subsurface burial of chemicals is not a feasible method of waste disposal for a wide variety of organic chemicals. However, a great deal more care must be used in site selection relative to aquifer recharge areas and heights above the water table, and in selection of types of chemicals that can be placed in these burial sites. Clearly, because of the example of DDT, much more attention should be devoted to examining degradation pathways by microorganisms that will be found in both the saturated and unsaturated zones of the soil. Because degradation in saturated soils probably occurs by anaerobic bacteria, the techniques developed by Roethling and Alexander [20] provide a useful beginning for methods to examine these phenomena in a laboratory setting.

The single-chemical, one-dimensional model can provide guidance in the analysis of hydrodynamic and reaction rate data collected from a potential site, and aid in the development of a monitoring plan for the operation of a new site. For low concentrations of chemicals in groundwaters, the model can be used to estimate the distance from the burial site at which the concentration will be reduced to a specified level as a function of hydrodynamic properties and reaction rate properties of the soil—solute system. Implicit in this analysis, adsorption to soil constituents is defined by a Freundlich adsorption process. If adsorption is not reversible, attenuation as a function of distance will be less than predicted by reaction kinetic processes. The dimensionless term that contains hydrodynamic and reaction rate properties describes the interactions between the important processes that control transport and degradation, and provides a rapid method for estimating the suitability of a particular site for subsurface burial of organic chemicals. When this term has a value less than 0.01, the site is unsuitable because the chemicals are unreactive; a value between 0.1—0.01 is marginally suitable; and a value greater than 0.1 should be more extensively evaluated.

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