Evaluation of Simple Methods for Estimating Contaminant Removal by Flushing

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Abstract

The purpose of this work was to briefly outline and evaluate simple methods used for estimating the volume of water and the time required to remove contaminants from the subsurface by flushing (e.g., "pump-and-treat," "soil washing"). The methods are based on three general approaches to treating flow and transport: perfectly mixed flow, hydraulic, and advective-dispersive. Data obtained from a small field experiment designed to evaluate aquifer flushing was used to illustrate the performance of the estimation methods. The methods based on the hydraulic and ideal advective-dispersive transport approaches will generally provide estimates that underpredict the actual time. The magnitude of the underprediction will depend, in part, on the degree of nonideal behavior influencing contaminant removal (e.g., heterogeneity, rate-limited mass transfer) and on the ratio of target to initial contaminant concentration. The perfectly mixed flow reactor approach, because of its asymptotic removal curve, may be useful in providing rough approximations of required pore volumes and times. However, it cannot be overemphasized that all estimation techniques are prone to failure as long as the conceptual models upon which they are based do not accurately represent field-scale contaminant transport.

Introduction

The advent of federal and state sponsored programs for restoration of contaminated sites has fomented the design and use of various subsurface remediation techniques. The availability of alternative remediation techniques necessitates a comparison of expected performances during preparation of a site restoration plan. The time required to accomplish the proposed restoration (e.g., attainment of desired concentration) is a principal criterion used for performance evaluation. The purpose of this work is to briefly outline and evaluate simple methods used for estimating the time required for contaminant removal by flushing. Data obtained from a small field experiment designed to evaluate aquifer flushing will be used as a benchmark with which to illustrate the performance of the estimation methods.

Estimation Methods

A primary factor influencing hydraulic based remediation systems (e.g., pump and treat, in situ soil flushing) is the transport and fate behavior of contaminants, especially as affected by the imposition of induced hydraulic gradients (cf., Keely, 1989; Mackay and Cherry, 1989; Brusseau, 1993; NRC, 1994). Hence, attempts to estimate contaminant-removal times focus on predicting water flow and solute transport under specified conditions. The alternative methods differ by the approach used for predicting water flow and solute transport and by the assumptions inherent to each. For purposes of discussion, the alternative methods will be grouped into three categories: mixed reactor, hydraulic, and advective-dispersive. The discussion will focus on removal of dissolved and sorbed contaminant; the impact and removal of immiscible liquids, while often critical, will not be considered.

Mixed-Reactor Approaches

Several investigators have used estimation methods based on a representation of the aquifer as a mixed-reactor system (cf., Fogg et al., 1988; Zheng et al., 1991). This approach is widely used in chemical engineering and is based on the behavior of a "perfectly mixed flow reactor" or a "continuous stirred tank reactor" (Froment and Bischoff, 1990). With this approach, it is assumed that incoming water (free of contaminant) mixes completely within the aquifer in a time interval that is very small relative to the hydraulic residence time.

The equation obtained by treating the subsurface as a perfectly mixed flow reactor is:

$$V_o \frac{dC}{dt} + \rho \frac{V_o}{n} \frac{dS}{dt} = -QC \tag{1}$$

where C is the concentration of contaminant in the water, S is the sorbed-phase concentration of contaminant, V_o is the volume of contaminated water associated with the subsurface (pore volume), ρ is bulk density of the porous medium, n is porosity, Q is discharge, and t is time. If sorption is assumed to be linear, reversible, and rapid, the following isotherm function can be substituted into (1):

$$S = KC \tag{2}$$

where K is the sorption coefficient. Substitution and rearrangement leads to:

$$RV_o \frac{dC}{dt} = -QC \tag{3}$$

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where the retardation factor, R, is defined as:

$$R = 1 + \frac{\rho}{n} K$$

By solving (3) one can obtain the following equations for calculating the number of pore volumes (T_t) and the time (t_t) required to reach the cleanup target (C_t):

$$T_t = R\left[-\ln \frac{C_t}{C_o}\right] \tag{4}$$

$$t_t = t_r T_t = \frac{V_o}{Q} T_t \tag{5}$$

where C_o is the initial concentration, and t_r is the hydraulic residence time.

An approach related to the one described above has been used by the U.S. Environmental Protection Agency (EPA, 1988) and by others (cf., Tabak and Lang, 1988) to estimate cleanup times. This approach, called the "Batch Flushing" model, is based on step-wise flushing, which is an approximation of the approach discussed above. Given the availability of an analytical solution to equation (3) and the concomitant simplicity of using equations (4) and (5), I will focus on this approach and disregard the less elegant batch flushing model.

The subsurface is not a perfectly mixed flow reactor and there is no reason, therefore, to expect estimation methods based on such a representation to be valid. In addition, it is possible that the assumption of rapid sorption may not be valid, especially under induced-gradient conditions. However, this approach will be evaluated since it is actively used.

Hydraulic Approach

Hydraulic methods are the simplest and, perhaps, the most widely used approach for estimating cleanup times. Briefly, this approach entails definition of the "pore volume" of contaminated water, and the rate at which a pore volume is replaced or displaced by uncontaminated water. These values are determined from knowledge of the hydraulic gradient, the hydraulic conductivity, and the distribution and sorption properties of the contaminant. Once these parameters are defined, the pore volumes of water and the time required for restoration can be estimated by use of the following two equations:

$$T_t = R \tag{6}$$

$$t_t = Rt_r = R \frac{V_o}{Q} \tag{7}$$

This method is simple and straightforward, which perhaps explains its widespread use. However, a major problem associated with this approach is the assumption of ideal transport (plug flow or piston displacement). The effects of aquifer heterogeneity on flow and transport (e.g., solute spreading) are not represented in this approach. In addition, sorption/desorption is assumed to be rapid. This approach will, therefore, provide estimates that represent the minimum, with expectations that the true volumes and times could be much greater.

Approaches Based on Advective-Dispersive Transport

The two preceding approaches were based on simplifications of flow and transport in subsurface systems. Estimation approaches have also been based on advective-dispersive transport theory, which presumably more closely represents contaminant transport in the subsurface. In keeping with our focus on simple estimation methods, the simplest form of the equation will be used. Major assumptions used to derive this form of the equation include homogeneous porous media, one-dimensional transport under steady-state flow, and linear, reversible, and rapid sorption. It is clear, of course, that these conditions would not be met in the field.

The nondimensional equation governing solute transport for the conditions described above is:

$$R \frac{\partial C^*}{\partial T} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \tag{8}$$

where $C^* = C/C_o$, $T = tv/L$, v is average linear pore-water velocity, L is system length, P (Peclet Number) $= vL/D$, D is the hydrodynamic dispersion coefficient, $X = x/L$, and x is distance. Solutions to this equation are widely available for various initial and boundary conditions.

Field Data

An induced-gradient experiment was undertaken by Whiffen and Bahr (1984) to assess the efficacy of water flushing as a means to remediate a contaminated aquifer. The test was performed in a confined, sand and gravel aquifer underlying the Gloucester landfill, which is located near Ottawa, Canada. An injection/extraction well couplet was used to introduce uncontaminated water into the aquifer, thereby inducing desorption and transport of the organic contaminants. Iodide and meta-trifluoromethylbenzoic acid were added to the injection water to delineate the advective-dispersive properties of the system. Breakthrough curves for the tracers, as well as the organic solutes, exhibited tailing, which indicates the influence of hydraulic-conductivity heterogeneity on transport (Brusseau, 1992). Bahr (1989) showed that the breakthrough curves for iodide could be simulated using a one-dimensional, dual-porosity solute transport model. The data reported for the organic solutes were not, however, analyzed directly with such a model. Recently, Brusseau (1992) used a mathematical model that accounted explicitly for, among other factors, physical heterogeneity and rate-limited sorption/desorption to successfully predict the data of Whiffen and Bahr.

The elution curve measured for diethylether at a sampling point located on the longitudinal centerline of the couplet and 2.5 m from the injection well will be used as the basis for the analyses performed herein. It has been shown that the streamlines in the vicinity of the centerline of an injection-extraction well couplet are nearly linear, and that water flow can therefore be reasonably approximated as one-dimensional (cf., Chrysikopoulos et al., 1990). Hence, error associated with application of a one-dimensional model to the data obtained from the induced-gradient experiments should be minimal. The applicability of a one-dimensional model for simulating breakthrough curves obtained from the Gloucester experiment has been previously demonstrated (Bahr, 1989; Brusseau, 1992).

Results and Discussion

The elution curve reported by Whiffen and Bahr (1984) for diethylether is presented in Figure 1. Values for the retardation factor (R = 3.3), initial concentration ($C_o = 2.5$ mg/l), and average linear pore-water velocity (v = 0.15 m/d) were obtained from Whiffen and Bahr (1984) and Brusseau (1992). The predicted curve obtained by Brusseau (1992), which accounts for the influence of aquifer heterogeneity and rate-limited sorption/desorption, is also shown in Figure 1. Clearly, this independent prediction provides an excellent simulation of the experimental results. Based on this performance, the predicted curve is used to obtain values for the number of pore volumes required to reach specified concentrations below relative concentrations of 0.05. This was done to extend the results of the field experiment.

The elution curves obtained for each estimation method are compared to the field data in Figure 2. The pore volumes required to reach relative concentrations of 0.1, 0.01, and 0.001 are listed in Table 1 for each estimation method. The results obtained from the field experiment are listed for comparison. For the 0.1 relative concentration, the hydraulic and advective-dispersive approaches provide estimates that are within a factor of two of the measured data. However, the difference between the estimates and the measured data increases greatly for lower concentrations. This is to be expected since neither method accounts for the tailing caused by the impact of heterogeneity and rate-limited sorption/desorption on transport. This asymptotic removal behavior can be a severe cost and time constraint when the specified cleanup target is very low, such as are many MCLs (maximum contaminant levels).

Interestingly, the estimates produced with the perfectly mixed flow reactor approach are relatively close to the measured data (Figure 2). This results from the form of the solution to equation (3), which asymptotically approaches relative concentration of zero. This behavior mimics the tailing observed for the field data. Given that tailing phenomena are observed at many pump-and-treat operations, the perfectly mixed flow reactor approach may be useful for providing rough approximations of cleanup times. However, the good match presented in Figure 2 should be considered as nothing more than fortuitous until additional cases can be evaluated.

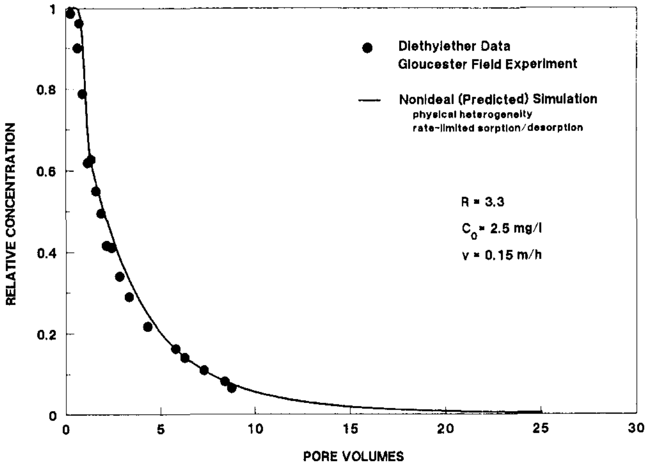

Fig. 1. Elution curve for diethylether obtained from field experiment and predicted curve obtained with nonideal transport model. Measured data from Whiffen and Bahr (1984); predicted simulation from Brusseau (1992), wherein is discussed the model and parameters used to obtain the prediction.

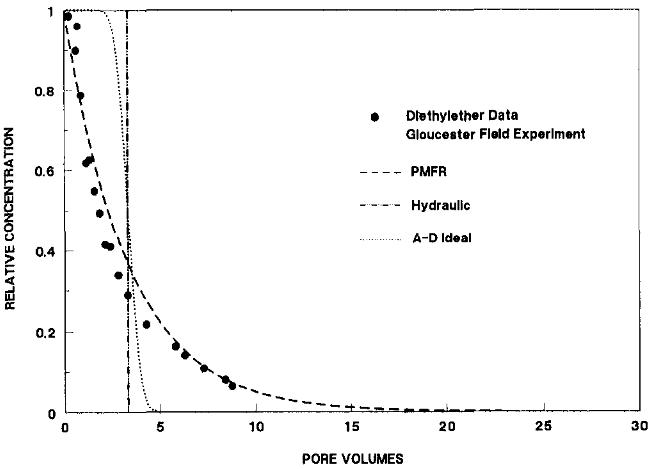

Fig. 2. Elution curves obtained for the estimation methods compared to field data. PMFR = perfectly mixed flow reactor; ADIDEAL = ideal advective-dispersive. For the ideal advective-dispersive transport case, the dispersivity was set at 2.5 cm.

Mathematical models based on advective-dispersive transport are considered more accurate than the hydraulic and mixed-reactor approaches. The latter two can, however, be considered as limiting cases of advective-dispersive transport. For example, the hydraulic model is equivalent to transport with no dispersive component (i.e., piston flow). Conversely, the perfectly mixed flow model is equivalent to transport governed by infinite dispersion. This latter equivalency helps explain the potential usefulness of the approach based on the perfectly mixed flow reactor. The spreading observed during field-scale transport is often represented by scale-dependent macrodispersivity terms that are much larger than laboratory measured values. The equivalent of infinite dispersion associated with the perfectly mixed flow model roughly approximates the macrodispersion of field-scale advective-dispersive transport.

Despite their limitations, mathematical models will continue to be used for evaluating the performance of remediation systems and for estimating contaminant removal

Table 1. Comparison of Pore Volumes Required to Reach Cleanup Target

Method	*$C/C_o = 0.1$*	*$C/C_o = 0.01$*	*$C/C_o = 0.001$*
PMFR	7.6	15.2	22.8
Hydraulic	3.3	3.3	3.3
ADIDEAL	4.3	5.3	6
Measured[1]	7.5	17.4	29

PMFR = perfectly mixed flow reactor; ADIDEAL = ideal advective-dispersive.

[1] Measured value for $C/C_o = 0.1$, extrapolated values for $C/C_o = 0.01$ and 0.001 based on predicted nonideal simulation.

times. The principal factors controlling the reliability and usefulness of modeling are the design of the model and how closely it represents the site of interest, and the availability of data for specifying values of input parameters. Models developed with the assumptions of homogeneous properties and rapid mass transfer are the simplest solute-transport models and have been the type used most often for estimating the time required for subsurface remediation. However, the application of models based on these assumptions to real systems is prone to failure because the assumptions of homogeneity and instantaneous mass transfer are rarely met at real field sites. Realistic time estimates will be obtained only with the use of models that account for all the factors influencing solute transport, including heterogeneity, rate-limited mass transfer, and the existence of nonaqueous-phase liquids (when present). Major advantages of the use of complex transport models include the capability to explicitly represent the factors that influence contaminant transport and the ability to evaluate the impact of data (input) uncertainty on the uncertainty of output. A major constraint to the widespread use of these complex transport models at most sites is the lack of sufficient information to fully "parameterize" the models (Brusseau, 1994).

Conclusion

Three alternatives for estimating the volume of water and the time required for contaminant removal were evaluated, and their performance was illustrated by comparison to the results obtained from a field experiment. Each has associated advantages and disadvantages. The choice of which to use depends upon the circumstances and upon the desired results. The methods based on the hydraulic and ideal advective-dispersive transport approaches will generally provide estimates that underpredict the actual time. The magnitude of the underprediction will depend, in part, on the degree of nonideal behavior influencing contaminant removal (e.g., heterogeneity, rate-limited mass transfer) and on the ratio of target to initial contaminant concentration. The perfectly mixed flow reactor approach, because of its asymptotic removal curve, may be useful in providing rough approximations of required pore volumes and times. However, it cannot be overemphasized that all estimation techniques are prone to failure as long as the conceptual models upon which they are based do not accurately represent field-scale contaminant transport.

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Notation

C is concentration of contaminant in the water $[M/L^3]$.
C_o is the initial concentration $[M/L^3]$.
$C^* = C/C_o$ is relative concentration.
D is hydrodynamic dispersion coefficient $(L^2/T]$.
K is the sorption coefficient $[L^3/M]$.
L is system length $[L]$.
n is porosity.
$P = vL/D$, the Peclet Number.
Q is discharge $[L^3/T]$.
$R = 1 + (\rho/n)K$ is the retardation factor.
S is sorbed-phase concentration of contaminant $[M/M]$.
t is time $[T]$.
t_r is the hydraulic residence time $[T]$.
t_t is the time required to reach the designated cleanup target $[T]$.
$T = tv/L$, nondimensional time.
T_t is the number of pore volumes (or nondimensional time) required to reach the designated cleanup target.
v is average pore-water velocity $[L/T]$.
V_o is the volume of contaminated water associated with the aquifer (pore volume) $[L^3]$.
x is distance $[L]$.
$X = x/L$, nondimensional distance.
ρ is bulk density of the porous media $[M/L^3]$.

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