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An Evaluation of Dual-Media Contaminant Transport for SRS Environmental Applications (U)

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Executive summary

The dual-media approach to contaminant transport modeling has emerged over the years as a clear improvement over the conventional Fickian advection-dispersion, or single-medium model, in an increasing number of settings. Recent application to the MADE-2 tracer test at Columbus Air Force Base has extended interest to field-scale plume migration in unconsolidated sediments. Subsequent application to tritium migration from the SRS F- and H-area seepage basins within this study also demonstrated improved transport predictions.

Both the single- and dual-media models are capable of reproducing the first-order, bulk behavior of plumes. However, the dual-media formulation reproduces second-order effects better than the conventional ADE, such as the leading and trailing tails of the plume. At the F- and H-area seepage basins, the dual-media model more accurately simulated plume arrival at Fourmile Branch, and plume attenuation from 1988 through 1998. In addition, excessive up-gradient dispersion exhibited by the single-medium model was absent in the dual-media simulations.

Use of the dual-media approach would be most important at sites driven by residual contamination at levels still exceeding regulatory limits (i.e. plume tail). Examples include "old" waste sites where the subsurface has been contaminated for decades and the bulk of the original source has already flushed through the aquifer, and pump-and-treat operations after initial treatment of high permeability zones. In these cases the dual-media approach can be expected to produce significantly different, and potentially more accurate, predictions of plume behavior. Accurate prediction of long-term residual contamination levels could be a critical component of a Monitored Natural Attenuation (MNA) program relying on dispersion and other hydrologic effects as a mechanism for attenuation (e.g. dilute tritium or TCE/PCE plumes).

Beyond technical merits, the dual-media formulation is appealing for SRS regulatory applications because its model complexity, input requirements, and computational demands are similar to single-medium modeling. Compared to high resolution geostatistical modeling, the dual-media approach is deterministic rather than stochastic, far less mathematically complex, and computationally efficient. Also, familiar commercial/ public-domain software offer a dual-media transport capability, such as the MT3DMS transport code supported by the Groundwater Modeling System (GMS).

While promising for SRS regulatory applications, selection of optimal values for dual-media input parameters is a challenge, as field-experience and theoretical study are limited. Empirical model calibration to site-specific plume monitoring data is the most reliable method for determining transport parameters in preparation for future predictions. Lacking historical data, the values of mobile volume fraction and mass transfer coefficient derived for the F- and H-area seepage basins in this study provide guidance for other SRS waste sites. Also, analyses performed in this investigation suggest that mobile volume fraction can reasonably be estimated from borehole flowmeter characterization data and/or known statistical properties of an aquifer system, independent of model calibration. Order of magnitude estimates can made for mass transfer coefficient.

Contents

Tables

Figures

Acronyms

ADE	Advection-Dispersion Equation
BTC	Break-Through Curve
CKLP	C, K, L, P reactor area
EBF	Electromagnetic Borehole Flowmeter
FACT	Flow And Contaminant Transport (code)
FMB	Fourmile Branch
GCG	Generalized Conjugate Gradient
GMS	Groundwater Modeling System
GSA	General Separations Area
HTO	Hydrogen-Tritium-Oxygen molecule (tritiated water)
LAZ	Lower Aquifer Zone
MADE	MAcro-Dispersion Experiment
MNA	Monitored Natural Attenuation
MOC	Method Of Characteristics
MODFLOW	MODular three-dimensional finite-difference ground-water FLOW model (code)
MT3DMS	Modular Three-Dimensional Transport Model - Multi-Species (code)
NATS	Natural ATtenuation Study
PCE	Perchloroethylene
PTR	Pump-Treat-Reinject
RCRA	Resource Conservation & Recovery Act
ShRINE	Savannah River Information Network Environment
SRS	Savannah River Site
TCCZ	Tan Clay Confining Zone
TCE	Trichloroethylene
TVD	Total Variation Diminishing (numerical algorithm)
UAZ	Upper Aquifer Zone
VERSE	VErsatile Reaction SEparation (code)
WSRC	Westinghouse Savannah River Company

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Introduction

Dispersion of a conservative tracer at field-scale is primarily the result of small-scale advective processes resulting from natural heterogeneity in permeability, rather than molecular diffusion that might dominate at smaller scales in a homogeneous setting. Fully incorporating physical heterogeneity into a field-scale model is extremely challenging because subsurface variability is pervasive, being present from pore-scale through regional-scale. Characterization data can only define a small fraction of actual variability, especially at smaller scales. Furthermore, computational resources usually limit the model grid resolution to a relatively coarse scale in typical regulatory applications. As a result, a typical approach is to incorporate only the largest scale hydraulic conductivity variations in the groundwater model flow model, and use a Fickian dispersion term in the contaminant transport model to deal with plume spreading from heterogeneity at all smaller scales. Although the classical Fickian advection-dispersion equation (ADE) has been effective and widely used, the formulation has well-known and long-standing deficiencies that continue to produce significant biases in highly heterogeneous aquifers, such as encountered at the Savannah River Site. These include non-physical up-gradient dispersion and the absence of long plume tails observed in the field.

More accurate predictions of contaminant migration can be achieved by employing finer-scale model grids capable of explicitly representing finer-scale heterogeneity and resulting small-scale advective processes. A geostatistical technique is commonly used to generate random synthetic variability based on assumed statistical properties for the aquifer. While such high resolution modeling can be technically effective, the large computational resources and sophisticated mathematical/statistical capabilities required are often not appropriate for routine regulatory applications. Alternatively, sub-grid modeling can be used to handle heterogeneity at scales smaller than one can, or desires to, explicitly represent with the model hydraulic conductivity field, whether due to characterization data, grid size, run-time, or other limitations. The conventional Fickian dispersion term is an example of a sub-grid model accounting for advective processes not reproduced through the model conductivity field.

An alternative sub-grid approach is the dual-media concept, the focus of this study. The dual-media concept of a porous volume being comprised of two interacting regions, one containing mobile water and the other immobile water, originated in chemical engineering studies of fixed/packed bed reactors in the early 1950's. Initial efforts to predict solute movement through such engineered porous media using the classical Fickian advection-dispersion model proved ineffective in capturing the asymmetric shape of concentration break-through curves (BTCs) at the outlet. The long "tails" typically observed were attributed to a "bed capacitance" effect resulting from the presence of relatively stagnant regions of somewhat isolated fluid, a phenomenon not considered by the advection-dispersion equation (ADE). This interpretation lead to the basic dual-media concept of co-existing regions of relatively "mobile" and "immobile" water. Advection, and possibly Fickian dispersion, occur only in the mobile water region, while the immobile water region participates through a local mass transfer mechanism between the two regions. Introduced in the late 1950's, the dual-media approach proved effective at reproducing experimental break-through curves.

Since then, the dual-media concept has been increasingly used with success in a variety of applications including fractured geologic media, especially in the petroleum industry, chromatography, aggregated/structured soils, stratified soils, field-scale solute transport, and multiphase applications. Along the way, a wide variety of terms have been used to identify the same or similar concept, including "dual-porosity", "dual-domain", "dual-media", "bi-continuum", "mobile-immobile", "two-region" and "rate-limited mass transfer". The term "dual-media" is preferentially used in this report. Among earth science applications, the bulk of the published literature on the dual-media approach for solute transport involves soil behavior and/or laboratory column tracer studies. Here an abundance of experimental data has been used to demonstrate a clear advantage in using the dual-media concept to reproduce break-through curve behavior.

Very recently, large-scale, natural-gradient tracer tests conducted at the Columbus Air Force Base have been used to show similar advantages for field-scale solute transport in unconsolidated heterogeneous geologic formations. Harvey and Gorelick (2000) showed that a dual-media model without dispersion provides a significantly better explanation of observed bromide and tritium plume behavior in the MAcroDispersion Experiments (MADE, MADE-2) than the classical advection-dispersion model. Their analytical dual-media model, coupled with interpreted measurement biases consistent with the concept of mobile and immobile water, accounts for previously reported overestimation of solute mass at early times, and underestimation at later times. The dual-media also reproduced the extremely asymmetric plume profiles observed, unlike the ADE. Subsequently, Feehley and others (2000) modeled the MADE-2 tritium tracer test using numerical ADE and dual-media models. They found that the classical Fickian ADE could reproduce bulk plume behavior reasonably well, but not the lower concentration leading tail. On the other hand, the alternative dual-media model reproduced both the bulk plume behavior and the lower concentration tail. Julian and others (2001) found the dual-media approach to be equally effective in reproducing bromide tracer test data from the Natural ATtenuation Study (NATS) at the same site.

The present investigation is motivated by a number of apparent advantages offered by the dual-media concept. Compared to the conventional ADE, the dual-media approach appears to be capable of significantly more accurate predictions of plume behavior, especially the lower concentration leading and trailing tails. The model complexity, input requirements, and computational demands are similar. Also, familiar commercial software incorporating a dual-media capability are available (e.g. MT3DMS, FACT). Compared to high resolution geostatistical modeling, the dual-media approach is deterministic, far less mathematically complex, and computationally efficient. While the dual-media method is promising, selection of optimal values for input parameters is a significant challenge, as field-scale experience and theoretical study are limited.

With these motivations and challenges, the present study explores the feasibility of applying the dual-media approach to SRS environmental applications. The investigation includes a literature review of the origin, development and application of the concept, a presentation of mathematical formulations, a comparison of break-through curve behavior for the ADE and dual-media approaches with and without decay, application to tritium migration from F- and H-area seepage basins, an analysis of optimal parameter settings, and suggested future applications of the technique at the SRS.

Literature review

Some of the earliest efforts to model solute transport through porous media occurred in chemical engineering studies of fixed/packed bed reactors, where inherent flow non-uniformities lead to axial (longitudinal) dispersion. Lapidus and Amundson (1952) proposed an advection-dispersion equation (ADE) based on Fick's Law

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad (1)$$

for predicting the behavior of fixed bed reactors (van Genuchten and Wierenga, 1976). The ADE or Fickian dispersion model produces a nearly symmetric break-through curve (BTC) at the outlet of a packed bed in response to a solute pulse at the inlet.

Early experimental data indicated the ADE was effective in reproducing the behavior of gas phase systems, but discrepancies were observed for liquid systems. Ebach and White (1958) suggested "increased by-passing, trapping, and short-circuiting of liquid" as a reason for the differences. Carberry and Bretton (1958) observed asymmetric BTCs with long tails, which they considered to be experimental evidence of a "bed capacitance effect". They attributed the effect to "trapping of fluid in low-velocity or stagnant areas from which removal occurs by a much slower mechanism than the primary dispersion one". Experimental observations such as these lead to the basic concept of interacting mobile and immobile fluid regions in subsequent mathematical developments. A wide variety of terms have been used to identify the same or similar concept, including "dual-porosity", "dual-domain", "dual-media", "bi-continuum", "mobile-immobile", "two-region" and "rate-limited mass transfer".

Turner (1958) analyzed flow through a packed bed with stagnant pockets of fluid with a particular geometry. Mass exchange between the flowing and stagnant liquid occurred by molecular diffusion. Aris (1959) developed a mathematical model that included a capacitive effect. Deans and Lapidus (1960) developed a general two-dimensional model that incorporates a two-region, mobile-immobile fluid concept, and proposed the model could be used to accommodate the observed differences between gas and liquid systems. Gottschich (1963) developed a model incorporating a stagnant film layer, and used it to explain the published gas and liquid data.

At about the same time in the petroleum industry, Warren and Root (1963) developed a double-porosity flow model to describe pressure build-up/fall-off data, noting earlier recognition that reservoirs can contain regions which contribute significantly to pore volume but negligibly to flow capacity. Deans (1963) proposed a two-region, mobile-immobile solute transport model with first-order inter-region mass transfer but neglecting dispersion in the mobile region. Coats and Smith (1964) expanded Deans' model to include longitudinal dispersion resulting in the common formulation of the mobile-immobile water concept for a conservative, non-decaying tracer:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} \quad (2a)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \zeta \left(C_m - C_{im} \right) \quad (2b)$$

Coats and Smith (1964) also performed column experiments using geologic media, as opposed to engineered materials. They observed asymmetric BTCs and achieved better agreement with their laboratory data using the mobile-immobile water formulation.

Following initial successes reported in chemical engineering and petroleum literature, application of the dual-media approach expanded to include aggregated/structured soils, solute transport in fractured media, stratified soils, field-scale transport, and multiphase processes. Extension of the concept to aggregated/structured soils occurred early because mobile and immobile regions could be clearly identified in the physical system and soil column tracer tests indicated clear improvements over the ADE (e.g. Passioura, 1971; Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976, 1977; van Genuchten and others, 1977). Application to solute transport in fractured media was also natural in that fracture and matrix porosities clearly correspond to mobile and immobile regions respectively. However, field-scale data providing a basis for the dual-media approach (e.g. Biddy, 1981) are rare compared to soils studies and have slowed its application (e.g. Painter and others, 2001).

Sudicky and others (1985) conducted experiments involving a stratified porous medium (silt-sand-silt layers). As with earlier studies involving aggregates, their solute break-through curves were strong dispersed and skewed indicating a significant departure from the Fickian dispersion model. Subsequently, Herr and others (1989), Brusseau (1991) and Li and others (1994) among others validated use of the dual-media concept for stratified media at the laboratory scale, despite conceptual ambiguity in defining the mobile and immobile regions. More recently, the mobile-immobile concept has attracted considerable attention for field-scale solute transport in unconsolidated sediments through successful application at the MADE-2 and NATS sites at Columbus Air Force Base (Harvey and Gorelick, 2000; Feehley and others, 2000; Julian and others, 2001). And, the basic concept is promising for multiphase phenomena, such as air sparging (Falta, 2000).

Starting from the Coats and Smith (1964) formulation given by equations (2), numerous mathematical extensions have accompanied expanding application of the dual-media concept. These include sorption (van Genuchten and Wierenga, 1976), dual-permeability (Skopp and others, 1981), first-order degradation (van Genuchten and Wagenet, 1989), unsteady flow with variable saturation (Gerke and van Genuchten, 1993), competive sorption (McGinley and others, 1996), multi-rate mass transfer (Haggerty and Gorelick, 1995), colloidal transport (Corapcioglu and Wang, 1999), and random walk transport (Liu and others, 2000). The dual-media approach has been increasingly used to the extent that commercial/public-domain software are now readily available, such as VERSE-LC (Whitley and Wang, 1998), MT3DMS (Zheng and Wang, 1999) and FACT (Hamm and Aleman, 2000).

Griffioen and others (1998) point out that although the dual-media approach "is being applied with increasing frequency and under a variety of physical conditions with considerable success, the question of interpreting parameters associated with the model must be addressed". The issue is raised because successes have mostly come in the form of improved empirical fits to laboratory or field data (i.e. calibration or inverse modeling). Using the dual-media concept in a predictive manner requires independent estimation of model parameters however. The dual-media formulation given by equations (2) can be viewed as a generalization of the ADE given by equation (1), as the latter is a special case obtained by setting the mass transfer coefficient in equation (2b) to either zero or infinitely. Therefore, from the standpoint of empirically fitting data , it is not surprising that the dual-media formulation provides a better match given its two additional parameters (second porosity and mass transfer coefficient).

Recognizing the need for independent measurements of dual-media parameters, soil scientists have proposed various techniques (Clothier and others, 1992; Jaynes and others, 1995; Casey and others, 1997; Casey and others, 1998; Jaynes and Shao, 1999; Casey and others, 1999; Lee and others, 2000). Others have used first-principles to define dual-media parameters or investigate scaling properties (Gerke and van Genuchten, 1993; Li and others, 1994; Brusseau and others, 1994; Haggery and Gorelick, 1995; Gerke and van Genuchten, 1996; Bajracharya and Barry, 1997; Griffioen and others, 1998). Much of the progress in these areas is relevant to smaller scales, that is, laboratory columns and field soils. For larger scales, accurate estimates of dual-media parameters depend on historical plume data (e.g. Bibby, 1981) or field-scale tracer tests (e.g. Feehley and others, 2000).

A more complete citation of peer-reviewed literature pertaining to the dual-media approach is provided in Appendix A for reference purposes.

Dual-media approach

From a conceptual standpoint, the dual-media approach is a natural extension of the conventional ADE model as illustrated in Figure 1. For a homogeneous porous medium, groundwater moves uniformly through the cross-section at a rate equal to the Darcy velocity (volumetric flux) divided by total porosity ($v = U/\theta$ in equation (1)). However, geologic media are almost invariably heterogeneous. As a typical example for unconsolidated sediment, distinct sand and clay layers are depicted in Figure 1. As a result of large variations in permeability, groundwater effectively flows only through the sand layers. Use of the total porosity in this context leads to well-known modeling biases in the form of late arrival times and inaccurate concentration levels (depending on the boundary and initial conditions). Improved predictions are typically achieved by replacing total porosity with an effective porosity for transport, $\theta_{eff} < \theta$. This is the conventional practice in field-scale contaminant transport modeling.

While a definite improvement, the ADE coupled with an effective porosity excludes the possibility of some contamination entering the finer-grain, low-permeability sediment, whether due to diffusion, small-scale advective processes (hydrodynamic dispersion), or bulk advection. Longer than expected plume tails and groundwater clean-up times have been attributed to residual contamination in fine-grained sediment, a phenomenon not accounted for by the ADE. Residual tritium contamination in clayey sediment has been observed at the SRS by Orebaugh (1987). The dual-media concept is to capture this effect by allowing local mass transfer to occur between "mobile" and "immobile" regions, as depicted by the bi-directional arrows in part 3 of Figure 1. The terms "dual-media", "dual-domain", "dual-porosity", etc. arise from the fact that, at the scale of observation, the mobile and immobile regions co-exist and comprise a mathematical dual continuum.

While most dual-media formulations include Fickian dispersion, the dual-media concept can be formulated without dispersion as a strict alternative to the ADE model:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = -\theta_m v_m \frac{\partial C_m}{\partial x} \tag{3a}$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \zeta \left(C_m - C_{im} \right) \tag{3b}$$

Note that equation (3a) is equation (2a) omitting the second-order Fickian dispersion term. This approach has been taken with success by Deans (1963), Skopp and Warrick (1974) and Harvey and Gorelick (2000) in early applications to fractured media, soils, and field-scale transport in unconsolidated sediments, respectively. However, more often classical Fickian dispersion is incorporated as shown in equation (2a), in which case the ADE or "single-medium" model is a special case of the more general dual-media formulation.

A general formulation of the dual-media approach for saturated media that includes Fickian dispersion in the mobile region, sorption, first-order decay, and internal sources/sinks is implemented in the popular MT3DMS code (Zheng and Wang, 1999) and specified by

$$\begin{aligned} \theta_m R_m \frac{\partial C_m}{\partial t} + \theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} &= \frac{\partial}{\partial x_i} \left(\theta_m D_{ij} \frac{\partial C_m}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left(\theta_m v_m C_m \right) + q_s C_s - q_s' C_m \\ &- \lambda_{1,m} \theta_m C_m - \lambda_{1,im} \theta_{im} C_{im} - \lambda_{2,m} f \rho_b K_d C_m - \lambda_{2,im} (1 - f) \rho_b K_d C_{im} \end{aligned} \tag{4a}$$

$$\theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \zeta \left(C_m - C_{im} \right) - \lambda_{1,im} \theta_{im} C_{im} - \lambda_{2,im} (1 - f) \rho_b K_d C_{im} \tag{4b}$$

where the subscripts *m* and *im* denote the mobile and immobile regions and

C = concentration

θ = volume fraction (porosity)

v_m = pore or seepage velocity, U / θ_m

D_{ij} = dispersion coefficient tensor

q_s = fluid source/sink

q_s' = transient fluid storage, $\partial \theta_m / \partial t$

f = fraction of sorption sites in contact with mobile region

λ_1 = first-order reaction/decay rate for solute

λ_2 = first-order reaction/decay rate for sorbed contaminant

ρ_b = bulk density

K_d = soil-solute distribution coefficient

ζ = first-order mass transfer coefficient between mobile and immobile regions

R_m = $1+ f\rho_b K_d / \theta_m$, retardation coefficient for mobile phase

R_{im} = $1+(1-f)\rho_b K_d / \theta_{im}$, retardation coefficient for immobile phase

Version 2.0 of the FACT code offers a similar capability for saturated, unsaturated, and/or mixed conditions (Hamm and Aleman, 2000).

The focus of the present investigation is tritium, for which equations (4) can be simplified. Assuming no sorption, $K_d = 0$ and the retardation coefficients are one. Also the first-order decay rates are the same for the mobile and immobile regions for radioactive decay. Further assuming no internal sources exist, and for the moment considering only steady flow one-dimensional flow and transient one-dimensional transport, equations (4) become

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} - \lambda(\theta_m C_m + \theta_{im} C_{im}) \tag{5a}$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \zeta(C_m - C_{im}) - \lambda \theta_{im} C_{im} \tag{5b}$$

where

D_m = $\alpha_L v_m$

α_L = longitudinal dispersivity

The ADE or single-medium model can be obtained from the dual-media model as a special case by setting the inter-region mass transfer coefficient to either zero or infinity.

This fact can be demonstrated for the former case by setting $\zeta = 0$, subtracting equation (5b) from (5a), dividing by mobile volume fraction, and omitting the now unnecessary mobile region subscript. The result is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \lambda C \tag{6}$$

which is the same as equation (1) with the addition of radioactive decay. When $\zeta \to \infty$, the mobile and immobile region concentrations become $C_{im} = C_m = C$ by equation (5b), and equation (5a) becomes

$$(\theta_m + \theta_{im})\frac{\partial C}{\partial t} = \theta_m D_m \frac{\partial^2 C}{\partial x^2} - \theta_m v_m \frac{\partial C}{\partial x} - \lambda(\theta_m + \theta_{im})C$$

Recognizing that $\theta_m + \theta_{im} = \theta$, replacing $\theta_m v_m$ with the Darcy velocity (U), and dividing by total porosity yields

$$\frac{\partial C}{\partial t} = \frac{\alpha_L U}{\theta}\frac{\partial^2 C}{\partial x^2} - \frac{U}{\theta}\frac{\partial C}{\partial x} - \lambda C \tag{7}$$

Substituting $U/\theta = v$ and $\alpha_L U/\theta = \alpha_L v = D$ again results in the single-medium equation given by equation (6).

Although the dual-media formulation reproduces ADE behavior at limiting values of the mass transfer coefficient, its behavior at intermediate values differs from the single-medium approach, as shown by van Genuchten and Wierenga (1976) for example. These unique characteristics are most conveniently illustrated by considering a non-dimensional counterpart to equations (5) derived in Appendix B

$$\phi\frac{\partial C_m'}{\partial t'} + (1-\phi)\frac{\partial C_{im}'}{\partial t'} = \alpha_L'\frac{\partial^2 C_m'}{\partial x'^2} - \frac{\partial C_m'}{\partial x'} - \lambda'\left[\phi C_m' + (1-\phi)C_{im}'\right] \tag{8a}$$

$$(1-\phi)\frac{\partial C_{im}'}{\partial t'} = \zeta'\left(C_m' - C_{im}'\right) - \lambda'(1-\phi)C_{im}' \tag{8b}$$

where

$$t' = \frac{U}{\theta L}t$$

$$x' = \frac{1}{L} x$$

$$Pe = \frac{L}{D} v_m = \frac{LU}{D\theta_m}$$, Peclet number

$$\zeta' = \frac{L}{U} \zeta$$

$$\lambda' = \frac{\theta L}{U} \lambda$$

$$C_m{}' = \frac{1}{C_0} C_m$$

$$C_{im}{}' = \frac{1}{C_0} C_{im}$$

$$\phi = \frac{\theta_m}{\theta}$$

and

$$\frac{1}{Pe} = \frac{D}{v_m L} = \frac{\alpha_L v_m}{v_m L} = \frac{\alpha_L}{L} = \alpha_L{}' \tag{9}$$

The non-dimensional time, t', can be interpreted as the number of pore volumes advected through the system based on total porosity.

The Fickian ADE is obtained from equations (8) by setting $\zeta' = 0$, and re-interpreting the mobile phase porosity θ_m as the effective porosity for transport, θ_{eff}. The result is

$$\phi \frac{\partial C_m{}'}{\partial t'} = \alpha_L{}' \frac{\partial^2 C_m{}'}{\partial x'^2} - \frac{\partial C_m{}'}{\partial x'} - \lambda' \phi C_m{}' \tag{10}$$

which is a two-parameter transport model in terms of ϕ and $\alpha_L{}'$. Typical values for effective porosity and non-dimensional dispersity would be 25% and 0.10 (i.e. dimensional dispersivity, α_L = 10% of the travel length, L). The most basic dual-media model is obtained by omitting Fickian dispersion in the mobile region as in equations (3), and assuming the total porosity of aquifer is relatively well known. The result is also a two-parameter transport model

$$\phi\frac{\partial C_m{}'}{\partial t'}+(1-\phi)\frac{\partial C_{im}{}'}{\partial t'}=-\frac{\partial C_m{}'}{\partial x'}-\lambda'\left[\phi C_m{}'+(1-\phi)C_{im}{}'\right] \tag{11a}$$

$$(1-\phi)\frac{\partial C_{im}{}'}{\partial t'}=\zeta'\left(C_m{}'-C_{im}{}'\right)-\lambda'(1-\phi)C_{im}{}' \tag{11b}$$

where the input parameters are mobile porosity θ_m and non-dimensional mass transfer coefficient, ζ'. Values of these parameters appropriate for field-scale conditions in unconsolidated sediments are not well established. However, limited experience gained at the MADE-2 site and the SRS F- and H-area seepage basins, to be presented later in this report, suggests approximate nominal values of θ_m = 15% ($\phi = 1/3$) and ζ' = 1.0 as discussed below.

For comparing the behavior of the single- and dual-media models, consider the parameter matrices shown in Table 1. No-decay conditions are considered to illustrate the predicted behavior of a conservative tracer, and for comparison to similar results presented by van Genuchten and Wierenga (1976). Radioactive decay at a rate corresponding to tritium is considered in anticipation of subsequent investigation of the F- and H-area seepage basins and other tritiated SRS waste sites. The non-dimensional parameters are based on an assumed typical travel distance of 1000 ft and a 3 year groundwater travel time for the fastest flow paths. Total porosity is assumed to be 45%. The MADE-2 tracer test (Harvey and Gorelick, 2000; Feehley and others, 2000) and present SRS F- and H-area seepage basins study suggest a nominal value of 10^{-4} day^{-1} for the dimensional mass transfer coefficient, ζ, and 15% for mobile porosity, θ_m. For tritium, which has a half-life of 12.3 years, the decay rate coefficient is 1.54×10^{-4} day^{-1}. The corresponding non-dimensional mass transfer and decay coefficients are computed in Table 1 to be 0.730 and 0.507, respectively.

Figures 2 through 9 illustrate the break-through curves (BTCs) resulting from the parameter settings in Table 1, and solute injection for 3 non-dimensional time units starting at time zero following van Genuchten and Wierenga (1976). The BTCs were generated using MT3DMS (version DoD_3.5) and the Groundwater Modeling System (GMS v3.1, 12Jun01 build). The numerical discretization was chosen as $\Delta x' = 0.01$ and $\Delta t' = 0.001$, and the TVD solution algorithm was used. In the dual-media runs, the non-dimensional dispersivity was set to 0.001, which eliminated Fickian dispersion for practical purposes. Note that the BTCs generally differ in shape between the two formulations, such that the dual-media behavior is not reproduced by the Fickian ADE model. Figures 10 and 11 provide a direct comparison of the single- and dual-media formulations with nominal parameter settings under no decay and decay conditions, respectively. Following the progression of conceptual models depicted in Figure 1, the first BTC shown in each figure is a single-medium model with $\theta = \theta_{total} = 0.45$ (cases SN9 and SD9 in Table 1). The second curve is a single-medium model using an effective porosity, $\theta = \theta_{effective} = 0.25$ (cases SN3 and SD3). The third BTC is a nominal dual-media model without Fickian dispersion (cases DN3 and DD3). The fourth BTC is a dual-media model that includes Fickian dispersion in the mobile region with $\alpha_L' = 0.1$, which would be the next stage in the progression shown in Figure 1. Note that the dual-media models produce early breakthrough like the effective porosity single-medium model, similar peak concentrations as the total porosity model, and much heavier tails than either ADE model. These characteristics of the dual-media formulation have been demonstrated in the literature to better match the observed behavior of laboratory and field data, and motivate application of the technique at the Savannah River Site as discussed previously.

Application to the F- and H-area seepage basins

Ideally, the dual-media approach would be evaluated for SRS conditions using the results of an on-site field-scale tracer test, similar to the MADE-2 study of physical heterogeneity at Columbus Air Force Base (Boggs and others, 1992; Adams and Gelhar, 1992; Rehfeldt and others, 1992; Boggs and Adams, 1992). Unfortunately, data of this nature is not available at the SRS. However, tritium migration from the F- and H-area seepage basins can be viewed as *de facto* tracer tests because basin inputs and discharges to surface water have been quantitatively monitored over time, albeit with less precision than a carefully-controlled experiment. Tritium is an ideal tracer of groundwater movement because it is non-sorbing and can be accurately measured. The potential merits of the dual-media approach are investigated by calibrating groundwater flow and contaminant transport models of each set of basins against surface water monitoring data at Fourmile Branch (i.e. observed tritium break-through).

Background information

The F- and H-area seepage basins are located within the General Separations Area (Figure 12). Three basins were constructed in F-area and four in H-area. The basins received low-level radioactive waste water from the 200-F and 200-H separations facilities from

1955 through 1988, after which they were closed and capped under the Resource Conservation & Recovery Act (RCRA). From 1989 through 1998, mounding of the water table at the basins dissipated and head gradients reverted to more natural conditions while large-scale pump-treat-reinject (PTR) systems were designed and constructed. The PTR systems began continuous operation in 1999 and provide hydraulic control of tritium and treatment of other radionuclides and metals. Fenimore and Horton (1972) provide an excellent summary of the operating history and environmental effects of the seepage basins through 1972. More recent information is provided by Looney and others (1993) and GeoTrans (1993).

Tables 2 and 3 summarize tritium source, migration and related data for each set of basins assembled from WSRC (1991), annual environmental monitoring reports (e.g. Arnett and Mamatey, 1999), and the SRS Weather Center through ShRINE. An error in the volumetric flowrate recorded for F-area in 1987 was identified through the assistance of Paul Dentremont and Joe Odum. The correct value was not determined, so the long-term average flowrate is shown as a placeholder in Table 2. Approximately 30% of tritium discharged to the basins was lost to the atmosphere through evaporation and diffusion according to WSRC (1991), and each table shows the net amount entering the subsurface under this assumption. The flux of tritium discharging with groundwater to Fourmile Branch has been monitored at H-area since 1958 and at F-area since 1967. Monitoring in H-area apparently captured plume arrival, whereas in F-area tritium apparently arrived before 1967. The locations of the surface water monitoring stations are shown in Figure 13. Contaminant migration from the basins is approximated by the following differences:

F-area seepage basins	FMA7 - FM3A - FM2B
H-area seepage basins	FM2B - FM1C

Absolute and relative variations in liquid volume to the basins and rainfall are provided in the tables as potential explanations of perturbations in the surface water monitoring data. Figure 14 illustrates the estimated net flux of tritium entering and leaving the groundwater systems associated with each set of seepage basins. The latter are the "break-through curves" for these *de facto* tracer tests. Radioactive decay and storage in the aquifer result in fluxes to Fourmile Branch that are dampened and lagged relative to the sources.

Knowing the flux of activity entering and leaving the groundwater systems associated with the basins, total activity within the systems can be estimated through a mass balance accounting for radioactive decay. In exact differential form, the mass balance for a system containing a decaying contaminant is

$$\frac{dA}{dt} = F_{net} - \lambda A \tag{12}$$

where

$A \equiv$ total activity of the system (Ci)

$F_{net} \equiv$ net flux into system (Ci/yr)

$\lambda \equiv$ radioactive decay coefficient ($\ln 2 / \tau_{half-life}$), (yr^{-1})

$t \equiv$ time (yr)

Assuming the initial activity of the system is A_0, the solution to equation (12) is

$$A = A_0 e^{-\lambda t} + \frac{F_{net}}{\lambda}\left(1 - e^{-\lambda t}\right) \tag{13}$$

Tables 2 and 3 provide an estimate of the activity remaining in each groundwater system using the exact solution, equation (13), and an approximate discrete solution based on one year increments as an independent check. The "exact" results are plotted in Figure 15. The activity remaining in the F- and H-area groundwater systems in substantially lower than the historical peaks.

Several modeling studies have been conducted at the F- and H-area seepage basins over the years, mainly focused on tritium transport and design of the pump-treat-reinject remediation systems. Among those conducted within the past 10 years, Looney and others (1993) predicted tritium migration from the F- and H-area basins under no-action and PTR scenarios using a log-normal transfer function approach calibrated to historical data through 1992. In the same year, GeoTrans (1993, Figures 5.31 and 5.32) developed a three-dimensional numerical model of groundwater flow and tritium transport at the basins and forecast tritium migration to Fourmile Branch for various remedial strategies. Sadler (1995) and Boltz (1997) subsequently refined the GeoTrans (1993) models, but did not publish revised forecasts of total tritium migration to Fourmile Branch. In 1999, GeoTrans (1999a, Figure 4.22; 1999b, Figure 4.22) upgraded the existing numerical models of the basins and generated new predictions of tritium migration to Fourmile Branch under unstressed and active remediation conditions. For the present study, the saturated flow models developed by GeoTrans (1999a,b) are taken as the starting point for numerical simulations.

Net water and tritium flux to water table

For saturated groundwater flow and contaminant transport modeling, transient recharge and tritium flux to the water table are needed. The volumetric and tritium fluxes provided in Tables 2 and 3 are inputs to the surface water in the basins, as well as rainfall. Evaporation reduces fluxes to the water table, and travel time through the vadose zone delays arrival.

Fenimore and Horton (1972) report that the SRS lies in a region where "the average annual rainfall and evaporation usually balance each other". This statement is supported by field experience with H-area basin 3. Basin 3 became practically impermeable by the early 1960's and was removed from active service. From January 1964 through December 1966 the level in Basin 3 fluctuated, but was the same at the start and end of the three-year period (Horton and others, 1971). So, recharge to the water table can be approximated by the volumetric flow into the basins divided by surface area.

The net flux of tritium activity to the water table is more difficult to estimate, but has been thoroughly explored by Horton and others (1971) and Fenimore and Horton (1972). The water evaporative flux is given by

$$f_{evap} = K\left(P_{wi} - P_w\right) \tag{14}$$

where

K ≡ mass transfer coefficient

P_{wi} ≡ partial pressure of water vapor at liquid-gas interface between basin waters and the atmosphere

P_w ≡ partial pressure of water vapor in the atmosphere

Here P_{wi} would correspond to 100% humidity whereas P_w would be lower on average, perhaps 68% the SRS 30 year average humidity reported by Weather Center on ShRINE. The tritium (HTO) evaporative flux is given by

$$m_{evap} = K\left(P_{ti} - P_t\right) \cong K\left(P_{wi}\, y_t\right) \tag{15}$$

where

P_{ti} ≡ partial pressure of HTO vapor at liquid-gas interface between basin waters and the atmosphere

P_t ≡ partial pressure of HTO vapor in the atmosphere (approximately zero)

y_t ≡ mole fraction of HTO at the basin

Note that the practical absence of HTO in the atmosphere creates a proportionally larger driving force for evaporative transport of HTO. Using equations (14) and (15), Horton and others (1971) derived the following analytical expression for basin HTO concentration

$$\frac{C}{C_0} = \exp\left(-\frac{\beta A}{Q}\right) \tag{16}$$

where

C ≡ concentration of tritium in basin

C_0 ≡ concentration of tritium input to the basin

β ≡ rate coefficient

A ≡ basin area

Q ≡ basin flowrate

Calibration to field data from H-area Basin 3 over a two year period indicates the rate coefficient is approximately $\beta = 6 \times 10^{-6}$ cm/s (Horton and others, 1971). Basin surface areas are defined by Fenimore and Horton (1972) and average flowrates are computed in Tables 2 and 3. Application of equation (16) to the F- and H-area basins results in estimated HTO evaporative losses of 27% and 36%, respectively, as shown in Table 4.

Fenimore and Horton (1972, pp. 9 and 17) report that the water table beneath the F-area basins is 60-65 ft below ground surface, and that vertical movement through the vadose occurs at a rate of 0.1 ft/d or less. This suggests a travel time of approximately 2 years between the basins and water table. In H-area, the water table is 15 to 25 ft below ground surface, with the lower number being more representative of the largest, most active basin, Basin 4. Considering the depth of the excavation, the travel time is estimated to be less than 1/2 year and can be neglected at the time scale to be considered in numerical simulations.

In summary, water table recharge is assumed to equal volumetric flux input to the basin. Travel time to the water table is assumed to be 2 years in F-area and negligible in H-area. Tritium losses due to evaporation are assumed to be 27% in F-area and 36% in H-area. These assumptions combined with the data presented in Tables 2 and 3 define the source terms for saturated zone flow and transport modeling.

Groundwater flow modeling

Local-scale saturated flow models were developed by GeoTrans (1999a,b) for the purpose of assessing the effectiveness of pump-treat-reinject operations at the F- and H-area seepage basins. As these were the most recent models developed for the area, the corresponding MODFLOW input files were taken as the starting point for groundwater flow and contaminant transport modeling in this study. The MODFLOW input files were first imported into the Groundwater Modeling System (GMS v3.1 12Jun01 build). Each model was translated into the "true layer", and to the extent feasible, "conceptual modeling" frameworks of GMS. In particular, recharge boundary conditions were converted to the conceptual modeling approach to allow easy specification of spatial and temporal variations. MODFLOW was retained as the flow simulator code for the present study. The version packaged with GMS v3.1 is MODFLOW-96 (Harbaugh and McDonald, 1996).

Preliminary conventional ADE transport runs indicated that modifications to the flow models were necessary to achieve agreement between simulated and measured cumulative activity discharging to Fourmile Branch from 1955 through 1998. Effective porosity values well in excess of the assumed total porosity of 45% were required in both GeoTrans models to slow pore velocities to a point where radioactive decay reduced simulated fluxes to Fourmile Branch to the measured levels. For H-area an effective porosity on the order of 80% was needed. In F-area, the value was approximately 55%.

This implied too much groundwater flow through the upper aquifer zone (UAZ) in both models.

Recharge in the GeoTrans (1999a,b) models was set to 17 in/yr. Other modeling efforts covering the area (GeoTrans, 1993; Sadler, 1995; Boltz, 1997; Flach and Harris, 1997; Flach and others, 1999), and nearby hydrologic budget and lysimeter studies (Parizek and Root, 1986; Hubbard and Emslie, 1984, Hubbard, 1986; Denehy and McMahon, 1985; Cahill, 1982) suggest that recharge should be in the range of 12 to 15 in/yr. The most reliable estimate of recharge for average SRS conditions is probably the value used in a large-scale groundwater flow model calibrated to stream baseflows. A recent example is the groundwater flow model developed for the C, K, L and P-reactor areas by Flach and others (1999). The CKLP model was calibrated to both hydraulic head and stream baseflow data, and resulted in an estimated recharge of 12.5 in/yr. Based on the prior literature, recharge in the F- and H-area flow models were reduced from 17 to 12.5 in/yr. In order to maintain agreement with well water level data, horizontal and vertical conductivities in the UAZ were reduced to 70% of the GeoTrans (1999a,b) values. These changes resulted in reasonable values of effective porosity in the F-area model (i.e. <45%). However, H-area still required an effective porosity greater than 45%.

Further flow and transport simulations suggested that groundwater flow through the UAZ in H-area was still excessive, while flow through the lower aquifer zone (LAZ) was low. In the GeoTrans (1999b) model the horizontal conductivity of the LAZ is 1 ft/d, which is lower than prior models of the area. GeoTrans (1993) reported a calibrated estimate of 13.18 ft/d for LAZ conductivity around the H-area basins in groundwater flow models of the regional General Separations Area (GSA) and more localized F- and H-area seepage basins area. In a subsequent refinement of the local model, Boltz (1997) used a value of 5 ft/d in the vicinity of the H-area basins. In a GSA model by Flach and Harris (1997), LAZ conductivity averaged approximately 7 ft/d near the basins. These observations suggested raising LAZ conductivity from 1 ft/d to 5 ft/d to allow a greater fraction of surface recharge to discharge to Fourmile Branch through the LAZ rather than the UAZ. The effect would be to slow pore velocities in the UAZ. After making this modification, calibration to water level data resulted in a further 30% reduction in UAZ conductivity, and a two-fold increase in tan clay confining zone (TCCZ) conductivity. The combined effect of reducing recharge and increasing LAZ conductivity was a UAZ conductivity 50% lower than the GeoTrans (1999b) model. With these modifications, the transport model could be calibrated to the monitoring using an effective porosity less than 45%.

The modifications to the GeoTrans (1999a,b) conductivity fields are summarized in Table 5 in the form of multipliers to the original values. Hydraulic head contour maps for the original and re-calibrated groundwater flow models under steady-state capped conditions are shown in Figures 16 through 21 for comparison. From visual inspection, the revised results are in close agreement with GeoTrans (1999a,b). Transient groundwater flow simulations were performed by specifying transient recharge boundary conditionsm for the seepage basins in a manner consistent with the volumetric flows in Tables 2 and 3. Also, recharge over the Old Burial Ground and sedimentation basin was varied to reflect uncapped, capped and/or water-filled conditions.

Contaminant transport modeling

Transient transport was simulated by specifying the concentration of tritium in net recharge to the water table in a manner consistent with the activities (Curies) recorded in Tables 2 and 3. MT3DMS (version DoD_3.5) supported by GMS v3.1 was chosen as the transport simulation code. MT3DMS offers both the conventional Fickian ADE (single-medium) and dual-media transport formulations and interfaces conveniently with MODFLOW using the GMS v3.1 interface. Minor modifications were made to the MT3DMS source code to print cumulative mass balance data to a separate file for convenient post-processing.

The computational mesh employed by GeoTrans (1999a,b) and retained in this study has thin grid cells near seepage areas that impose severe time step (Courant) limitations. To avoid excessively small time steps, the fully implicit standard finite difference algorithm was chosen over total variation diminishing (TVD), method of characteristics (MOC) and hybrid algorithms. A time step of 0.1 year or 36.5 days was chosen. The convergence criterion for generalized conjugate gradient (GCG package) iterations was set to 0.0001.

For the conventional Fickian ADE or single-medium formulation, the primary input parameters are effective porosity θ_{eff} and longitudinal dispersivity α_L ($D = \alpha_L v_m$). Based on modeling experience at a number of SRS sites, a nominal value of effective porosity would be 25% (cf. Flach and others, 1999). A nominal value of longitudinal dispersivity is 10% of the plume travel distance (cf. Fetter 1993). The travel distance is approximately 1600 ft in F-area, and 500 ft in H-area for Basin 4. Transverse horizontal and transverse vertical dispersivities are assumed to be 10% and 1% of longitudinal dispersivity. Optimal values of effective porosity and longitudinal dispersivity can be determined empirically by calibrating the transport model to tritium break-through at Fourmile Branch. Table 6 defines the parameter matrices chosen for this purpose.

For the general dual-media formulation given by equations (5), which incorporates both the mobile-immobile water and Fickian dispersion concepts, the primary inputs are mobile porosity θ_m, immobile porosity θ_{im}, mass transfer coefficient ζ, and longitudinal dispersivity α_L ($D = \alpha_L v_m$). Assuming that total porosity θ is relatively well known, the immobile porosity can be defined as $\theta_{im} = \theta - \theta_m$, leaving a three parameter dual-media model. Further simplification occurs if Fickian dispersion is omitted ($\alpha_L = 0$), as Deans (1963), Skopp and Warrick (1974) and Harvey and Gorelick (2000) have done. The result is a two parameter dual-media model in terms of mobile porosity and mass transfer coefficient. The two parameter model has the advantage of requiring the same number of inputs as the conventional ADE model, but does sacrifice some flexibility.

Field-scale experience with the dual-media technique in heterogeneous, unconsolidated sediments is limited. Through empirical fits to the MADE-2 tracer test at Columbus Air Force Base, Harvey and Gorelick (2000) and Feehley and others (2000) estimated the ratio of mobile to total volume θ_m / θ to be 1/7 and 1/8, respectively. For mass transfer coefficient ζ the estimates were 0.003 and 0.0006 day^{-1}. Preliminary dual-media simulations using these values suggested that a larger mobile fraction and smaller mass transfer coefficient were needed for the F- and H-area seepage basins. The parameter matrices shown in Table 7 were judged to be sufficiently broad to capture the optimal settings for dual-media simulations. The H-area dual-media matrix was broadened during the parametric study as indicated because the initial matrix did not clearly capture the range of optimal settings.

Optimal parameter estimation

The primary criterion chosen for measuring the performance of the single- and dual-media transport models is the extent of agreement between simulated and measured tritium discharge to Fourmile Branch. A secondary criterion is presence or absence of non-physical up-gradient dispersion. Agreement between simulated and measured break-through at Fourmile Branch was assessed by observing the cumulative activity discharged from 1955 through 1998, the time of plume arrival, and plume attenuation after basin closure in 1988. Toward this end, paired plots showing a cumulative mass/activity balance and tritium flux to Fourmile Branch were prepared for each case identified in Tables 6 and 7. Appendix C contains a complete compilation of these plots, and the first single-medium parametric case for F-area (FS01 in Table 6) is shown in Figure 22 as an example.

In the cumulative mass/activity balance the following quantities are plotted:

Historical data curves:

"Source" =	cumulative activity entering the water table based on historical data
"FMB activity" =	cumulative activity discharged to Fourmile Branch based on historical data

Numerical simulation curves:

"Rech" =	cumulative activity entering the water table through recharge boundary conditions
"RivDrn" =	cumulative activity discharging through river or drain boundary conditions
"Decay" =	cumulative activity lost through radioactive decay
"Mobile" =	activity presently residing in the mobile region of the aquifer
"Immobile" =	activity presently residing in the immobile region (zero for single-medium transport)

The mass balance for the numerical simulation is

$$\text{Rech} = \text{RivDrn} + \text{Decay} + \text{Mobile} + \text{Immobile} \tag{17}$$

The "Source" and "Rech" amounts are identical in principle, but differ slightly in practice due to temporal discretization in the models. Under ideal conditions, the "RivDrn" model prediction would match the "FMB activity" data curve. The bottom plot in Figure 22 shows the year by year variation in tritium flux to Fourmile Branch.

In evaluating the results compiled in Appendix C, the most fundamental comparison is cumulative activity discharged to Fourmile Branch through 1998 ("RivDrn" and "FMB activity" curves). The parameter settings for which good agreement is observed in this regard are shaded in Tables 6 and 7. The five or six best parameter settings for each area and modeling technique are specifically:

F-area / Single-medium:	FS 4, 9, 13, 17, 22
H-area / Single-medium:	HS 4, 9, 13, 18, 22
F-area / Dual-media:	FD 5, 10, 14, 18, 22
H-area / Dual-media:	HD 29, 30, 15, 17, 18, 19

Note that the optimal input parameters for both transport formulations are correlated. For the single-medium model, increasing effective porosity can be offset by decreasing dispersivity to maintain model calibration, and vice versa. For the dual-media formulation, increasing mobile porosity can be compensated by decreasing the mass transfer coefficient, and vice versa.

The single best parameter settings for each area and modeling technique were selected by comparing the leading and trailing tails of the simulated and observed plumes, and considering upgradient dispersion. These were judged to be cases FS-13, HS-18, FD-18 and HD-30. Figures 23 through 28 compare the optimal single- and dual-media simulations for H- and F-areas, respectively. In H-area, the optimal dual-media simulation is observed to better match plume arrival at Fourmile Branch, and plume attenuation from 1988 through 1998, compared to the optimal single-medium model. The plume maps for 1988 show that the single-medium model exhibits excessive up-gradient dispersion, which is absent in the dual-media model.

In F-area, comparison of the single- and dual-media break-through curves is inconclusive as neither formulation was able to accurately reproduce the bulk plume behavior, much less the lower concentration tails. Both models overpredict transport to Fourmile Branch through the early 1980's, and then underpredict afterward until closure. Prior transport models have exhibited similar biases (GeoTrans, 1993, Looney and others, 1993; Sadler, 1995). Looney and others (1993) discuss a number of operational changes and nearby activities that may account for the discrepancy. In particular, the basins experienced periods of slow seepage through the early 80's that was eventually overcome by constructing higher banks and initiating algae control through oxalic acid treatment. These actions presumably affected tritium flux to the water table. Also, logging between the seepage basins and Fourmile Branch may have affected discharge to Fourmile Branch through changes in evapotranspiration. None of these factors have been included in the present flow and transport models. Note that, as in H-area, the single-medium model exhibits excessive up-gradient dispersion while the extent of the dual-media plume is more realistic.

Non-physical up-gradient dispersion is a well known deficiency of the Fickian ADE when large values of the diffusion coefficient $D = \alpha_L v_m$ are used, as is the typical case in field-scale modeling (cf. de Marsily, 1986, pp. 242, 243). Up-gradient dispersion in the single-medium formulation effectively serves to "hold up" some tritium, which allows for sufficient radioactive decay to occur. In the dual-media model, some tritium is accumulates in the immobile region, where sufficient radioactive decay occurs. The dual-media result is a sharp plume boundary on the up-gradient side, which is more consistent with reality. Single-medium simulations with less dispersion could be generated by reducing the dispersivity. However, the result would be an over-prediction of cumulative flux to Fourmile Branch.

The optimal parameter settings and corresponding simulation results depend on a number of uncertain inputs to the overall flow and transport modeling effort. These include recharge, hydraulic conductivity fields, stratigraphic surfaces, tritium source amounts and timing, and monitoring data. Also, grid geometry and resolution, time step size, and numerical algorithm selection have an effect on the calibrated transport predictions. A formal analysis was not conducted to quantify these uncertainties. However, refinement of modeling inputs, assumptions and choices is not expected to change the basic conclusions.

In summary, both the single- and dual-media models are apparently capable of reproducing the bulk behavior of the F- and H-area tritium plumes through 1998 given sufficient input information. However, the dual-media formulation reproduced second-order effects better than the conventional ADE. These include the leading and trailing tails of the plume, and an absence of excessive dispersion (e.g. up-gradient).

Implications for groundwater remediation

Predicting bulk plume behavior may be sufficient for designing effective remediation strategies at particular waste sites, in which case the conventional ADE approach would likely be adequate (Li and Brusseau, 2000). However, remediation at many other sites will be driven by residual contamination at levels still exceeding regulatory limits. Examples include "old" waste sites where the subsurface has been contaminated for decades and the bulk of the original source has already flushed through the aquifer, and pump-and-treat operations after initial treatment of high permeability zones. In these cases the dual-media approach can be expected to produce significantly different, and potentially more accurate, predictions of plume behavior (Li and Brusseau, 2000). Accurate prediction of long-term residual contamination levels could be a critical component of a Monitored Natural Attenuation (MNA) program relying on dispersion and other hydrologic effects as a mechanism for attenuation (e.g. dilute tritium or TCE/PCE plumes).

The implications of employing single- versus dual-media modeling in this context can be explored by extending the F- and H-area calibration runs discussed above. Figure 29 shows the five best single- and dual-media predictions discussed previously, but extended out to year 2050. The five best simulations are shown to provide a sense of the uncertainty inherent in any single prediction using either modeling approach. Note that at future times, the single-medium predictions do not capture the behavior of the dual-media results. At some times the difference is a factor of 2 to 3. This implies that single-medium predictions may not predict actual plume behavior even after considering model uncertainty/sensitivity.

Given the inability of either approach to provide a good match to the F-area break-through curve, consider only the H-area results for further discussion. The dual-media predictions differ from the single-medium results in two ways. During the first several years after basin closure, the dual-media model predicts a steeper reduction in concentration, consistent with the monitoring data. This occurs because the mobile zone, which occupies a third or less of the total volume (see Table 7), is rapidly flushed with clean groundwater through advection. After this initial advective flushing stage, the rate of further attenuation slows markedly with plume behavior being controlled by mass transfer from the immobile to mobile region. The H-area data and calibrated dual-media results indicate that conventional transport modeling may underpredict the initial rate of groundwater cleanup, and then produce overly optimistic long-term cleanup rates, as similarly noted by Haggerty and Gorelick (1995).

Selection of optimal dual-media parameters

While the dual-media formulation clearly has the potential to improve contaminant transport modeling, accurate predictions depend on selection of optimal input parameter values. At Columbus Air Force Base, optimal dual-media parameters were determined empirically from tracer test data. In this study of the F- and H-area seepage basins, optimal parameters were empirically derived from model calibration to historical data. At sites lacking such plume monitoring data, the predictive capability of a dual-media model will depend on an analyst's ability to select optimal site-specific values based on experience at similar sites, characterization data, and/or first principles. This challenge is widely recognized and forms the motivation for active research (e.g. Jaynes and others, 1995; Casey and others, 1999; Lee and others, 2000; Li and others, 1994; Brusseau and others, 1994; Haggerty and Gorelick, 1995; Bajracharya and Barry, 1997; Griffioen and others, 1998; Painter and others, 2001).

Conventional use of the Fickian ADE (single-medium) model in field-scale applications relies heavily on past experience that has been cast into "rules of thumb". At the Savannah River Site, the rules of thumb are to set longitudinal dispersivity to 10% of plume travel distance and effective porosity to 20 - 30%. Characterization data are rarely used to define these parameters, an exception being Flach and others (1999) who used core descriptions to justify effective porosity values.

Laboratory-scale experience with the dual-media formulation has become extensive and Griffioen and others (1998) have recently compiled much of the data. Theoretical developments have also advanced as reviewed by Griffioen and others (1998). Unfortunately, field-scale experience in heterogeneous unconsolidated sediments is very limited as discussed previously. Therefore, rules of thumb applicable to SRS field-scale applications have not been established for the dual-media approach, although the MADE-2 and F- and H-area seepage basins studies do provide guidance. Over time this situation will improve, but for now alternative approaches are needed for selecting values for each dual-media parameter.

Mobile volume fraction

The partitioning of total volume into "mobile" and "immobile" regions is uncertain, although perhaps no more so than defining an "effective" porosity. The proper breakpoint between these regions, whether cast in terms of permeability or pore velocity, has not been theoretically established for unconsolidated sediment. For a starter, the two regions should be thought of as containing *relatively* mobile and *relatively* immobile groundwater. Unfortunately, the determination is complicated by the fact that physical heterogeneity alone does not define the distinction between "mobile" and "immobile". Rather, optimal partitioning also apparently depends on the spatial and temporal scales of the contaminant plume in relation to scales of heterogeneity, and groundwater flow directions in relation to anisotropy and structural features.

As an example of scale dependence, consider a three component porous medium containing both small and large scale regions of low permeability sediment along with high permeability zones. For a large-scale plume passing through the medium over a long period, the characteristic time scale might be sufficiently large for molecular diffusion to keep solute concentrations in the high permeability and small-scale low permeability zones approximately equilibrated. In this case, the small-scale low permeability zones should be included in the "mobile" domain, despite the fact that the groundwater in these zones is relatively stagnant. The reason is that the high permeability and small-scale low permeability composite system would behave as though the entire volume was experiencing advection. This can be realized by recalling earlier discussion of the limiting behavior of the dual-media mathematical formulation. If mass transfer between the mobile and immobile regions is large enough, then the system behaves identically to a single porosity system from a transport perspective, even though advection is only occurring in a fraction of total volume. On the other hand, consider a contaminant plume of short duration. In this case, the time scale is too short for diffusion to produce equilibrium between the high permeability and small-scale low permeability zones. The immobile domain would then encompass both of the low permeability zones. Alternatively, one might employ an "effective porosity" concept by omitting the large scale low permeability zones altogether.

This example demonstrates that the mere presence of relatively stagnant water does not necessarily imply an "immobile" designation. Rather, in addition to being relatively stagnant, the "immobile" region must also be somewhat isolated from "mobile" region in a chemical sense. The degree of isolation will depend on the characteristic time scale of the plume in relation to the scale of heterogeneity. In a natural aquifer, variability is typically observed at many scales. Therefore mass transfer between high and low permeability zones will be occurring at many different rates from the dual-media perspective, and one should not expect a single partitioning to work over all time scales (Haggerty and Gorelick, 1995). The example above illustrated this for heterogeneity occurring at two scales. In response, Haggerty and Gorelick (1995) have proposed a multiple-rate mass transfer model in which the immobile domain is divided into a series of sub-regions, all experiencing first-order mass transfer, but at different rates. The concept is capable of predicting plume behavior over multiple time scales. Nevertheless, the single-rate (i.e. dual-media) formulation is effective at predicting behavior over a single time scale of interest provided optimal parameter settings are chosen.

As an example of groundwater flow direction affecting mobile-immobile partitioning, consider groundwater flowing parallel and perpendicular to a perfectly layered system. In the former case, low permeability layers above a certain thickness (based on the discussion above) would be assigned to the immobile domain. In the latter case, the flow field would be uniform despite the heterogeneous setting, and no zones of relatively stagnant groundwater could be identified as candidates for an immobile domain.

To summarize discussion so far, the immobile region in a dual-media model should be comprised of zones containing relatively stagnant groundwater, and also having a spatial scale consistent with the plume time scale. This observation suggests a two-stage approach to mobile-immobile partitioning. The first step would be to identify zones of relatively mobile and immobile water based on heterogeneity and groundwater flow directions in relation to anisotropy and/or structural features. The second step would be to examine the scales of heterogeneity, and potentially include the smallest scale stagnant zones with the "mobile" domain and exclude the largest scale stagnant zones altogether. The "immobile" domain in the model would then be comprised only of stagnant zones of a certain scale controlling plume behavior at the time scale of interest.

Before exploring some specific approaches for mobile-immobile partitioning, it should be noted that analogous difficulties exist with the conventional single-media model in defining effective porosity. In the case of small-scale low permeability zones and a large-scale plume, the mere presence of low permeability does not necessarily dictate exclusion from the effective porosity volume (cf. de Marsily, 1986, p. 259, K' = 0 and 1 cases). In the case of groundwater flow perpendicular to heterogeneous layers, the effective porosity concept breaks down in contrast to the parallel flow case for example.

Harvey and Gorelick (2000) present a plausibility argument for immobile regions comprising more than half of the aquifer at the MADE-2 site. They compare diffusion and advection time scales for a low permeability lens in a parallel flow field using the Peclet number

$$Pe = \frac{T_d}{T_a} = \frac{JK\tau w^2}{\theta D_m L} \tag{18}$$

where

T_d = diffusion time scale

T_a = advection time scale

J = hydraulic gradient

K = hydraulic conductivity

τ = tortuosity

w = half thickness of lens

θ = porosity

D_m = diffusion coefficient

L = length of lens

A small Peclet number would imply that diffusion dominates over advection and the lens can be classified as immobile. For representative values of these parameters, specifically with K set to an estimate of median conductivity and a half-thickness of 5 cm, the Peclet number is 0.28. Therefore well over half of the MADE-2 aquifer can be considered to be immobile, which is consistent with their calibrated model result, $\theta_{im} / \theta \cong 6/7$.

In partitioning total volume into "mobile" and "immobile" regions, one could hypothesize that the equivalent/effective conductivity is an appropriate cut-off value. In other words, regions of the appropriate scale containing groundwater flowing at velocities below average should be designated as immobile and the remainder mobile. With this assumption, characterization data and statistical models defining conductivity distributions can be used to estimate the mobile fraction θ_m / θ. The vertical scale of heterogeneity most relevant to field-scale plume migration at the Savannah River Site is assumed to be on the order of feet, as opposed to say inches or tens of feet. For this scale of interest, borehole flowmeter tests provide ideal characterization data as the typical resolution is 1-2 ft vertically.

Electromagnetic borehole flowmeter (EBF) testing has been performed at Savannah River Site wells RPC-2PR, RPT-2PW, RPT-30PZ, RPT-3PW, RPC-3PW, SWP-300A, SWP-200C, SWP-100D, DCB-25, P26-M1 and P26-M2 (Phifer, 1996; Boman and others, 1997; Flach and others, 2000a, b). Tables 8 through 18 present the variation in horizontal conductivity relative to the mean value for each well. In some cases, data are analyzed at a second coarser resolution to reduce noise from measurement error. In each table, lower than average permeability intervals are indicated with shading in the graphical depiction. By hypothesis, the remaining above average intervals correspond to the mobile domain. The fraction of intervals assigned by the mobile domain is identified in each table as "Vol. ratio", and the mean thickness of immobile layers is computed by non-weighted and weighted averaging. Table 19 summarizes the results, collectively and segregated by aquifer unit. The overall average mobile volume fraction is computed to be $\theta_m / \theta = 0.32$.

In comparison the optimal mobile porosity for F-area, determined empirically through model calibration, appears to lie within the range of $0.141 < \theta_m < 0.2$ based on cases FD 18 and 22. The equivalent mobile volume fraction is $0.31 < \theta_m / \theta < 0.44$. For H-area the result $0.22 < \theta_m / \theta < 0.31$ based on cases HD 15 and 30 apparently bracketing the optimal result. Hence, the above estimate based on EBF characterization data is consistent with the empirical model calibration results.

Much more extensive borehole flowmeter testing was conducted at the MADE-2 site. Rehfeldt and others (1992) reported a total 2483 estimates of hydraulic conductivity were obtained from 58 wells. Within the area traversed by the tracer plume, conductivity appeared to log-normally distributed, and the variance in natural log conductivity was estimated to be $\sigma^2_{\ln K} = 4.5$. The anisotropy ratio of horizontal to vertical correlation lengths was estimated to be $\lambda_h / \lambda_v = 12.8/1.6 = 8.0$. As discussed at length in Appendix D, the effective conductivity of statistically homogeneous, random, $\ln K$ field can be represented by

$$K_{eff} = e^{\mu + p\sigma^2} = K_g e^{p\sigma^2} \qquad (19)$$

where

K_{eff} = effective conductivity (cf. Sanchez-Vila, 1995)

K_g = geometric mean conductivity

μ = mean of $\ln K$

σ^2 = variance of $\ln K$

p = "power-average" exponent (Desbarats, 1992)

Values of p = +1, 0 and -1, produce arithmetic, geometric and harmonic averages of the K field, respectively. For a three-dimensional $\ln K$ field with an anisotropy ratio of

$\lambda_h / \lambda_v = 8$, the parameter p takes on the value 0.83 (Appendix D), which approaches arithmetic averaging as one would expect for flow parallel to a layered system.

Following the concept applied to SRS EBF data, let the immobile and mobile volume ratios for the MADE-2 site be defined as

$$\theta_{im} / \theta = \phi_{im} = \text{Prob}\left(K < K_{eff}\right) \quad \text{(20a)}$$

$$\theta_m / \theta = \phi_m = 1 - \text{Prob}\left(K < K_{eff}\right) \quad \text{(20b)}$$

The concept is illustrated in Figure 30. Note that the immobile volume fraction is simply the cumulative probability of the conductivity distribution evaluated at the value of effective conductivity. For the MADE-2 statistical distribution inferred by Rehfeldt and others (1992), the result is $\theta_m / \theta = 0.19$ according to the calculation shown in Table 7. As discussed earlier in the report, Harvey and Gorelick (2000) and Feehley and others (2000) independently estimated the optimal ratio of mobile to total volume to be 1/7 and 1/8, respectively. These optimal values are somewhat lower than $0.19 \cong 1/5$. However, Feehley and others (2000) observed from a sensitivity study that mobile volume ratios between 1/8 to 1/4 (0.125 to 0.25) produced very similar results. From this perspective, the estimate of $\theta_m / \theta = 0.19$ is consistent with the literature results derived from empirical model calibration.

The concept of using an effective conductivity estimate in conjunction with a conductivity distribution defined by borehole flowmeter data appears to be a promising approach for estimating mobile volume fraction in field-scale applications. To explore how the mobile fraction might vary with heterogeneity, consider the variation of equation (20b) as a function of $\ln K$ standard deviation as shown in Figure 31 and Table 7. The MADE-2 estimate is plotted as a reference ($\sigma_{\ln K} = \sqrt{4.5} = 2.12$). A dashed line is shown for small variances to indicate the concept apparently breaks down. Approaching zero variance, the conductivity field is becoming homogeneous and relatively immobile water no longer exists. In this case, the mobile fraction should presumably approach 1 instead of 0.5 (cf. Bajracharya and Barry, 1997). Inherent in equations (20) is the assumption that enough heterogeneity is present to produce a relatively stagnant zone. The predicted mobile fraction asymptotically approaches zero for high variances ($\phi_m \to 0$ as $\sigma^2 \to \infty$). A practical upper limit on standard deviation might be roughly 4. A dashed line is shown beyond this point, leaving the useable portion shown by a solid line.

Figure 31 in general, and experience at the MADE-2 and SRS sites in particular, indicate the ratio of mobile to total volume for heterogeneous field-scale settings will typically be much smaller than the range of values reported for laboratory soil columns containing sands and/or aggregated media (cf. Griffioen and others, 1998). A suggested range would be $0.2 < \theta_m / \theta < 0.3$ in the absence of site specific data.

Mass transfer coefficient

A number of researchers have considered idealized conditions in which molecular diffusion through a particular geometry is the mass transfer mechanism between mobile and immobile regions (e.g. Skopp and Warrick, 1974; Sudicky and others, 1985; (according to Brusseau1991: van Genuchten, 1985 Parker and Valocchi, 1986; Brusseau and Rao, 1989b); Brusseau, 1991; Haggerty and Gorelick, 1995; Gerke and van Genuchten, 1996). However, Griffioen and others (1998) have shown from examination of published experimental data that mass transfer in laboratory columns containing sands and/or aggregated media is governed by the mobile phase velocity rather than by molecular diffusion. The mass transfer coefficient was found to be proportional to velocity divided by a characteristic particle size. This suggests that hydrodynamic dispersion dominates inter-region mass transfer for geologic materials even at relatively small scales. Under most field scale conditions involving unconsolidated sediments, molecular diffusion is clearly insignificant compared to dispersion.

As demonstration, consider purely diffusive mass transfer to an immobile region from a surrounding, constant concentration, mobile region. This one-dimensional, transient, mass diffusion problem in the immobile domain can be stated as

$$\begin{aligned} &\frac{\partial^2 C}{\partial x^2} = \frac{1}{D^*}\frac{\partial C}{\partial t} \\ &C(0,t) = C(L,t) = C_\infty \\ &C(x,0) = C_i \end{aligned} \tag{21}$$

An analytical solution is readily available by analogy to plane-wall transient heat conduction (Myers, 1971, section 3.1.1; Appendix E). The corresponding dual-media mass transfer coefficient would be defined by

$$\theta_{im}\frac{\partial \overline{C}}{\partial t} = \zeta(C_\infty - \overline{C}) \tag{22}$$

where

$$\overline{C} = \frac{\int_0^L C\theta_{im} dx}{\theta_{im} L} = \frac{1}{L}\int_0^L C dx \tag{23}$$

Solving equation (22) for ζ and making use of the analytical solution for C in equation (23) and the time derivative yields (Appendix E).

$$\zeta = \frac{\theta_{im} D^*}{L^2} \cdot \frac{\sum_{m=0}^{\infty} e^{-\beta_m^2 \tau}}{\sum_{m=0}^{\infty} \frac{1}{\beta_m{}^2} e^{-\beta_m^2 \tau}} \tag{24}$$

where

$$\beta_m = (2m+1)\pi \tag{25}$$

$$\tau = D^* t / L^2 \tag{26}$$

The mass transfer coefficient as defined by equation (24) is time dependent. In the dual-media model defined by equation (2b), ζ is treated as a constant so diffusion cannot generally be represented by a single first-order mass transfer term. Haggerty and Gorelick (1995) show how an exact representation can be achieved by using a certain distribution of first-order mass transfer terms with constant rate coefficients. Nevertheless, equation (24) can be evaluated at representative times to estimate the magnitude of ζ required to approximate diffusive transport in a time-averaged sense.

Table 21 presents an example calculation for SRS conditions. The characteristic thickness of the immobile region is assumed to be 200 cm (6.6 ft) which is close to the average thickness of low permeability sediment estimated from SRS borehole flowmeter data (Table 19). The mobile volume fraction is taken from the calibrated models of the F- and H-area seepage basins. The diffusion coefficient and tortuosity are taken from de Marsily (1986, p. 233) and Freeze and Cherry (1979, p. 104) respectively. The total porosity is assumed to be 45%. A representative time is assumed to be 10 years. The estimated first-order mass transfer coefficient (0.000011 d^{-1}) is approximately an order of magnitude less than the empirical values determined at F- and H-area (≈ 0.0001 d^{-1}). This rough calculation suggests that purely diffusive transport is an unlikely mechanism for mass transfer between high and low permeability sediment layers.

An entirely different, but more likely, mechanism would be advective transport driven by a component of head gradient normal to sediment layering. The first-order mass transfer coefficient for pure advection can be computed following the same approach used above for pure diffusion. The result is (Appendix F)

$$\zeta = \frac{\theta_{im}}{t_b - t} \qquad (t < t_b) \tag{27}$$

where

$$t_b = \frac{L_{im}\theta_{im}}{U_{im}} \tag{28}$$

is the time required for the contaminant front to break-through the far side of the immobile layer. As before, the mass transfer coefficient defined by equation (27) is time-dependent. A representative calculation for SRS conditions is presented in Table 22. The hydraulic conductivity of the immobile region is assumed to be 10^{-5} cm/s. The normal component of the head gradient is assumed to be 0.01 (dimensionless). The computed equivalent first-order mass transfer coefficient is on the order of 0.0001 d^{-1}, which is similar to the empirical values determined at F- and H-area. Hence, advection normal to sediment layering is a plausible explanation for inter-region mass transfer at field-scale.

While it appears that mobile volume fraction can be reasonably estimated, little more than plausibility arguments can be made for mass transfer coefficient. The mass transfer coefficient depends on several factors including the selection of θ_m, the geometry of immobile water zones, the bulk flow field, and the time scale of plume migration. Experience at MADE-2 and the SRS F- and H-area seepage basins provide the best guidance at this time. The empirical results from these sites suggests $0.0001 < \zeta < 0.001$ d^{-1} as a starting point for field-scale applications. An encouraging observation is that sufficiently small and large values of mass transfer produce single-medium behavior, as discussed earlier. Therefore an analyst need not be concerned about the possibility of unfamiliar behavior occurring from a mass transfer setting that is too low or high.

Summary and conclusions

The dual-media approach to contaminant transport modeling has emerged over the years as a clear improvement over the conventional Fickian advection-dispersion, or single-medium model, in an increasing number of settings. Recent application to the MADE-2 tracer test at Columbus Air Force Base has extended interest to field-scale plume migration in unconsolidated sediments. Subsequent application to tritium migration from the SRS F- and H-area seepage basins within this study also demonstrated improved transport predictions.

Both the single- and dual-media models are capable of reproducing the first-order, bulk behavior of plumes. However, the dual-media formulation reproduces second-order effects better than the conventional ADE, such as the leading and trailing tails of the plume. At the F- and H-area seepage basins, the dual-media model more accurately simulated plume arrival at Fourmile Branch, and plume attenuation from 1988 through 1998. In addition, excessive up-gradient dispersion exhibited by the single-medium model was absent in the dual-media simulations.

Use of the dual-media approach would be most important at sites driven by residual contamination at levels still exceeding regulatory limits (i.e. plume tail). Examples include "old" waste sites where the subsurface has been contaminated for decades and the bulk of the original source has already flushed through the aquifer, and pump-and-treat operations after initial treatment of high permeability zones. In these cases the dual-media approach can be expected to produce significantly different, and potentially more accurate, predictions of plume behavior. Accurate prediction of long-term residual contamination levels could be a critical component of a Monitored Natural Attenuation (MNA) program relying on dispersion and other hydrologic effects as a mechanism for attenuation (e.g. dilute tritium or TCE/PCE plumes).

Beyond technical merits, the dual-media formulation is appealing for SRS regulatory applications because its model complexity, input requirements, and computational demands are similar to single-medium modeling. Compared to high resolution geostatistical modeling, the dual-media approach is deterministic rather than stochastic, far less mathematically complex, and computationally efficient. Also, familiar commercial/ public-domain software offer a dual-media transport capability, such as MT3DMS within GMS.

While promising for SRS regulatory applications, selection of optimal values for dual-media input parameters is a challenge, as field-experience and theoretical study are limited. Empirical model calibration to site-specific plume monitoring data is the most reliable method for determining transport parameters in preparation for future predictions. Lacking historical data, the values of mobile volume fraction and mass transfer coefficient derived for the F- and H-area seepage basins in this study provide guidance for other SRS waste sites. Also, analyses performed in this investigation suggest that mobile volume fraction can reasonably be estimated from borehole flowmeter characterization data and/or known statistical properties of an aquifer system, independent of model calibration. Order of magnitude estimates can made for mass transfer coefficient.

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