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NUREG/CR-4615
LA-10730-MS
Vol. 2

Modeling Study of Solute Transport in the Unsaturated Zone

Workshop Proceedings

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Manuscript Completed: February 1987
Date Published: April 1987

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Prepared for
Division of Waste Management
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555
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Modeling Study of Solute Transport in the Unsaturated Zone

Workshop Proceedings

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Edited by E. P. Springer, H. R. Fuentes

Los Alamos National Laboratory

Prepared for
U.S. Nuclear Regulatory Commission

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PREFACE

Regulations issued by the Nuclear Regulatory Commission, 10 CFR Part 61, require disposal of radioactive waste in unsaturated media above fluctuations in the water table (unless it can be conclusively demonstrated that site characteristics will result in molecular diffusion being the predominant mechanism of radionuclide migration) and that the disposal area is capable of being modeled. The Los Alamos National Laboratory (Los Alamos) has conducted intermediate-scale (large-caisson) studies, the scale between laboratory scale and field scale, to evaluate vertical transport of solutes in unsaturated media.

In validating mathematical models for flow and transport of solutes in porous media, three levels of experimental work are currently used: laboratory columns, large caissons (intermediate scale), and field scale. The large caissons are considered an attempt to observe phenomena at a larger scale than laboratory columns with the expectation of observing larger-scale heterogeneities but maintaining good control of variables and boundary conditions.

The experiments conducted at Los Alamos in large caissons (3-m i.d. x 6 m) to evaluate patterns of solutes migration in unsaturated porous media have provided data bases that can be used to validate state-of-the-art flow and transport models. The data bases contain more information than what is normally available from disposal site selection and characterization studies.

Los Alamos, under sponsorship of the Nuclear Regulatory Commission, conducted a modeling exercise initiated in January 1986. A group of modelers were selected on the basis of the modeling approach, their reputation and credibility, and the extent of use of their models. The individuals and groups who accepted the invitation and their modeling approach were as

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follows:

G. Cederberg

(TRANQL: Hydrogeochemical Numerical Analysis)

C. J. Duffy

(Frequency Domain Analysis)

P. S. Huyakorn

(Three-Dimensional Numerical Analysis)

M. Th. van Genuchten and J. C. Parker

(One-Dimensional Analytical and Semianalytical Solutions)

R. J. Wagenet

(Continuous-Time Markov Process Solution)

An organizational meeting was held at Los Alamos in January to present background information, and to introduce specific objectives to the modelers. The modelers had five months to complete their modeling of the provided data and to present their results in final papers at a workshop to be held on June 18 and 19, 1986, at Los Alamos. The modelers were provided with near-steady-state unsaturated flow information for four tracers, iodine and bromide (conservative tracers) and lithium and strontium (nonconservative tracers). These tracers were applied together in a six-day pulse to a caisson. The information consisted of moisture profiles, base-line chemical data, influent tracer concentrations, soil solution and effluent tracer concentrations, moisture tension and temperature profiles, and outflow.

A panel representing different interests and backgrounds was invited to attend the workshop and to produce a summary paper. The individuals and their affiliation who participated as panelists follow:

A. L. Gutjahr (New Mexico Institute of Mining and Technology)

C. T. Kincaid (Battelle Pacific Northwest Laboratory)

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J. W. Mercer (GeoTrans, Inc.)

I. P. Murarka (Electric Power Research Institute)

M. D. Siegel (Sandia National Laboratory)

P. J. Wierenga (New Mexico State University)

Some of the issues addressed during discussions at the June workshop were adequacy of the data for the various models, effectiveness of the models to represent the data, particular information provided by the models, the role of caisson experiments in providing fundamental knowledge of porous-media water flow and solute transport, and the importance of geochemistry to the transport of nonconservative tracers.

The benefits, besides state-of-the-art modeling evaluation, from this exercise were to provide information on the effectiveness of using controlled caisson experimental data to validate state-of-the-art models, as well as to improve the efficiency of caisson work in providing better tools for regulatory activities. In addition, it was intended to serve as a catalyst for the exchange of information between the nuclear waste community and other groups with similar challenges.

These proceedings include the presentations made by each of the modelers; the summary document written by the panel; and a transcript of the discussions, both the discussions that followed individual presentations and the general discussion held on the second day. This publication completes the series on the workshop. Volume I in the series (NUREG/CR-4615, Vol. I) contains background information and the data sets provided each modeler.

E. P. Springer

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MODELING STUDY OF SOLUTE TRANSPORT IN THE UNSATURATED ZONE

Workshop Proceedings

Edited by

E. P. Springer and H. R. Fuentes

ABSTRACT

These proceedings include the technical papers, a panel summary report, and discussions held at the workshop on Modeling of Solute Transport in the Unsaturated Zone held June 19-20, 1986, at Los Alamos, New Mexico. The central focus of the workshop was the analysis of data collected by Los Alamos under agreement with the U. S. Nuclear Regulatory Commission on intermediate-scale caisson experiments. Five different modeling approaches were used. The purpose was to evaluate models for near-surface waste disposal of low-level radioactive wastes. The workshop was part of a larger study being conducted by Los Alamos on transport in the unsaturated zone under agreement with the U. S. Nuclear Regulatory Commission.

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INTRODUCTION

If the state-of-the-art understanding of those processes that control the fate of contaminants in porous media (saturated or unsaturated) were representative of the complex subsurface reality, the task of predicting the movement of chemicals in the environment would be unchallenging, and the regulatory work would be effective and efficient. This utopian situation seems to be very far away and a satisfactory outcome may not be reached for decades.

In fact, deep gaps in knowledge hinder the efficiency of environmental protection decisions in the field of radioactive, hazardous, and nonhazardous waste disposal, as well as in reclamation of ground and ground waters. A lack of consensus on the best way to quantify hydrodynamic dispersion in porous

material requires suitable experiments to evaluate theoretical expectations for dispersion and to search for peculiarities in the near field. What is considered a difficult challenge in the area of physical processes is only being recognized as a research priority in the area of chemical and biological processes. For instance, the use of the distribution coefficient to represent the interactions of solid media and chemicals has not yet been subjected to a comprehensive evaluation. Much deeper understanding of processes like sorption, oxidation, hydrolysis, and microbial transformations, and their interactions is necessary for both equilibrium and nonequilibrium behavior. Needless to say, the interactions between physical, chemical, and biological processes offer equally comparable challenges to our understanding.

With all these needs, technical assistance studies focus their attention on a variety of experiments at various scales to improve the knowledge of individual or combined processes and to validate various theories through models that are expected to represent phenomena in porous media. The scale problems inherent in bench-scale laboratory experiments have spurred active experimentation at larger scales, namely, intermediate scale (field caissons, and natural subsurface systems), where peculiar physical, chemical, and biological heterogeneities can be more realistically addressed. This range of experimentation offers advantages and disadvantages at all levels, and it is characterized by better control of variables and boundary conditions at laboratory scale and decreased control at larger scales. Undoubtedly, each scale of experimentation plays a key role in improving the understanding of processes and present modeling capabilities.

In sum, a priority need remains for the immediate future to understand phenomena in porous media using various scale levels (from laboratory through field), to develop fundamental concepts, test their validity and application,

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and structure models that can be used for regulatory work in a framework characterized by reasonable handling of the sensitivity, the uncertainty, and the conservative estimates associated with model predictions.

In the modeling exercise reported herein, various approaches to modeling the transport of tracers through unsaturated porous material using data from a caisson experiment are presented and discussed. The caisson experiment was conducted by the Environmental Science Group at Los Alamos National Laboratory. The various modeling approaches represented a cross section of available techniques but by no means are they considered to be exhaustive. By comparing these approaches on a single data set, the reader will see how various complications are considered. Another facet of this effort is that the various modeling groups have different backgrounds in terms of applying their model. A summary report compiled by a panel that represented different interest groups adds another perspective of the study. Finally, discussions of individual presentations and a general discussion are included in transcript form for completeness. Again, various viewpoints are presented enhancing the overall report.

Our intentions were not to discredit nor elevate any particular modeling approach. We wanted to present the state of the art in terms of modeling and experimentation and discuss these in the context of large-caisson experiments.

We want to take this opportunity to thank those who participated in this study.

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ANALYSIS AND PREDICTION OF WATER AND SOLUTE TRANSPORT IN A LARGE LYSIMETER

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INTRODUCTION

Our purpose in this report is to undertake the deterministic description of properties governing water and solute transport for crushed Bandelier Tuff in lysimeter experiments carried out at Los Alamos National Laboratory, New Mexico. Specifically, we will consider experiments performed on compacted crushed tuff in caissons A and B of the experimental cluster described by DePoorter (1981). Our principal objective is to analyze the results of bromide (Br), iodide (I), lithium (Li), and strontium (Sr) tracer experiments performed in caisson B under near-steady flow conditions using selected analytical and numerical solutions of the classical deterministic convection-dispersion equation for steady flow in an assumed uniform velocity field. Although in the present analyses of transport we will treat the flow problem in a simplistic fashion, other studies currently being conducted parallel to this one, as well as anticipated future studies, will require a more rigorous treatment of the hydrologic behavior. Therefore, in addition to the analyses of the caisson B transport experiments, we have undertaken a number of analyses to characterize the hydraulic behavior of crushed Bandelier Tuff from water content and pressure head measurements obtained during transient drainage experiments on material in caisson A and, for some analyses, also employed selected laboratory data.

MODEL DESCRIPTION

Hydraulic Properties

Soil water retention and hydraulic conductivity functions are assumed to be represented by the model of van Genuchten (1980) as

$$\theta = \theta_r + \frac{\theta_s - \theta_r}{(1+|\alpha h|^n)^m} \tag{1}$$

and

$$K = K_s S_e^{\ell} [1 - (1 - S_e^{1/m})^m]^2, \tag{2}$$

where θ is the volumetric water content; θ_r and θ_s are residual and field-saturated water contents, h is the pressure head; α, ℓ, and n are empirical shape factors: m = 1-1/n; K_s is the field-saturated hydraulic conductivity; and S_e is effective fluid saturation defined by

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}. \tag{3}$$

Various methods of estimating the parameters K_s, θ_s, θ_r, α, n, and ℓ to describe the hydraulic properties of crushed Bandelier Tuff used in the caisson tracer experiments will be considered subsequently.

Transport Studies

Solute transport during steady state flow is described in this study by the one-dimensional deterministic convection-dispersion equation

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial s}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x}, \tag{4}$$

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where C is the solute concentration, s is the adsorbed concentration, D is the dispersion coefficient, ρ is the bulk density, θ is the water content, $v = q/\theta$ is the pore water velocity where q is the hydraulic flux density, x is distance, and t is time. Equilibrium adsorbed and solute concentrations are related by a Freundlich-type isotherm of the form

$$s = kC^{\eta}, \tag{5}$$

where k and η are empirical parameters. Assuming local equilibrium conditions exist, substitution of (5) into (4) yields

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

in which the nonlinear retardation factor R is given by

$$R = 1 + \rho k\eta C^{\eta-1}/\theta. \tag{7}$$

For linear adsorption, $\eta = 1$ and R becomes independent of concentration:

$$R = 1 + \rho k/\theta. \tag{8}$$

The parameter k in (8) is often referred to as the distribution coefficient K_d.

Equation (6) is solved subject to a uniform initial concentration C_i and a pulse-type boundary condition at the soil surface:

$$\left(-D\,\frac{\partial C}{\partial x} + vC\right)\Big|_{x=0} = \begin{cases} vC_o & 0 \le t < t_o \\ o & t \ge t_o \end{cases}, \qquad (9)$$

where C_o is the input concentration and t_o is the solute pulse duration. Assuming a semi-infinite profile ($0 \le x < \infty$), linear adsorption ($\eta = 1$), and solute detection in flux concentration mode [$c_f = c-(D/v)\ \partial c/\partial x$; see Parker and van Genuchten 1984a], the appropriate analytical solution to (6) subject to (9) is

$$C_f(x,t) = \begin{cases} C_o\ A(x,t) & 0 \le t < t_o \\ C_o\ A(x,t) - C_o\ A(x,t-t_o) & t \ge t_o \end{cases}, \qquad (10a)$$

where

$$A(x,t) = \frac{1}{2}\,\mathrm{erfc}\left[\frac{Rx - vt}{2(DRt)^{1/2}}\right] + \frac{1}{2}\exp\left[\frac{vx}{D}\right]\mathrm{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right]. \qquad (10b)$$

Equation (10) assumes that observed concentrations represent flux-averaged concentrations rather than volume-averaged resident concentrations. Observed concentrations determined in suction samplers may correspond precisely to neither flux nor resident concentrations; however, because of the generally small values of the dimensionless groups (vx/D) obtained in this study, differences between the two concentration modes should be extremely small (Parker and van Genuchten 1984a) so the distinction need not be of concern.

For cases of nonlinear adsorption, we solve (6) with an iterative numerical method based on a Crank-Nicolson-type finite difference formulation of the governing equations.

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METHODS OF ANALYSIS

Hydraulic Properties

Two parameter estimation methods employing different objective functions and input data were used to quantify the parameters in the hydraulic model described by Equations (1) and (2) for crushed Bandelier Tuff. In Method 1, K_s, θ_r, α, and n are estimated from water content and pressure head observations in caisson A during a transient drainage experiment (Abeele 1984). The average water content after ponding for more than one month provided an independent estimate for θ_s of 0.331. From Mualem (1976), the coefficient ℓ in Equation (2) was assumed to be 0.5, thus leaving four unknown coefficients including the saturated conductivity. Abeele (1984) estimated the latter to be about 12.4 cm/d from the steady state lysimeter drainage rate: however, owing to uncertainty in the parametric model near the transition from saturated to unsaturated conditions as well as to experimental uncertainties, we regard K_s to be an unknown in the present analysis.

The unknown parameters were estimated from measured water contents at 6 depths (0.4, 1.16, 1.91, 2.71, 3.47, and 4.23 m) and measured pressure heads at only one depth (0.4 m) observed over a period of 100 days as the caisson drained from saturation subject to a zero surface flux. The inverse problem was solved by combining a numerical solution of the one-dimensional unsaturated flow equation with a nonlinear least-squares optimization scheme based on the Levenberg-Marquardt method (Marquardt 1963). The unsaturated flow equation was taken as

$$C(h)\ \frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\ [K(h)\ \frac{\partial h}{\partial x} - K(h)], \qquad (11)$$

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where $C(h) = d\theta/dh$ is the soil water capacity, x is depth from the soil surface, and t is time.

The optimization program used in this study is a modification of the code of Kool et al. (1985). In this model, Equation (11) is solved with a fully implicit, Galerkin-type, mass-lumped linear finite element scheme. This scheme has proved to be considerably more efficient than the previously employed Hermitian cubic scheme. The objective function O(b) to be minimized was taken to be of the form

$$O(b) = \sum_{i=1}^{m} \sum_{j=1}^{p} [\theta_{ij}^{*} - \theta_{ij}(b)]^2 + \sum_{j=1}^{p} W[h_j^{*} - h_j(b)]^2, \quad (12)$$

where θ_{ij}^{*} represents measured water contents at m = 5 depths x_i and p = 6 times t_j: h_j^{*} is the measured pressure head at x = 0.4 m and times t_j: and $\theta_{ij}(b)$ and $h_j(b)$ are model-predicted θ and h corresponding to parameter vector $b = (\alpha, \theta_r, n, K_s)$. The weighting coefficient W was chosen such that the two composite terms of (12) attain roughly the same value (Parker et al. 1985).

The unknown parameters in Equations (1) and (2) were also estimated directly (Method 2) from the reported $\theta(h)$ and K(h) data listed in Table III of Abeele (1984). To obtain better resolution at relatively low water contents, we augmented the caisson data with laboratory-measured data for $h \leq -300$ cm from an earlier study by Abeele (1979). The objective function in Method 2 was taken to be

$$O(b) = \sum_{i=1}^{M} [\theta_i^{*} - \theta_i(b)]^2 + \sum_{j=1}^{N} V[\log(K_j^{*}) - \log(K_j(b))]^2, \quad (13)$$

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where θ_i^* and $\theta_i(b)$ are observed and predicted water contents at M pressure heads, K_j^* and $K_j(b)$ are observed and predicted conductivities at N heads, and V is a weighting factor that ensures roughly equal values of the two terms of (13). Two different analyses with Method 2 were performed with different unknown parameter vectors b. In Method 2a all six parameters (θ_r, θ_s, α, n, ℓ, K_s) were treated as unknown, while in Method 2b θ_s and K_s were fixed at their measured values and only θ_r, α, n, and ℓ were estimated.

Transport Studies

Observed concentration data in caisson B were analyzed using the CXTFIT program of Parker and van Genuchten (1984b). Subject to a few restrictions, this program can be used to optimize the unknown coefficients v, D, R, and t_o in Equations (6) and (9) from observed temporal and spatial concentration data. One restriction is that v and R cannot be optimized simultaneously because of similar effects on the effective transport rate v/R in the soil column. We assumed that iodide and bromide were not adsorbed on, nor excluded from, the solid phase, resulting in R=1. Table 1 lists all measured or independently estimated parameter values and indicates those parameters that were treated as unknowns in the parameter estimation process. For the iodide and bromide displacement experiments, the parameters v, D, and t_o were treated as unknowns, whereas R was taken to be unity with no adsorption. Similarly, the parameters D, R, and t_o were considered unknowns for the lithium tracer experiments, while v was fixed at 11.7 cm/d as estimated from the iodide and bromide data (to be discussed later). To simulate strontium transport, nonlinearity in the adsorption behavior was explicitly considered. From Polzer et al. (1985), the Freundlich exponent η for Sr was taken to be 0.835. Values for v and D

were assumed to be the same as those in the iodide and bromide experiments. Since independent estimates for θ, ρ, and t_o were also available, the only unknown parameter that remained to be estimated from the tracer experiments was the Freudlich k-value in Equation (5), which was obtained by matching observed and predicted concentrations during initial breakthrough.

Table 1. Assumed unknown parameters (indicated by "?") and measured data (indicated by value) for the iodide, bromide, lithium, and strontium tracer experiments.

Parameter	Iodide	Bromide	Lithium	Strontium
θ (cm^3/cm^3)	-[a]	-	0.28	0.28
ρ (g/cm^3)	-	-	1.60	1.60
C_i (mg/L)	0.2	0.0	0.04	0.2
C_o (mg/L)	170.0	79.0	6.80	70.0
v (cm/d)	?	?	11.70[b]	11.70[b]
D (cm^2/d)	?	?	?	4.72[c]
t_o (days)	?	?	?	6.0
R	1.0	1.0	?	?
k ($\mu g^{1-\eta} cm^{3\eta} g^{-1}$)	-	-	-	?
η	-	-	1.0	0.835

[a] Not needed in estimation process.

[b] Estimated from iodide and bromide experiments.

[c] Estimated from iodide, bromide, and lithium experiments.

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RESULTS AND DISCUSSION

Hydraulic Properties

Values for parameters in the soil hydraulic functions [Equations (1) and (2)] estimated by Methods 1, 2a, and 2b are given in Table 2. Figure 1 compares the fitted retention and hydraulic conductivity curves of Method 2a with the laboratory and caisson-derived data of Abeele (1979, 1984). The estimated curves for Method 1 are not shown on the figure but nearly duplicate the calculated curves for Method 2a, even though some of the parameter values for Method 1 were quite different (notably ℓ). Small deviations occurred at lower water contents because of the difference in estimated θ_r values (Table 2) and at the higher water contents because of somewhat different K_s estimates. Note the relatively wide 95% confidence limits on K_s in Table 2 for both methods, indicating poor identifiability of K_s.

Figure 2 compares observed water content distributions in the caisson after 1, 4, 20, and 100 days (Abeele 1984) with the predicted curves using parameter estimates from Method 1 (dashed lines) and Method 2a (solid lines). Predictions were obtained by assuming that the tuff and underlying sand layer had the same hydraulic properties. The bottom boundary of the sand layer at the interface with the underlying gravel was maintained at saturation (h=0), while a no-flux condition was imposed at the soil surface. Note that the observed data are underpredicted after 1 day of drainage but are predicted very well at all other times, with Method 1 parameters generating somewhat higher water contents than those obtained with Method 2a parameters. Deviations between computed and observed distributions at 1 day are likely due to the high estimated K_s values. Abeele (1984) estimated K_s to be only about 12.4 cm/d, which would result

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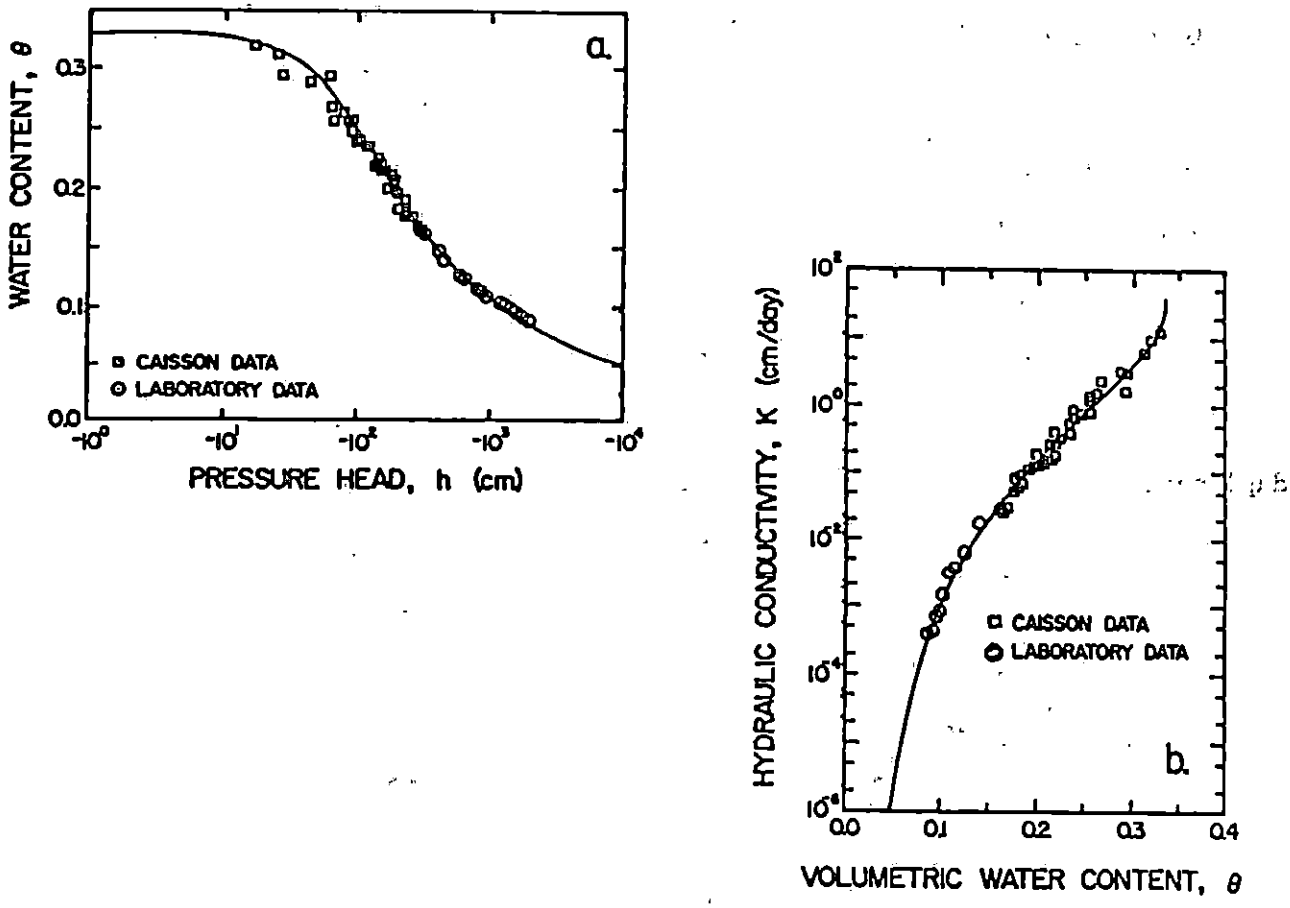

Figure 1. Measured hydraulic properties of crushed Bandelier Tuff (data points) and model-predicted properties using Method 2a parameter estimates (smooth curves).

in high predicted water contents at one day. This is shown in Figure 3 where predicted water contents using Method 2b hydraulic parameters are compared with the observed data. While predicted water contents at 1 day in this case are larger than those shown in Figure 2, drainage at later times proceeds too slowly and causes the water contents to remain high, notably at intermediate times. We conclude that the Method 1 or 2a parameters are the preferred ones for most calculations, except for near-saturated conditions.

Table 2. Parameters in Equations (1) and (2) for Bandelier Tuff estimated from in situ drainage data (Method 1) and from previously measured hydraulic data (Method 2).

Parameter	Method 1	Method 2a	Method 2b
θ_r	0.01[a]	0.0255 (±0.0185)[b]	0.0451 (±0.0066)
θ_s	0.3308[c]	0.3320 (±0.0059)	0.3308[c]
α (cm^{-1})	0.01433 (±0.0030)	0.01545 (±0.0022)	0.01339 (±0.0090)
n	1.506 (±0.105)	1.474 (±0.744)	1.636 (±0.0438)
ℓ	0.5[c]	0.4946 (±0.3713)	-1.129 (±0.2575)
K_s (cm/d)	25.0 (±12.6)	33.71 (±16.92)	12.4[c]

[a] Converging towards negative value; set to zero during estimation process.

[b] Values in parentheses indicate 95% confidence limits.

[c] Assumed to be known.

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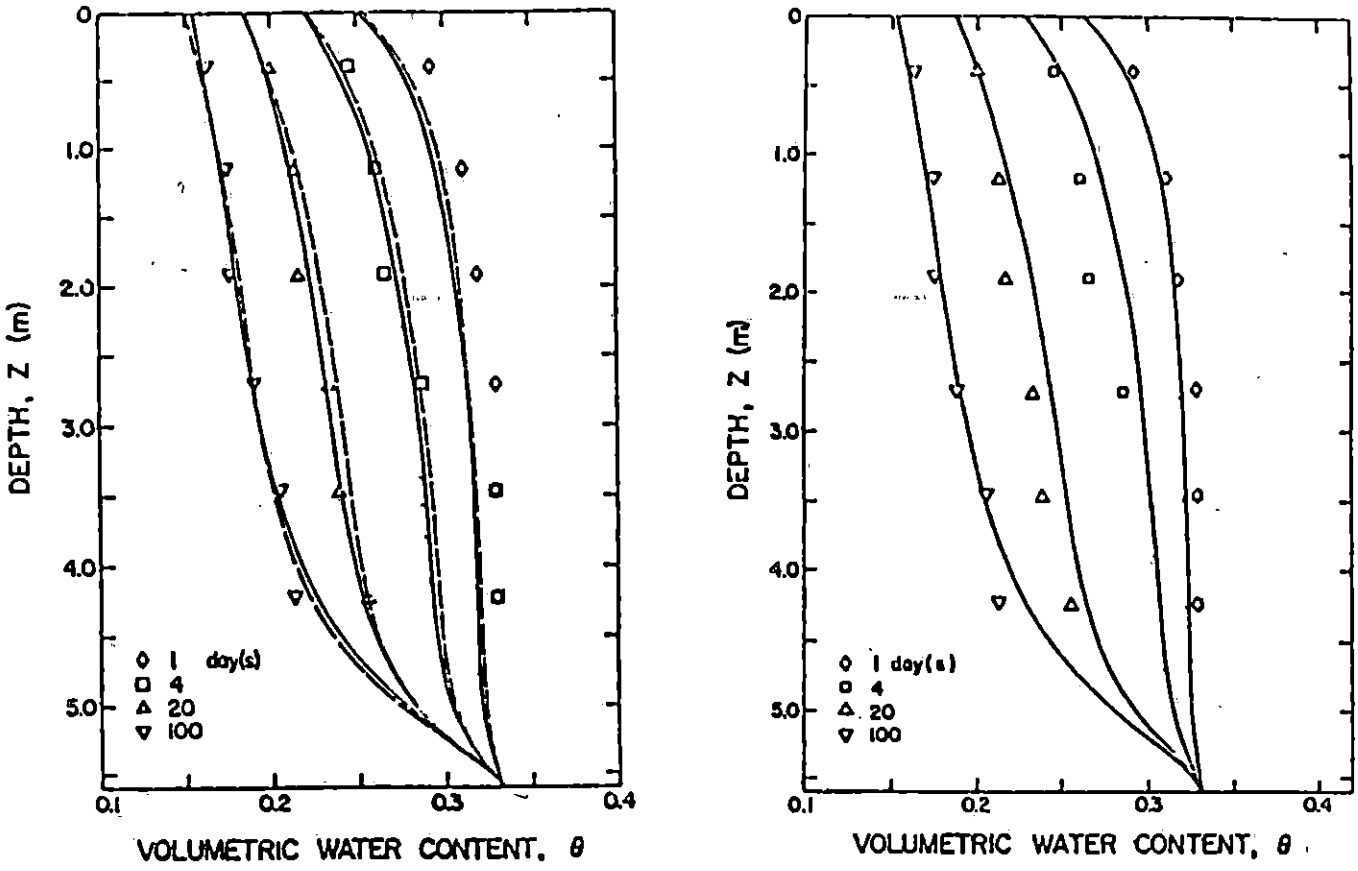

Figure 2. Measured water content profiles at different times during transient drainage under zero-flux surface condition in caisson A (data points) and predicted distributions using Method 1 parameters (a, dashed lines), Method 2a parameters (a, solid lines), and Method 2b parameters (b, solid lines).

Transport Studies

Observed tracer breakthrough curves obtained with hollow fiber suction samplers at six depths are shown in Figures 3 and 4 for bromide and iodide, respectively. All data considered here are for the tracer pulses begun on December 6, 1984, under approximately steady flow conditions. Each depth was first analyzed individually to find optimal values for v, D, and t_o assuming R = 1; these results are summarized in Table 3. For both tracers the first depth shows a relatively large D-value, probably as a consequence of the uneven application of water and tracers at the soil surface through multiple point sources. Values of v and D at this depth are relatively poorly defined as reflected by large 95% confidence intervals. As the tracers move downwards, the estimated parameters, in particular the pore water velocity, become better defined. The fitted value for t_o is in most cases significantly less than the target value of six days. Because of this discrepancy, we elected to keep t_o as an unknown parameter in this study. Note also that the peak concentrations of the 36- and 113-cm-depth observed bromide breakthrough curves are much higher than the input concentration C_o. Too few input concentration measurements were carried out during the six day pulse application to verify the accuracy of C_o. Since we are assuming C_o is known, any error in this value will effectively be accommodated by adjusting t_o to obtain apparent mass balance.

The data in Table 3 also reveal much higher fitted v-values for iodide and bromide at the 264-cm-depth port compared with the other depths. Vertical variations in the pore water velocity, due for example to differences in compaction, might be suggested as a possible explanation of this behavior. If the average pore water velocity between 0 and 188 cm is taken to be about 12.6 cm/d (see the 188-cm data in Table 3), then an

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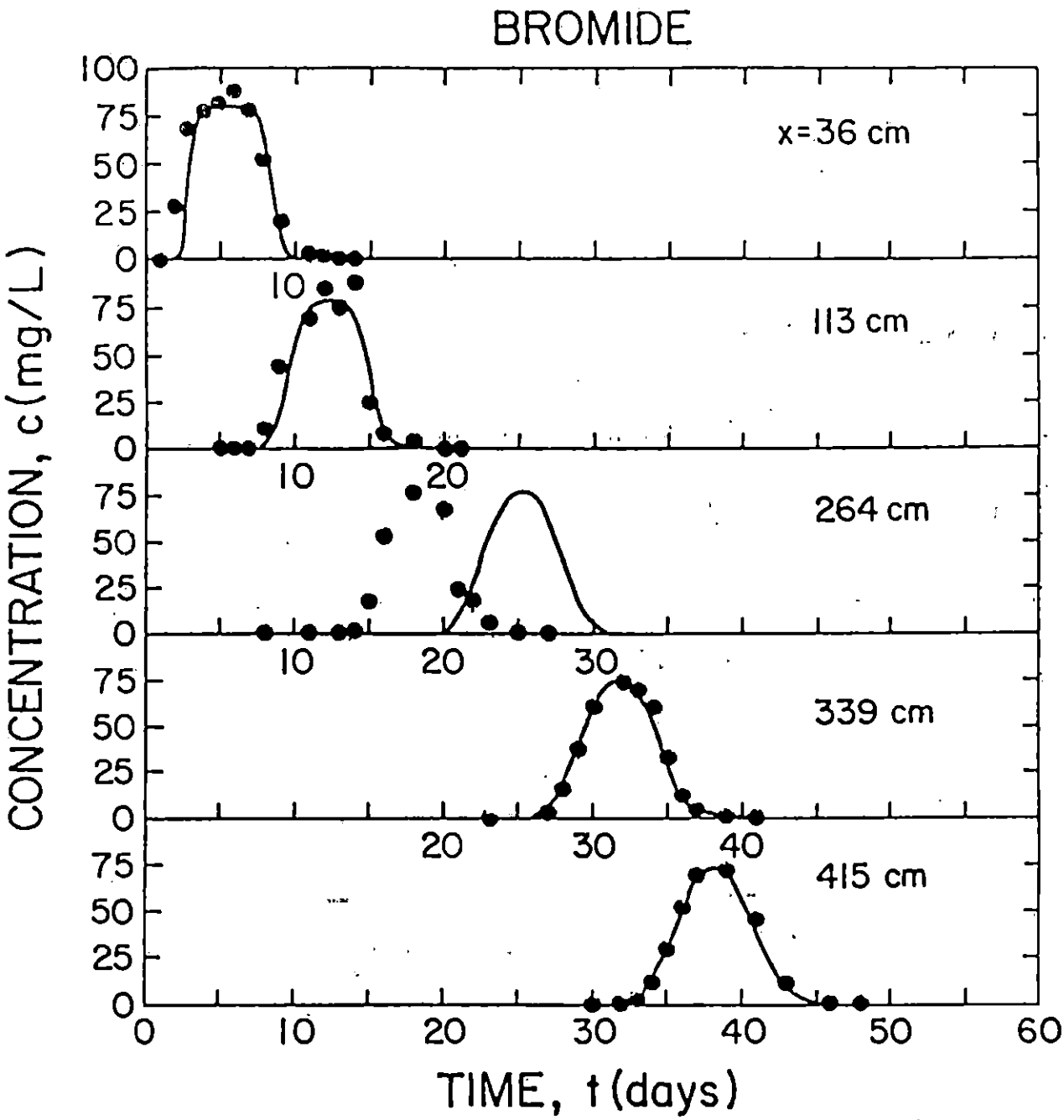

Figure 3. Bromide breakthrough curves measured at various depths in hollow fiber samplers and predicted curves using parameter values estimated from pooled iodide, bromide, and lithium data.

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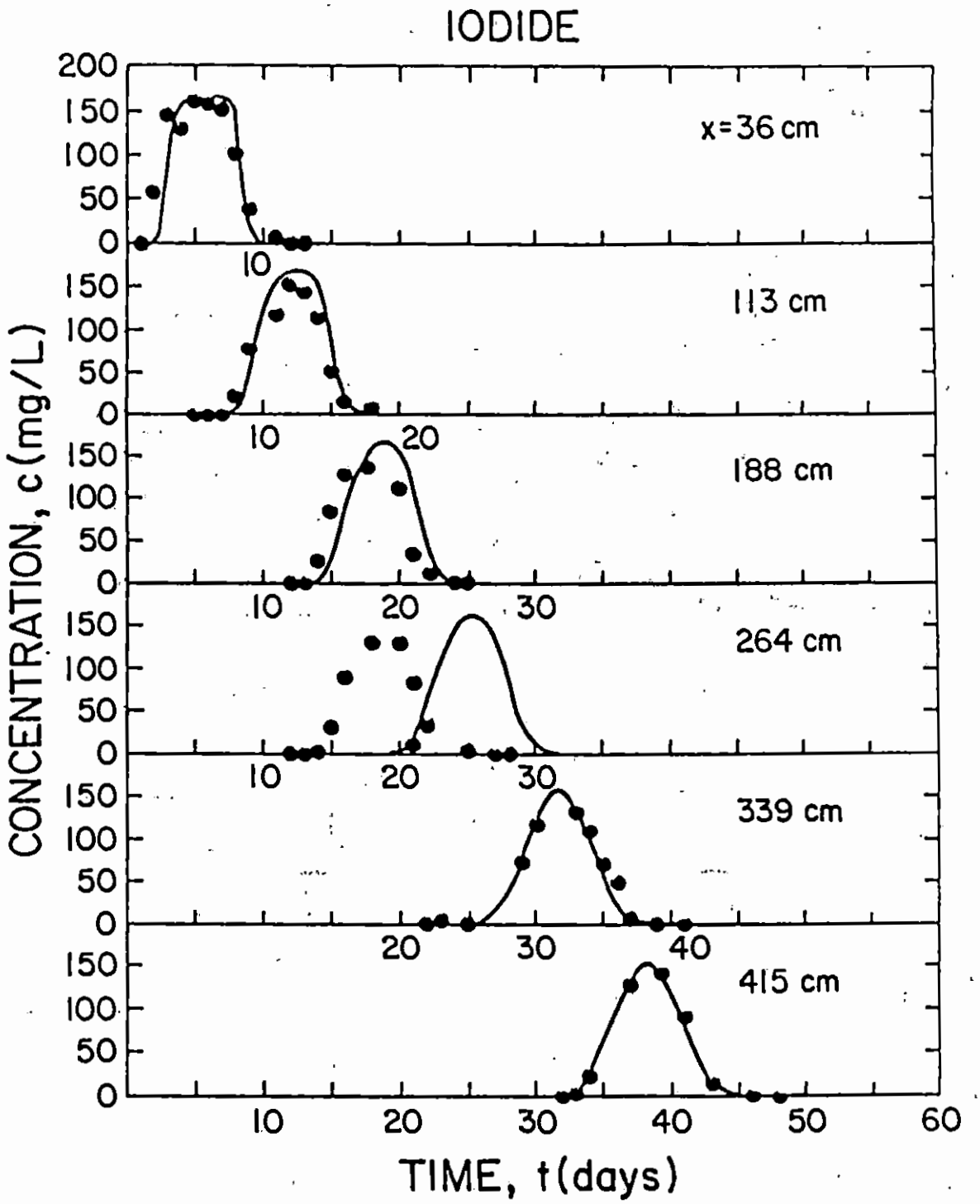

Figure 4. Iodide breakthrough curves measured at various depths in hollow fiber samplers and predicted curves using parameter values estimated from pooled iodide, bromide, and lithium data.

Table 3. Estimated values for the pore water velocity v, the dispersion coefficient D, and the pulse time t_o, for the iodide and bromide experiment in caisson B, assuming R=1 for both tracers.

Depth (cm)	v (cm/d)	D cm^2/d)	t_o (day)
	IODIDE		
36	14.45 (±1.33)[a]	53.07 (±28.37)	5.93 (±0.31)
113	11.88 (±0.36)	15.93 (± 5.07)	5.06 (±0.36)
188	12.44 (±0.15)	6.87 (± 2.53)	5.23 (±0.27)
188[b]	12.80 (±0.14)	11.06 (± 2.62)	4.98 (±0.25)
264	16.38 (±0.46)	14.47 (± 9.42)	4.45 (±0.55)
339	11.58 (±0.04)	5.89 (± 0.79)	5.36 (±0.13)
415	11.58 (±0.03)	4.90 (± 0.39)	5.34 (±0.12)
all data[c]	11.74 (±0.14)	11.29 (± 3.09)	5.11 (±0.22)
	BROMIDE		
36	15.38 (±0.85)	30.94 (±12.23)	6.09 (±0.17)
113[d]	12.57 (-)	0.0 (-)	5.96 (-)
264	16.83 (±0.20)	8.05 (± 3.38)	5.09 (±0.25)
339	11.66 (±0.03)	3.98 (± 0.41)	5.72 (±0.09)
415	11.71 (±0.02)	4.09 (± 0.33)	5.90 (±0.09)
all data[e]	11.66 (±0.10)	5.92 (± 1.91)	5.39 (±0.20)

[a]Values in parentheses represent 95% confidence limits for parameter estimates.

[b]Teflon cup data; all others hollow fiber samplers.

[c]Simultaneous fit to all data except the 188-cm Teflon cup data and the 64-cm depth data.

[d]Best estimates; optimization program failed to converge.

[e]Simultaneous fit to all bromide data, except those of the 264-cm depth.

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effective tracer velocity of about 65 cm/d is needed between 188 and 264 cm to give an average v of 14.6 between 0 and 264 cm. This value of 65 cm/day is unrealistically high. Therefore, it seems more likely that the pore water velocity varies significantly horizontally across the caisson and that the 264-cm depth sampler is located in a section of markedly higher hydraulic flux. All of the samplers except the 188- and 264-cm depth hollow fiber units were placed in the left hemisphere of the caisson. Since neither the Teflon sampler in the left hemisphere at the 188-cm depth nor the hollow fiber sampler in the right hemisphere at 188-cm exhibit the apparent high velocity of the 264-cm depth sampler, it must be concluded that the flow path for the fast zone is rather tortuous and not strictly vertical.

The anomalous behavior of the 264-cm depth data may be further elucidated by investigating the behavior of the effluent breakthrough curves for leachate collected from the column exit. Only iodide was measured with sufficient frequency in the effluent to warrant analysis. Observed iodide effluent concentration data are shown in Figure 5. Inspection of these data indicates two distinct peaks suggesting zones in the porous medium moving at two distinctly different velocities. To analyze the data we make the simple and expedient assumption that two flow regions exist which interact negligibly so that the observed effluent concentration C_e is given by

$$C_e = \frac{\sum_{i=1}^{2} A_i q_i c_i}{\sum_{i=1}^{2} A_i q_i} \qquad (14a)$$

$$= \frac{\sum_{i=1}^{2} A_{ri} v_i c_i}{\sum_{i=1}^{2} A_{ri} v_i} \qquad (14b)$$

where A_i is the proportional area of region i with hydraulic flux density q_i from which the local exit concentration is c_i, v_i is the pore water velocity in region i, and $A_{ri} = A_i \theta_i$ is the effective hydraulic area where θ_i is the water content in region i. We take $c_i = c_i(x,t;v_i,D_i,t_o,C_i,C_o)$, fix C_i and C_o at their previous values, and estimate v_i, D_i and A_{ri} (i=1,2) and t_o by nonlinear regression analysis of the observed effluent data against (14) with c_i computed via (10). An effective column length of 570 cm was employed assuming the tuff and underlying 25-cm thick sand layer to

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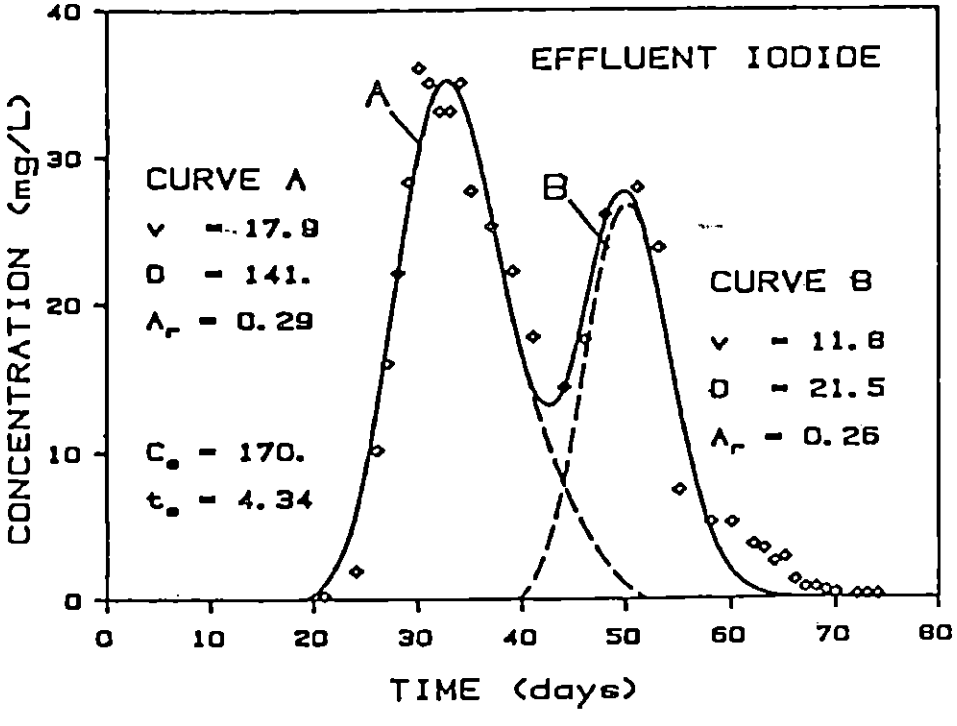

Figure 5. Observed iodide concentrations in effluent from caisson B and fitted curves, assuming two distinct and noninteracting flow regions with different pore water velocities and cross-sectional areas.

have similar properties and the resident time in the lower gravel layer to be insignificant. The results are given in Figure 5. The two apparent flow regions are found to have velocities of 17.9 and 11.8 cm/d corresponding very closely to velocities observed in suction samplers at the 264-cm depth and at the other depths, respectively. The results indicate the effective hydraulic cross-sectional areas of the two regions are nearly equal (A_r=0.29 for the fast zone and 0.26 for the slower zone). In order to elucidate the mechanisms underlying this heterogeneity in the flow field, more detailed spatial resolution of concentrations, water contents, and hydraulic fluxes would be needed.

A simultaneous fit of v, D, and t_o to suction sampler data from all depths, excluding that from the anomalous 264-cm depth and from the 188-cm Teflon sampler (all other data were obtained with hollow fiber samplers), was carried out for iodide and bromide and results are summarized in Table 3. Note that the fitted velocities for iodide and bromide are very similar. Thus, we conclude that the average pore water velocity of 11.7 cm/d estimated from the iodide and bromide tracers is representative of the hydraulic conditions experienced by the majority of the samplers and that this value should be applicable also for the lithium and strontium experiments. As expected, the simultaneously fitted D-values for iodide and bromide are somewhat higher than those for the individual depths because of small differences in local v-values. We also note that the fitted D-values in Table 3 do not indicate any increases with depth due to scale effects. The reverse effect is in fact observed, with D generally decreasing with depth reflecting, as previously suggested, the gradual amelioration in point-source application effects at greater distances. Dispersion coefficients for the iodide effluent data, however, are

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considerably higher than for the suction sampler data even without the high flow zone. This is not an unexpected result, since the effluent data reflects heterogenieties over the caisson cross section, whereas suction samples provide a rather localized perspective on the medium.

Using the measured hydraulic flux density of 4.0 cm/d from caisson outflow rate measurements and the estimated average pore water velocity of 11.7 cm/d fitted to the pooled suction sampler data (Tables 3 and 4), we may estimate the effective water content of caisson B during the tracer experiments to be 0.34 cm^3/cm^3. This is greater than the water content measured in the caisson by neutron backscatter, which averaged about 0.28 cm^3/cm^3. If we estimate the mean pore water velocity for the caisson from the iodide effluent data (Figure 5), an area-weighted average of 15 cm/d is obtained corresponding to a water content of 0.27 cm^3/cm^3 which is clearly in better agreement with the observed water contents and thus gives further credence to the postulation of a bimodal velocity distribution.

Observed lithium concentration data for each depth are shown in Figure 6. Individual depth-fitted as well as pooled depth-fitted parameter values of the estimated parameters R, D, and t_o are given in Table 4. Note that the pooled depth-fitted R is 1.18, indicating a small amount of lithium adsorption.

Inspection of the data in Tables 3 and 4 reveals relatively large differences in D for the different ports. In part this may be due to somewhat poor identifiability of D, as evidenced by the relatively wide 95% confidence intervals, especially for the lithium data. The average of the D-values of iodide and bromide at 339- and 415-cm depths is 4.72 cm^2/d. This value is well within the 95% confidence range for the lithium data.

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Because D-values at greater depths also partially reflect transport properties of the soil medium closer to the soil surface, we chose to fix D at the above-average value of 4.72 cm^2/d independently of depth or tracer to simulate all suction sampler data. Given this estimate for D, the previously estimated value for v of 11.7 cm/d, and a mean value for t_o of 5.43 d derived from all fitted pulse times in Tables 3 and 4, the sampler breakthrough curves for iodide, bromide, and lithium can be calculated.

Table 4. Estimated values for the dispersion coefficient D, the retardation factor R, and the pulse time t_o for the lithium experiments in caisson B assuming v=11.7 cm/d.

Depth (cm)	D (cm^2/d)	R (-)	t_o (d)
36	27.50 (±24.34)	0.789 (±0.102)	6.42 (±0.41)
113	10.57 (±5.73)	1.133 (±0.039)	5.46 (±0.55)
188	9.96 (±3.52)	1.138 (±0.024)	5.44 (±0.52)
188[a]	5.96 (±3.11)	1.070 (±0.025)	5.33 (±0.50)
264[b]	14.80 (±5.18)	0.844 (±0.018)	5.24 (±0.59)
264[c]	20.99 (±7.35)	1.197 (±0.026)	5.24 (±0.59)
415	8.69 (±5.40)	1.227 (±0.025)	4.89 (±1.04)
all data[d]	12.58 (±5.43)	1.180 (±0.027)	5.25 (±0.42)

a Teflon cup data.

b Assuming v=11.7 cm/d.

c Assuming v=16.6 cm/d.

d Simultaneous fit to all observations except the 188-cm teflon cup data and the 264-cm-depth data.

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Results are shown as the solid lines Figures 3, 4, and 6. The observed data are fairly well described at all depths except at 264 cm where the previously noted fast flow zone was observed.

To predict strontium transport, we employed the values for v and D estimated from the pooled iodide, bromide, and lithium data and independently estimated values of all other parameters except the Freundlich coefficients k. The last of these was estimated from the initial breakthrough part of the 188-cm hollow fiber sampling data to be 1.486 in units consistent with those of c (mg/L) and s(mg/g). Observed and calculated breakthrough curves for all depths are shown in Figure 7. The observed data, especially the peak concentrations, at different depths are extremely erratic and inconsistent. Despite these inconsistencies, the assumed parameters lead to surprisingly accurate predictions of initial breakthrough at most depths, except again for the 264-cm port. Peak concentrations are accurately described in only one or two cases (at 188 and 339 cm), with severe deviations occurring at the 36-, 113- and 264-cm depth ports. Poor apparent mass balance is obtained at several depths.

The exact reasons for this behavior are not clear. Strontium adsorption on the samplers might be suggested as an explanation, except that two of the hollow fiber samplers do show reasonable mass balances. Another explanation could be that local compaction of soil around the samplers results in stagnant liquid zones in which transport is controlled largely by diffusion. While immobile water zones can have marked effects on transport of strongly adsorbed tracers (van Genuchten 1985), we tend to discount mobile-immobile effects in this case for two reasons. First, there is not evidence of similar behavior for the iodide, bromide, and

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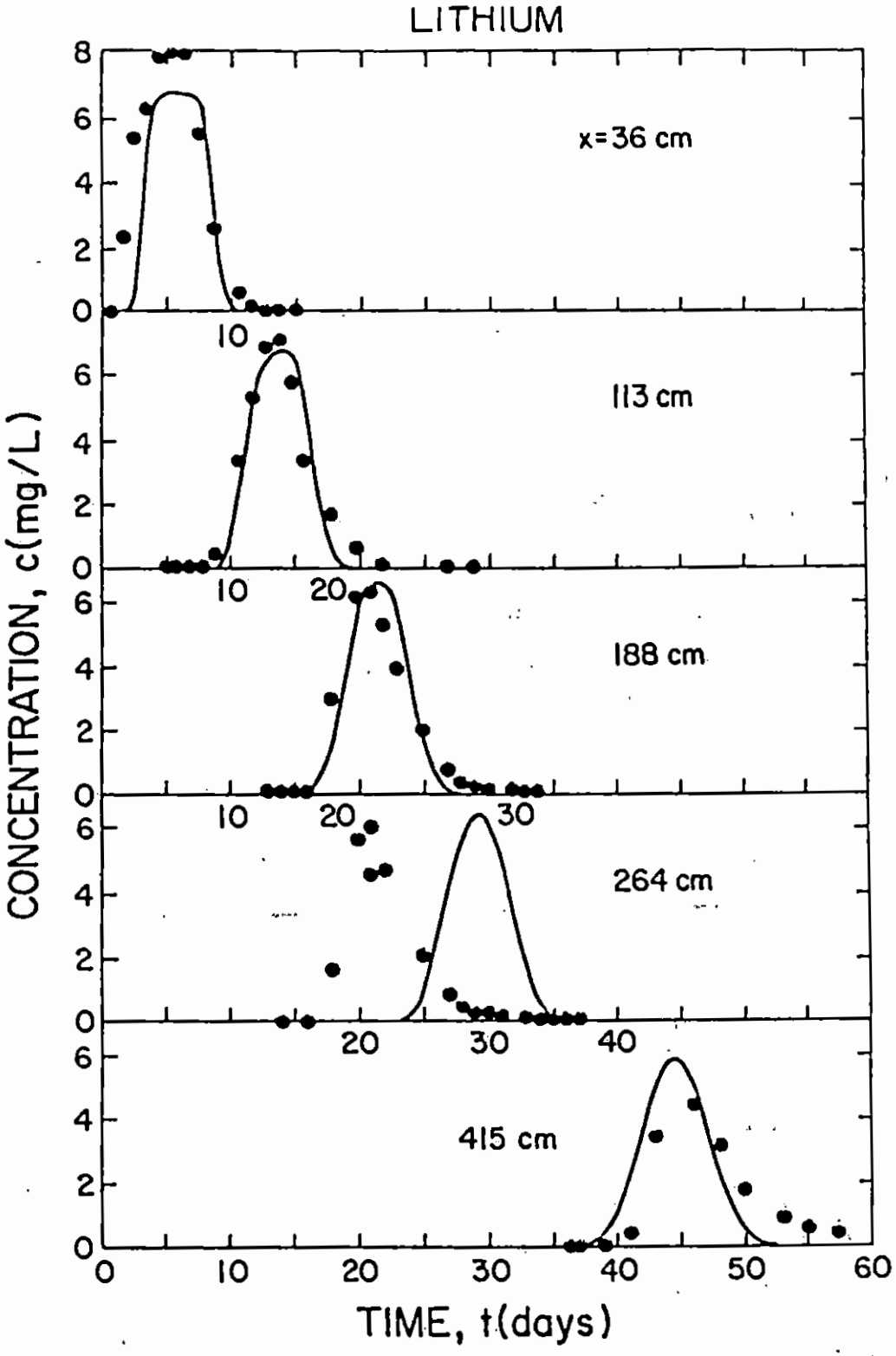

Figure 6. Lithium breakthrough curves measured at various depths in hollow fiber samplers and predicted curves using parameter values estimated from pooled iodide, bromide, and lithium data.

lithium tracer data. Minor tailing in the lithium breakthrough curves could have been caused by immobile water but also by some nonlinear adsorption effects (data are insufficient to draw definite conclusions). Second, if immobile zones were present, the observed breakthrough curves should have been displaced to the right of those in Figure 7 because of the slow diffusional processes. This is clearly not the case as the initial breakthrough at all depths (except at 264 cm) are reasonably well described.

A more probable explanation for the observed behavior of strontium is that the precipitation of $SrCO_3$, either in situ or in the solution samples after extraction from the caisson has occurred, results in apparent erratic mass balance. This explanation seems especially probable because of the high pH (approximately 8) and low temperatures (approximately 5°C) in the caisson during the experiment, which would favor the stability of $SrCO_3$. Furthermore, the fact that the tuff was crushed may have increased the potential for weathering and the possible release of additional alkalinity into the soil solution.....Tentative calculations based on measured chemical data suggest that the soil solution may have been supersaturated with respect to $SrCO_3$. Degassing of the extracted soil solution during sampling may have promoted even higher pH-values and thus further increased the likelihood of $SrCO_3$ precipitation (Suarez 1986a), which could lead to erratic apparent solution concentrations. The use of extractors that limit or prevent degassing (Suarez 1986b) should be considered in similar studies that may be conducted in the future if strontium is employed as a tracer.

From the fitted k-value of 1.486 and the estimated η-value of 0.835 (Polzer et al. 1985), we obtain the following Freundlich isotherm for strontium adsorption on Bandelier Tuff:

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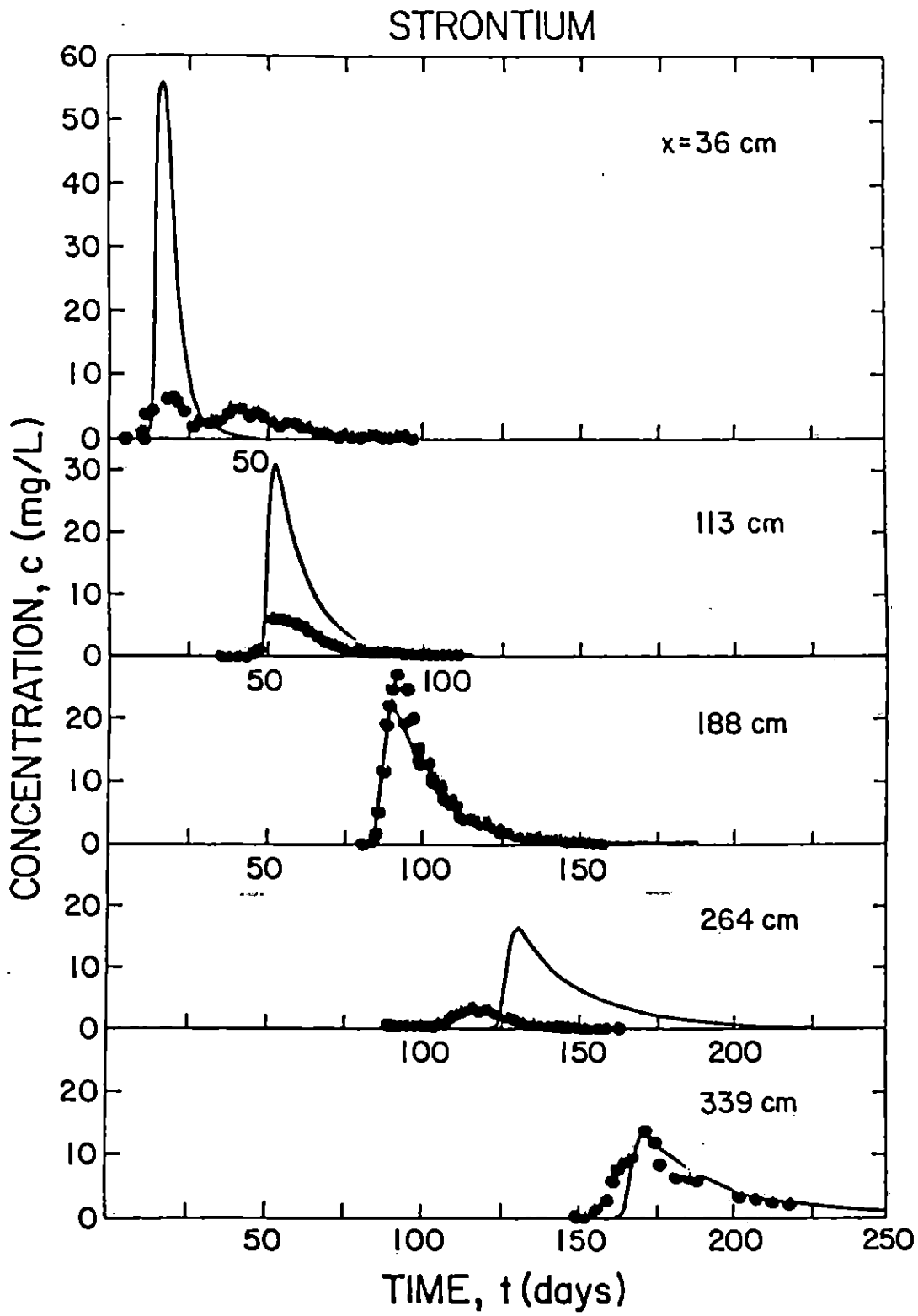

Figure 7. Strontium breakthrough curves measured at various depths in hollow fiber samplers and predicted curves using estimated parameter values.

$$s = 1.486\ C^{0.835}. \qquad (15)$$

This equation can be linearized in several ways. One way is to assume that the areas under the linearized isotherm ($s=k_dC$) and the nonlinear isotherm are the same for the range in concentration values used in the displacement experiment (van Genuchten 1981):

$$\int_0^{c_a} k_dC\ dC = \int_0^{c_a} 1.486\ C^{0.835} dC\ . \qquad (16)$$

Assuming an average peak concentration c_a of 50 mg/L during the leaching experiment results in a k_d value [Equation (16)] of 0.85 g/mL corresponding to a retardation factor R of about 5.85. When substituted into Equation (10), this R-value leads to reasonable predictions of the locations of the peak concentration in the caisson (results not shown here). The strontium peak concentration at the 188-cm port was actually predicted somewhat better than with the more rigorous nonlinear model. However, the asymmetrical shape of the observed breakthrough curves will not be described well by the linear model, which produces relatively symmetric curves for the magnitude of hydrodynamic dispersion in these experiments. The value of K_d estimated in the above manner from the caisson tracer experiments is observed to be much higher than that estimated by Polzer et al. (1985) from batch equilibrium studies. Occurrence of $SrCO_3$ precipitation in the caisson experiments may explain the high apparent distribution coefficient for Sr. At the higher temperatures and much lower solid-solution ratios of the laboratory batch studies, the stability of $SrCO_3$ may be anticipated to be much lower than in these field studies.

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SUMMARY AND RECOMMENDATIONS

In this study we have investigated the use of various simple deterministic models to describe flow and transport behavior of crushed Bandelier Tuff in large lysimeters. Parameter estimation methods have been found to facilitate accurate model calibration. In many respects, the simple flow and transport models have provided quite adequate description of the observed behavior. However, it is evident that even in this fabricated and presumably rather homogeneous medium, considerable variability in flow and transport behavior occurs that complicates the description and prediction of these processes. A number of specific observations and suggestions for subsequent studies follow:

1. The hydraulic properties of Bandelier Tuff appear to be well characterized by the assumed parametric model. The model provides reasonable predictions of transient unsaturated flow behavior except when very near to saturation.

2. Considerable ambiguity occurred in the interpretation of influent concentrations and pulse durations, which had to be adjusted rather arbitrarily to obtain apparent mass balances even for presumably nonreactive tracers. In future experiments greater precision in characterizing the input function should be sought by making more frequent measurements of influent concentrations, feed rates, and pulse durations.

3. A few additional concentration measurements during the time interval in which the pulses pass given depths would allow for a better definition of v, t_o, and especially D for species with little or no retardation (iodide, bromide, and lithium).

4. More detailed geochemical analyses should be performed to investigate the possibility of $SrCO_3$ precipitation in these or similar experiments.

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There are indications that the soil solution was supersaturated with respect to $SrCO_3$ resulting in erratic apparent mass balances for strontium and larger than expected retardation. In order to study this phenomenon experimentally, consideration will need to be given to the use of extractors that limit the degassing of samples.

5. Attention should be addressed to the evaluation of variability in transport behavior. The results indicate that even in this relatively homogeneous, artificially constructed medium, significant variations in water contents and/or hydraulic fluxes occur within the caissons. Multiple sampling ports should be placed at each depth to evaluate the structure of the heterogeneity and isolate its cause; to conserve effort, it may be satisfactory to reduce the number of depths sampled while increasing the number of ports per depth.

6. The water/tracer application system should be redesigned to obtain a more uniform addition of solution at the caisson surface. This would better simulate natural conditions and eliminate the apparent high dispersion at shallow depths. Uneven distribution may also contribute to transverse velocity variations by encouraging local fingering of the flow paths.

7. In order to preclude any uncertainty in measured water contents in future studies, it may be advisable to obtain a few gravimetric samples to check the neutron probe calibration.

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DISCUSSION

C. J. Duffy — How much of the spatial variability and the dispersion coefficients could you explain just through the variations in the velocity?

J. C. Parker — The dispersivity would be more constant than the dispersion coefficient. In all cases that I can recall, where we have high dispersion coefficients, there were relatively high velocities also. The correlation is not perfect by any means, but it is significant.

P. J. Wierenga — We assumed transport in a homogeneous material in a uniform velocity field. As Peter Huyakorn will later show, if you simulate the one-dimensional steady flow problem, the result is virtually a constant water content through the profile until you get to the bottom few centimeters in the column when it goes over to saturation. Where was the soil saturated?

J. C. Parker — The bottom few centimeters were saturated. It was analyzed using both assumptions, using the variable water content distribution through the column calculated from the steady flow analysis and using a constant water content, and it was virtually indistinguishable. The bottom 50 cm was where the water content distribution bends over out of the 5.5-m zone.

D. J. Goode — For the dispersion coefficients that you get at each depth, if there is any general trend, it seems to me that the dispersion coefficients decrease with depth except the outflow dispersion coefficients, which are much higher than anything you get at individual depths. It seems that the outflow is what is of concern because that is what is going to come out of the bottom of a unit.

J. C. Parker — These results are probably to be expected. One samples a fairly small environment in the vicinity of these suction samplers, and the fitted dispersion coefficients reflect the relative homogeneity within these confined volumes. In the effluent data, you are seeing the average behavior of the entire caisson. Volume and dispersion effects are due to the fact you have velocity variations within the media and some mixing between the

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flow zones. So it is reasonable when you analyze these kind of point measurements that you get smaller dispersion coefficients than when you analyze something that is averaged over a larger domain.

I. P. Murarka — How much of the total mass was accounted for by the analysis?

J. C. Parker — Disregarding the strontium data, the way it was modeled, the mass balance was very close. To get that mass balance, we had to juggle around the pulse duration. If you used the advertised injection concentration and assumed it was correct when you analyzed the data, then you would account for only about 80% of the mass. That is, it looks like you have less mass than what was thought to have been put in.

I. P. Murarka — In that particular vein then, a dispersion estimate for an average velocity of 12 cm/d. At the depth of 36 cm with six days of continuous injection of the chemicals doesn't really mean much from the standpoint of our confidence in the parameter values.

J. C. Parker — I agree that doing a one-dimensional analysis when you inherently have some three-dimensional effects will lead to parameters that are going to have dubious physical significance.

I. P. Murarka — It is worse than that in the sense that you have six days of 12-cm/d introduction rate. The earliest application would automatically go, if there were no dispersion, 72 cm anyway. To try to estimate dispersion at 36 cm or 50 cm, I wouldn't worry about dispersion coefficients and make any particular judgment about the parameter values at shallow depths. But leaving that aside, if you really get to the total analysis of the whole experiment, wouldn't it be that the most distant observation already gives you an integrated result where basically all the estimated parameters based on the final observation should be the predictor parameters (the most reliable) because you have already averaged out all that you couldn't assume or know about?

J. C. Parker — It appears that the two apparent flow regions are discrete enough that mixing between them is not complete by the time you get to the

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bottom of the column, so you still see some effects of those two zones. I don't really know what has caused these two zones.

I. P. Murarka

Well, for either prediction you used the average values based on individual analysis, and what I am saying is that, numerically, they don't look that far apart. There would be very little difference because the velocities are almost the same and the dispersion coefficients would show little difference. Once you calculated your predicted value, did you try to calculate the residual between the calculated and observed values, take the absolute values, and find the average residual for each of the depths so that we can see other than qualitatively that the corresponding numbers look alike?

J. C. Parker

No, that was not done. Another way we could have analyzed the data is to fit a single set of parameters from the pooled set of data for all depths, but again, this was not done.

I. P. Murarka

You used this data to derive the parameters and then you used the parameters to predict--is that correct?

J. C. Parker

Yes, that is correct.

J. Steele

Did I understand you saying that the two-path effect is the explanation for the 264-cm discrepancy? Any time you pack a cylindrical bed you have a fast path down the surface and the path length should have a correlation to that depth in a sense. If you have two paths and one is a surface, then you have a fast path with a path length to get to that depth. When you pack a bed, the surface effect is going to create a fast path in a more open packing. Unless you shake the whole caisson, you have a surface effect that is a fast path. The distance to get to the centroid of that cylinder ought to have a correlation with the diameter of the caisson and that depth and when you mix the two, you will have some optimum depth where that mixing produces the most because you took the single or the worst case. Below that your mixing from your radial condition will take that away from you. There ought to be a correlation in the 264-cm length and the fast-path length which has to do with the diameter of the caisson because it will pack more densely in the center than in the wall.

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J. C. Parker

I think what you are saying is that you have a dense compaction in the center of the caisson which results in velocity differences radially.

There is a problem with this hypothesis. Almost all the samplers were on one-half of the caisson at different depths down one hemisphere. Then there were two down the other side, one at 264 cm and one immediately above that at 188 cm. All on one side gave velocities of about 12 or so, and on the other side, the 188 gave 12 and the 264 gave 17 or 18, so the velocity distribution was not radially symmetric.

W. A. Jury

How uniform is the water application regime at the surface? Could there have been one or more of these emitters creating a regime that was slower, that wouldn't move solute as rapidly?

J. W. Nyhan

One of the slides that Hector showed were a series of metal cups around each one of the emitters, and for almost three months, we tested the uniformity of the application of the solution to the surface of the caisson. Over that three-month time period, the emitters varied by + or -5% in terms of the amount of solution delivered to any one location across the 96-point distribution.

W. A. Jury

Well, I will now say that this is just a classic field observation which we have encountered many times leaching solutes under uniform applications on homogeneous soils. I tend to favor your explanation that there is a highly complicated three-dimensional flow path connecting that particular sampler and not the one near it for reasons yet to be determined.

I. P. Murarka

Did you analyze the two sets of different observations separately or did you only use the average values?

J. C. Parker

There are two different entries for the depths on the tables. One was a Teflon sampler and the other, a hollow fiber. The figures were all for the hollow fiber ones.

C. T. Kincaid

Based on the fact that you are constrained to use one-dimensional tools in fitting parameters, how heavy-handed do you think you

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have been in fitting parameters to this experiment?

J. C. Parker

Pretty heavy-handed.

C. T. Kincaid

Based on the fact, then, that the NRC, DOE, and others employ these types of tools to form very long-term predictions, do you think it is germane?

J. C. Parker

I think the problems that have been pointed out are germane. There are some obvious problems in a deterministic approach like this. I can fit some parameters to the data to obtain some mean properties, and they may describe the mean behavior. However, if the sampler at 264 cm had been missing, the fast flow zone could have been entirely missed and any predictions based on the reduced data set would be quite misleading. This points out the problems in using a simple deterministic approach to fit parameters and project short-term, much less long-term, behavior.

I. P. Murarka

Isn't it worse than that, though, because here you have data where you derived the parameters from and then tried to predict the same thing? In normal situations you wouldn't have that luxury, and all these dispersion velocity things are going to have to be pulled out from other sources and then try to predict before you place the controls. That is true prediction.

J. C. Parker

I would say that we are definitely not at a stage where I would feel comfortable making some reliable predictions for field behavior. Perhaps we never will be; we may have to settle for quantification of error bounds on our predictions, which due to indeterminancy of soil properties are likely to be rather broad.

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SIMULATION OF ION MOVEMENT IN SOIL USING A CONTINUOUS-TIME MARKOV PROCESS

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INTRODUCTION

A variety of approaches have been taken to model solute movement in soil. These models vary widely in their conceptualization of the soil-water-solute system and greatly reflect the environment, training, and preoccupations of their developers. Given that our understanding of the natural system is incomplete, all models of water and solute movement represent simplifications of the physical, chemical, and biological processes actually occurring in field soils.

As more measurements are made of field-scale movement of water and chemicals, it is becoming clear that the processes determining displacement are at the least spatially variable and are probably temporally variable as well. Modelers recognize the need to include consideration of this variability if their descriptions of water and chemical fate are to be accurate. However, previous modeling efforts, mostly deterministic in form and validated on laboratory soil column experiments, may not be adequate for description of such variability. Attention has therefore shifted to stochastic approaches as possible models of water and chemical movement under variable, incompletely understood field conditions.

One stochastic process that has been successful in modeling naturally occurring phenomena in many disciplines is the continuous-time Markov process

(CTMP) (Feller 1959, Bailey 1964, Chiang 1980). The Markov process requires that only the present value of the time-dependent random variable be known to determine the future value of the random variable. Processes such as births and deaths in a population, as well as immigration and emigration, have been successfully modeled using the Markov approach. For example, the population size can be considered as a random variable with the population either increasing or decreasing by one over a discrete time interval. The future size of the population is dependent only on the present size and not the population history. This concept of birth-death and immigration-emigration process was taken further by Fan et al. (1982) by modeling chemical reactions where molecules were considered as time-dependent random variables in a series of in-line batch reactors. A molecule could move to any reactor in a given time interval (emigration), a new molecule could enter any reactor (immigration), a molecule could be formed by chemical reaction (birth), and a molecule could exit the system or be consumed by chemical reaction (death). Movement to any of the reactors was conditional only upon the present location of the molecule in the series of batch reactors. In the Markov conceptualization of this flow system, each reactor was considered as a discrete representation in space. Using the Markov process, Nassar et al. (1983) discretized space-to-model soil movement and loss in the field from wind and through transporation by surface flow due to rainstorms. The field was partitioned into sections beginning at the windward side and ending at the leeward side. Movement of soil resulted from transitional steps from section due to saltation and surface creep.

An extension of the Markov process into continuous space has been used extensively to model diffusive processes in porous media. The Fokker-Planck equation is one such example that has been used by man to describe diffusive

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processes (Gardner 1983). However, development of a Markov process model in a form useful to describe both steady state laboratory conditions and transient, variable field conditions probably requires use of a discretized approach. The model described here (and in greater detail by Knighton and Wagenet 1985a,b) uses a discrete space representation that more closely parallels methodologies for collecting soil and solute samples in both laboratory and field. The resulting theory can be used to describe solute movement under both steady state and transient conditions and in the presence of time-homogeneous chemical and biological reactions.

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DESCRIPTION OF THE MODEL

The soil is considered as a finite number of layers n with different processes occurring simultaneously within any layer. These processes might include the flow of water and dissolved chemicals, microbial degradation, adsorption, hydrolysis, and plant uptake of nutrients. This system is essentially continuous in time with respect to the individual processes but discrete in space. A random variable S(t) can be defined whose value indicates the state of the system at any time t, if $t \in (0,\infty)$. Here the system is defined as a molecule moving through a series of soil layers or states. The event S(t)=j defines the position of a single molecule of solute to be soil layer j at time t. If the molecule moves from any layer i to some other layer j within a small time element $(t, t + \Delta)$, there is a finite probability associated with that movement. The $P_{ij}(\tau, t)$ is used to denote the transition (or conditional) probability that the molecule will be in layer j at time t, given that it was in layer i at time τ. For $\tau < t$ and if τ and t are elements of the set $(0, \infty)$, then

$$P_{ij}(\tau, t) = \Pr\{S(t) = j \mid S(\tau) = i\},\ i, j = 1,2,\ldots,n. \quad (1)$$

A discrete-valued stochastic process is a Markov process if the conditional probability distribution of the future state of the system S(t), given the present state S(τ), is independent of past states S($\tau-\Delta$). Furthermore, a Markov process is time homogeneous if the transition probability depends only on the difference $t-\tau$ and not on the individual values of τ and t. The dependence of the Markov property on the present state but not on past states of the system implies a very useful relationship. If we consider three fixed points in the time interval (τ,t) such as τ, ξ, t, where ξ lies inside the interval so that $\tau<\xi<t$, then we can form three independent random variables: S(τ), S(ξ), and S(t). A conditional probability can be formed where

$$\begin{aligned} &\Pr\{S(t) = k/S(\tau)=i, S(\xi) = j \\ &\quad = \Pr\{S(t)=k/S(\xi)=j\}. \end{aligned} \tag{2}$$

The joint conditional probability of S(t) and S(ξ) given S(τ) can be written as

$$\begin{aligned} &\Pr\{S(\xi) = j \text{ and } S(t) = k/S(\tau) = i\} \\ &\quad = P_{ij}(\tau,\xi)\, P_{jk}(\xi,t). \end{aligned} \tag{3}$$

This last probability defines passage from S(τ) = i to S(t) = k through an intermediate state S(ξ) = j. If indeed passage has occurred through layer j at time ξ, then the event (S(ξ) = 1 or S(ξ) = 2 ...) has probability of occurrence equal to unity. This implies that the transition probability $P_{ik}(\tau,t)$ can be written as

$$P_{ik}(\tau,t) = \sum_j P_{ij}(\tau,\xi)\, P_{jk}(\xi,t) \quad i, k = 1,2\ldots n;\ \tau<\xi<t. \qquad (4)$$

Equation (4) is known as the Chapman-Kolmogorov equation (Chiang 1980) and can be rewritten for the time-homogeneous case as

$$P_{ij}(0,t+\Delta t) = \sum_k P_{ik}(o,t)\, P_{kj}(0,\Delta t)\ , \qquad (5)$$

where the subscript k now represents the intermediate state or soil layer.

As stated before, there are a number of processes that influence the layer a molecule of solute will be in at some time t. The transition probability from one soil layer to another is affected by the intensity of transition (or passage) from layer i to layer j. The intensities of transition are directly related to the above-mentioned processes, i.e., water and solute flow and plant uptake. From an application standpoint, the transition rate of, for example, a molecule of water from layer to layer over a short time interval is usually known and is deterministic. We can define this intensity of transition as the flow of water molecules through some pore volume. The intensity of transition for flow can be written as

$$v_{ij} = \frac{q_{ij}}{V_i}, \qquad (6)$$

where v_{ij} is the intensity of transition from layer i to layer j, q_{ij} is the volumetric flow rate between layers i and j, and V_i is the pore water volume of the soil layer i. This assumes that flow is well mixed with regard to water and solute molecules. Since v_{ij} represents an intensity of transition from layer i to layer j, then

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$$v_{ij} \Delta t + o(\Delta t) \qquad (7)$$

becomes the probability that a molecule in soil layer i at time t will be in soil layer j at time t + Δt, where o(Δt) represents higher-order insignificant terms.

Substracting $P_{ij}(0,t)$ from both sides of (5) and dividing by Δt, as Δt→ 0, gives

$$\frac{d}{dt} P_{ij}(0,t) = \sum_k P_{ik}(0,t)\, v_{kj}. \qquad (8)$$

Equation (8) is known as the Chapman-Kolmogorov forward differential equation and defines a system of ordinary differential equations that relates the rate of change of the transition probability to the intensity of transition. The initial boundary conditions for these forward differential equations are

$$P_{ij}(0,0) = \delta_{ij}, \qquad (9)$$

where δ_{ij} is the Kronecker delta. Using the Kronecker delta implies that the distribution of solute molecules at time equals zero is known throughout the soil profile. The solution of these differential equations also requires that

$$\sum_j P_{ij}(0,t) = 1. \qquad (10)$$

This constraint requires that the probabilities of transition out of any layer i to any other layer j must sum to 1. Equation (10) also implies

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$$v_{ii} = - \sum_{j \neq i} v_{ij} \quad , \tag{11}$$

where v_{ii} is the intensity of transition of a molecule starting in layer i at time 0 and remaining in layer i and time t.

These equations have, so far, only been developed based on intensities of transition for the flux of water and solute but can be modified to include other processes such as microbial degradation, plant uptake, and sorption. Of particular interest to the applications of the model in this study is sorption.

Sorption of solutes that interact with the soil matrix can be represented by retarding the flow of solute (Rao et al. 1976, Rose et al. 1978). The intensity of transition for flow v_{ij} therefore becomes v_{ij}/α_i where α_i, the retardation factor, is written as

$$\alpha_i = (1 + \frac{\rho \, K_d}{\theta_i}) \quad , \tag{12}$$

and where ρ is soil bulk density (Mg/m^3), K_d is the adsorption partition coefficient (m^3/Mg), and θ_i is the volumetric water content (m^3/m^3) in each layer. For this relationship to hold, we must assume a linear and reversible adsorption model. For the case of a noninteracting solute ($K_d = 0$), $\alpha_i = 1$, and $v_{ij}/\alpha_i = v_{ij}$. Equation (11) can now be written as

$$\lambda_{ii} = - \sum_{i \neq j} v_{ij}/\alpha_i \quad , \tag{13}$$

where λ_{ii} still represents the negative sum of all probabilities of exit from layer i. Additional sources or sinks of solute would be considered by adding

terms to the right side of (13). Since for the time-homogeneous process v_{ij} is constant, λ_{ii} will be used to represent the intensity of transition for the general case.

The forward differential equation given in (8) can be more conveniently written in matrix notation by recognizing that i,j = ,1,2...n forms an N x N matrix. In matrix notation, Equations (8) and (9) can be written as

$$\frac{d}{dt} \underline{P}(0,t) = \underline{P}(0,t)\, \underline{\Lambda} \tag{14}$$

and

$$\underline{P}(0,0) = \underline{I} = \text{identity matrix} , \tag{15}$$

where

$$\underline{P}(0,t) = \begin{bmatrix} P_{11}(0,t) & P_{12}(0,t) & \cdots & P_{1n}(0,t) \\ P_{21}(0,t) & P_{22}(0,t) & \cdots & P_{2n}(0,t) \\ \vdots & & & \vdots \\ P_{n1}(0,t) & P_{n2}(0,t) & \cdots & P_{nn}(0,t) \end{bmatrix} \tag{16}$$

and

$$\Lambda(0,t) = \begin{bmatrix} \lambda_{11}(0,t) & \lambda_{12}(0,t) & \cdots & \lambda_{1n}(0,t) \\ \lambda_{21}(0,t) & \lambda_{22}(0,t) & \cdots & \lambda_{2n}(0,t) \\ \vdots & & & \vdots \\ \lambda_{n1}(0,t) & \lambda_{n2}(0,t) & \cdots & \lambda_{nn}(0,t) \end{bmatrix} \tag{17}$$

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The solution of the ordinary differential equation (14) is

$$\underline{P}(0,t) = \underline{P}\ (0,0)\ \exp\ (\Lambda t) \qquad (18)$$
$$= \underline{I}\ \exp\ (\Lambda t) = \exp\ (\Lambda t).$$

PROBABILITY DISTRIBUTIONS OF MOLECULES

The main objective in using a Markov process to describe chemical movement is to be able to predict the concentration of a chemical in any soil layer over time. Transition probabilities formed above give the conditional probability of the movement of a single molecule to any layer in the system, given the position of the molecule at the start of the time interval. The distribution of all the molecules in the soil and within any soil layer is a function of the transition probability of each molecule.

The number of individual molecules within a soil layer at time = 0 can be represented by a constant vector,

$$\underline{M} = (M_1, M_2, \ldots, M_n); \qquad (19)$$

and at time = t by a random vector,

$$\underline{X}(t) = (X_1, X_2, \ldots, X_n). \qquad (20)$$

Each of the components of $\underline{X}(t)$ represents the number of molecules remaining in each layer that survived movement out of the soil or, if appropriate, microbial degradation or crop uptake. The vector $\underline{X}(t)$ can be simplified further by breaking it into two independent random vectors $\underline{Y}(t)$ and $\underline{Z}(t)$, where

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$$\underline{X}(t) = \underline{Y}(t) + \underline{Z}(t). \tag{21}$$

The vector components of $\underline{Y}(t)$ represent the number of molecules initially present in each layer at time = 0 that remained in the soil to time = t. The components of $\underline{Z}(t)$ represent the number of "survivor" molecules that entered the soil during the time interval (0,t) due to application and still remained. Molecules in $\underline{Z}(t)$ represent new additions and are not due to initial molecules from $\underline{M}$.

In this application of the model, there are no sources or sinks of solute. Therefore, any of the molecules found in $\underline{M}$ at time = 0 ($\underline{M} = \underline{X}(0)$) will be in a soil layer $\underline{n}$ at some later time t. We can then write

$$\underline{M} = \sum_{j=1}^{n} Y_{ij}(t) + E_i(t) \ , \tag{22}$$

where $Y_{ij}(t)$ is a random variable representing the number of molecules remaining in layer j at time t, which were in layer i at time = 0; $E_i(t)$ is the number of molecules that exited layer i by time t. The distribution of $Y_j(t)$ at time = t is essentially a multinomial distribution. That is, there are $\underline{M}$ independent molecules that can be distributed in n soil layers. The expectation and variance of $Y_j(t)$ follow using familiar formulae of the multinomial distribution, where

$$E(Y_j(t)) = \sum_{i=1}^{n} M_i \ P_{ij}(0,t) \tag{23}$$

and

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$$\mathrm{Var}(Y_j(t)) = \sum_{i=1}^{n} M_i \, P_{ij}(0,t) \, (1 - P_{ij}(0,t)). \qquad (24)$$

These last two parameters allow us to make statistical inference as to the predictive ability of the model, which is a valuable property in any model.

The vector $\underline{Z}(t)$ defined in Equation (21) is composed of the outcome of sequences of events initiated by the introduction of new molecules and determined by the internal movement of these same molecules. If we let molecules flow into a layer at the rate of $\zeta_i(\tau)$, then $\zeta_i(\tau)$ is equal to the volumetric flow rate of material into layer i. If we multiply $\zeta_i(\tau)$ by the molar concentration of the flow and by Avogadro's number we obtain the number, of molecules entering the layer per unit time. The number of new molecules that has entered the system is $\zeta_i(\tau)\, d\tau$. A binomial distribution can be formed for these new molecules. If we let z_i denote the number of molecules that has successfully entered a layer i, with its respective probability of entering or remaining there, then $P_{ij}(0, t-\tau)$. If we let $Z_i(t)$ represent a random variable, which is the number of molecules available for entry to layer i in the time interval (τ, t), where $0<\tau<t$,

$$\Pr\{Z_i(t) = z_i\} = \qquad (25)$$

$$\frac{(\zeta_i(\tau)d\tau)!}{((\zeta_i(\tau)d\tau) - z_i)!z_i!} \; P_{ij}(0,t-\tau)^{z_i}(1-P_{ij}(0,t-\tau))(\zeta_i(\tau)d\tau - z_i).$$

It can be shown that the binomial distribution approximates the Poisson if $\zeta(\tau)d\tau$ is large and $(\zeta(\tau)\, d\tau\, P_{ij}(t-\tau))$ is moderate. Therefore,

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$$\Pr\{Z_i(t) = z_i\} = \tag{26}$$

$$\exp\left(-(\zeta_i(\tau)d\tau\ P_{ij}(0,t-\tau)\right)\ \frac{\left((\zeta_i(\tau)d\tau\ P_{ij}(0,t-\tau)\right)^{z_i}}{z_i!},$$

where $(\zeta_i(\tau)d\tau\ P_{ij}(0,t-\tau)$ is the expected number of molecules in layer j at time = t that entered from $\zeta_i(\tau)d\tau$ molecules. Since molecules could conceivably enter through any layer and each of these events are independent for distinct values of τ, the Poisson distribution is a very good approximation. Hence,

$$E(Z_j(t)) = \mathrm{Var}(Z_j(t)) = \int_0^t \sum_{i=1}^{n} \zeta_i(\tau)\ P_{ij}\ (0,t-\tau)\ d\tau. \tag{27}$$

The distribution of $X_j(t)$, the number of molecules remaining in each layer that survived, is the sum of the two independent distributions $Y_j(t)$ and $Z_j(t)$; therefore,

$$E(X_j(t)) = \sum_{i=1}^{n} M_i\ P_{ij}(0,t) + \int_0^t \sum_{i=1}^{n} \zeta_i(\tau)\ P_{ij}(0,t-\tau)d\tau \tag{28}$$

and

$$\mathrm{VAR}\ (X_j(t)) =$$

$$\sum_{i=1}^{n} M_i\ P_{ij}(0,t)(1-P_{ij}(0,t)) + \int_0^t \sum_{i=1}^{n} \zeta_i(\tau)\ P_{ij}(0,t-\tau)d\tau. \tag{29}$$

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Converting the number of molecules to a concentration is very straightforward:

$$C_j(t) = \frac{X_j(t)}{N\ V_j}. \tag{30}$$

where $C_j(t)$ is the concentration in layer j at time = t, N is Avogadro's number, and V_j is the pore water volume of layer j. The mean and variance of $C_j(t)$ are

$$E(C_j(t)) = \frac{E(X_j(t))}{N\ V_j} \tag{31}$$

and

$$Var(C_j(t)) = \frac{Var\ (X_j(t))}{N\ V_j}. \tag{32}$$

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METHODS

Caisson Experiments

The experiments were designed to provide data useful in developing a predictive capability for chemical transport under unsaturated conditions in soils and were conducted to assist DOE and NRC in improving the understanding of estimated leaching and transport scenarios used to assess the performance of low-level waste disposal sites.

The experiments are described in complete detail in Polzer et al. (1986) and are only outlined here for completeness. Two types of tracer migration data were measured in the caisson experiments (described below). In the simplest case, measurements of water and tracer inflow and outflow rates allowed mass balance calculations and determination of the existence of steady state water flow conditions. Additionally, soil solution samples were

collected from the caisson at various depths to determine tracer movement and dispersion rates as functions of time and depth. Volumetric water content was also determined as a function of horizontal distance from the edge of the caisson with six sampling ports located at incremental depth intervals of 75 cm.

Four tracers (iodide, bromide. lithium, and strontium) were used. A six-day pulse of the first three tracers added was under steady state flow conditions. The strontium had been added earlier as a pulse applied under unsteady flow conditions. A calcium chloride solution (0.01N) was added throughout the experiment to maintain a constant ionic strength and proper moisture and flow conditions. Soil solution samples were collected daily at incremental depths and analyzed for tracer concentrations, and outflow rates were measured. Water contents were measured biweekly as functions of depth and horizontal distance within the caisson.

The caisson used in this experiment was located in an experiment cluster on Los Alamos National Laboratory property. The experiment cluster consisted of six corrugated metal pipes (3-m diam and 6 m deep) surrounding a central instrument and access caisson of the same size. Access ports situated at 75-cm-depth intervals between the central caisson and the experimental caissons allowed the study of chemical transport as a function of depth in the caisson. The inside of each caisson was coated with Teflon paint to minimize tracer interaction with the surface of the caisson walls.

The caisson was filled with crushed Bandelier Tuff, which was obtained locally and consists mostly of silicic glass with a grain-size distribution similar to that of a silty sand. At the bottom of the caisson, the drain was covered with a coarse screen. Approximately 0.25 m of gravel (approximately

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2- to 3-cm diam) was placed over the screen, and above this was placed approximately 0.25 m of coarse sand. The rest of the caisson was filled with the Bandelier Tuff.

The tuff was screened at a cement batch plant after crushing. All material passing through a 0.0125-m screen was mixed with known amounts of water to give optimum water content for compaction in an attempt to provide uniformity of column packing and minimal subsidence. Water content as well as wet and dry densities were determined at several caisson depths during the filling operation. The tuff was compacted by use of tampers after each 0.2-m-thick layer was added. Dry densities varied with depth from 92.8 (at the 1.56-m depth) to 99.3% (at the 0.25-m depth) of what is considered optimum dry density for crushed tuff. Thus, maximum compaction was not obtained at the 1.56-m depth where the initial moisture content was too high for optimal compaction. Average void ratios, which were calculated from the dry density data, were 0.60, 0.67, 0.71, 0.67, 0.62, 0.64, and 0.64 for caisson depths of 0.25, 1.14, 1.56, 2.72, 3.59, 4.14, and 4.92 m, respectively.

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The water-solute distribution system used in these studies was composed of an assembly of four fluidic wafer switches, each of which was fitted with 24 outlet ports fed sequentially from a single peristaltic pump. The pump was fitted with an electronic flow metering system and the pump speed was adjusted as required to provide the necessary flow rate (about 200 $cm^3\ min^{-1}$).

A continuous application of 0.005 M calcium chloride solution (200 mg ℓ^{-1} as Ca) containing target concentrations of tracers of 0.001 M, was required for these experiments. Because of the volume of solution required for the size caisson used, it was necessary to provide for continuous blending and storage of the influent solution as a separate unit operation. The blended matrix was sampled manually at the point of introduction to the matrix storage

tank. Minor concentration fluctuations in the blended solution were found to be attenuated by the presence of about 1000-1600 ℓ of stored matrix solution. A sample of the matrix solution delivered to the caisson distribution system was analyzed to provide information on the constancy of the delivered influent.

Samples of soil solution were collected at several sampling depths in the caisson. One set of samples was collected at each of six access ports (at caisson depths of 43, 118, 194, 271, 347, and 421 cm, corresponding to soil sampling depths of 36, 113, 188, 264, 339, and 415 cm, respectively) with the idea of characterizing the relatively fast transport of the nonsorbing tracers such as iodide and bromide. A polyethylene centrifuge tube received the soil solution sample and was used to transport the sample to the laboratory for analysis and subsequent storage.

Iodide assays were performed with an ion-selective electrode and bromide using ion chromatography. Lithium and strontium assays were performed by flame atomic adsorption spectrophotometry procedures.

Volumetric water content was determined using a neutron meter. Measurements were made within aluminum access tubes located at each of the six access ports throughout the caisson at distances of 0 to 130 cm from the caisson wall in 10-cm increments. Volumetric water content was also determined in a vertical access tube for depths ranging from 20 to 560 cm in increments of 20 cm.

Model Application

The steady state form of the CTMP model was used to simulate the measured iodide, bromide, lithium, and strontium data. Movement of water and solute was considered to be downward and only between adjacent soil layers. This assumption denies any upward movement; therefore, evaporation was assumed to be negligible. Such an assumption is not required by the theory but was

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assumed for this application. It was assumed that no sources or sinks of the solutes were present and sorption was considered for strontium and lithium as formulated in Equations (12 and (13). Under these conditions the intensity of transition matrix was formulated as in Equation (17).

When used to describe a nonsorbing chemical (bromide, iodide) under steady state water flow conditions, inputs to the CTMP model consist only of the volumetric flow rate q and the pore water volume V_i of each layer. A layer size of 5-cm thickness was used in all cases on the basis of experience in applying the CTMP model to bromide transport in laboratory soil columns (Knighton and Wagenet 1985a). The entire caisson was therefore divided into 130 layers (650-cm total depth). Calculation of the transport of sorbing tracers (lithium, strontium) requires additional input of bulk density (1.7 g/cm^3), saturated water content (used also to calculate V_i -- see Table 1 below), and a distribution coefficient [Equation (12)] K_d for each inteacting chemical. Values of K_d = 0.9 cm^3/g and K_d = 0.08 cm^3/g were used for strontium and lithium, respectively, according to reasons discussed below.

Values of V_i (Table 1) were calculated from the average water content at each depth over the time of the study.

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Table 1. Values of V_i for layers in each depth interval.

Depth Interval (cm)	V_i (cm^3)
0-75	106,736
75-150	98,253
150-225	104,262
225-300	101,788
300-375	110,977
375-450	103,555
450-600	103,555

Each pulse was applied over a six-day period. The volumetric flow rate in the first unsteady state pulse, during which the strontium was added at C_o (strontium) = 70 mg/ℓ, was 134 cm^3/min. Measured outflow was used as the input volumetric flow rate to simulate the strontium movement for the remainder of the time period. These values of q (Table 2) were obtained by averaging over the smallest time intervals for which there were measured outflow data. The volumetric flow rate during the first steady state pulse, 12/6/84 to 1/27/85, was q = 191 cm^3/min. The initial concentrations C_o of the three tracers applied in this pulse were lithium = 7 mg/ℓ, bromide = 89 mg/ℓ, and iodide = 173 mg/ℓ.

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Table 2. Volumetric flow rates used in CTMP model.

Dates	q(cm^3/min)	Dates	q(cm^3/min)
9/18 - 10/2	134	2/4 - 2/20	171
10/2 - 10/18	93	2/20 - 3/6	203
10/18 - 10/31	145	3/6 - 3/21	211
10/31 - 11/28	166	3/21 - 4/1	240
11/28 - 1/3	197[a]	4/1 - 4/8	209
1/3 - 1/17	198[a]	4/8 - 4/25	212
1/17 - 2/4	197[a]	4/25 - 4/28	208

[a]Average value from 12/6/84 to 1/27/85 was 191 cm^3/min.

RESULTS AND DISCUSSION

All measured data of bromide, iodide, lithium, and strontium were converted to relative concentration C/C_o using the influent concentration of each ion. All comparisons with the CTMP model were made on this basis.

Bromide and Iodide

The CTMP model does not distinguish bromide or iodide during the simulation of a nonsorbing solute. Hence, calculated distributions of bromide and iodide were identical. The strong correlation between measured bromide and iodide resulted in very similar results for the ability of the CTMP model to describe both these ions.

Agreement between predicted and measured bromide and iodide (Figures 1-3) was generally good for the upper three sampling depths (36, 113, 188 cm), with less acceptable description of measured values (Figures 4-6) at deeper depths (264, 339, 415 cm). All predicted concentrations include the expected mean value of the ion, as indicated by open squares connected with a solid line, and one standard deviation on each side of the expected value, as indicated by the surrounding dashed lines. The discontinuity in the CTMP predictions at the 36-cm depth is due to the inability of the CTMP model, because of the assumptions used in solving the equations, to provide calculated solute distributions during the time of pulse application.

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At the upper three depths, the time of maximum observed concentration was predicted within one or two days, and the dispersion about the maximum was well described. Disagreement between measured and calculated concentrations was first apparent at the 264-cm depth, with both bromide and iodide moving more quickly past that depth than was predicted with the model. The peak concentration for both ions was observed at the 264-cm depth at about 19 days, while the model did not predict the peak would arrive at that depth until 23 days. The discrepancy between calculated and measured distributions was reversed by the time the two ions had leached to the 339-cm depth. Samples from both these depths indicated that the bromide and iodide were moving more slowly past these depths than predicted by the CTMP model. The difference

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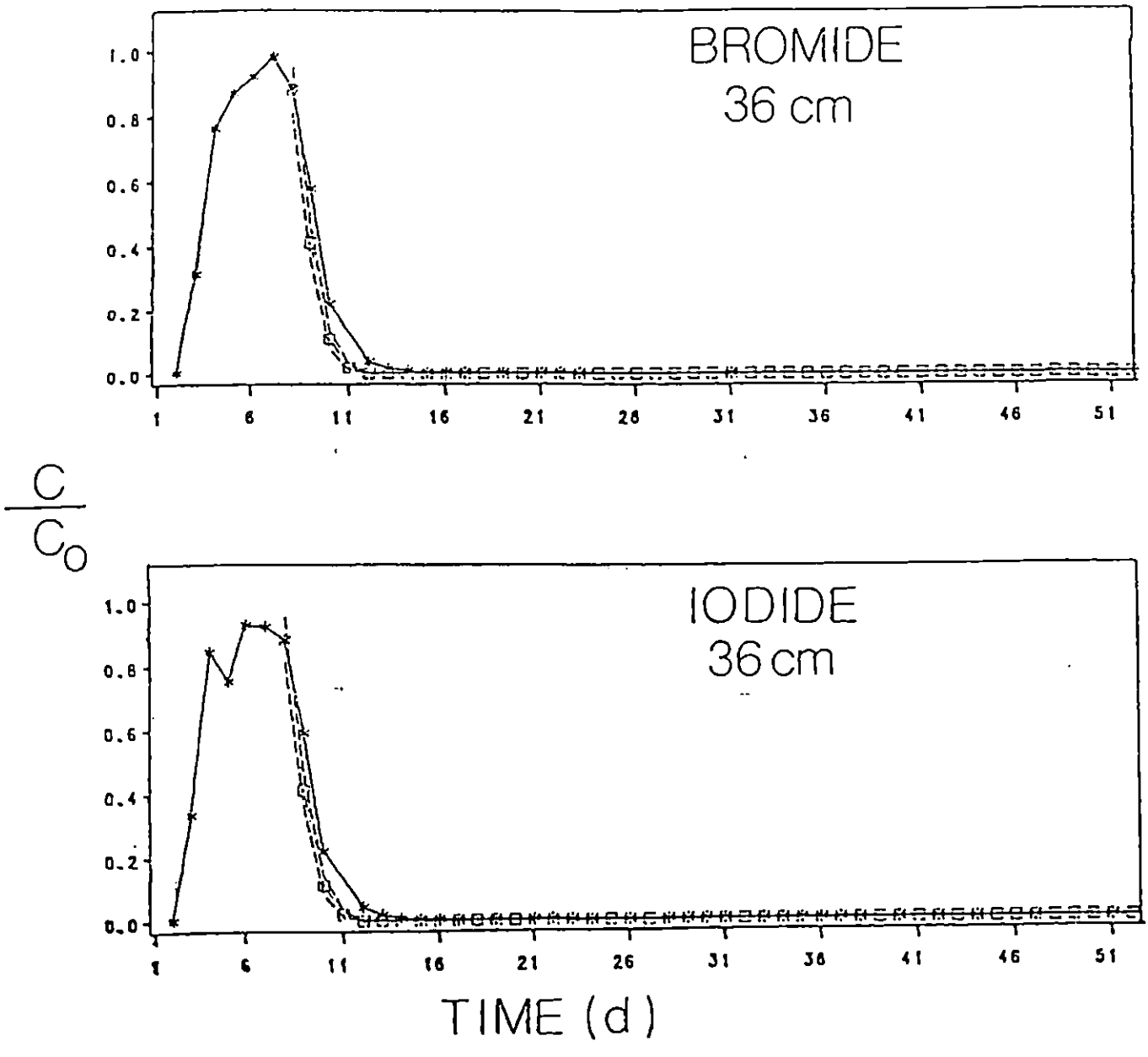

Figure 1. Comparison of measured (*) and predicted (□) bromide and iodide at the 36-cm depth.

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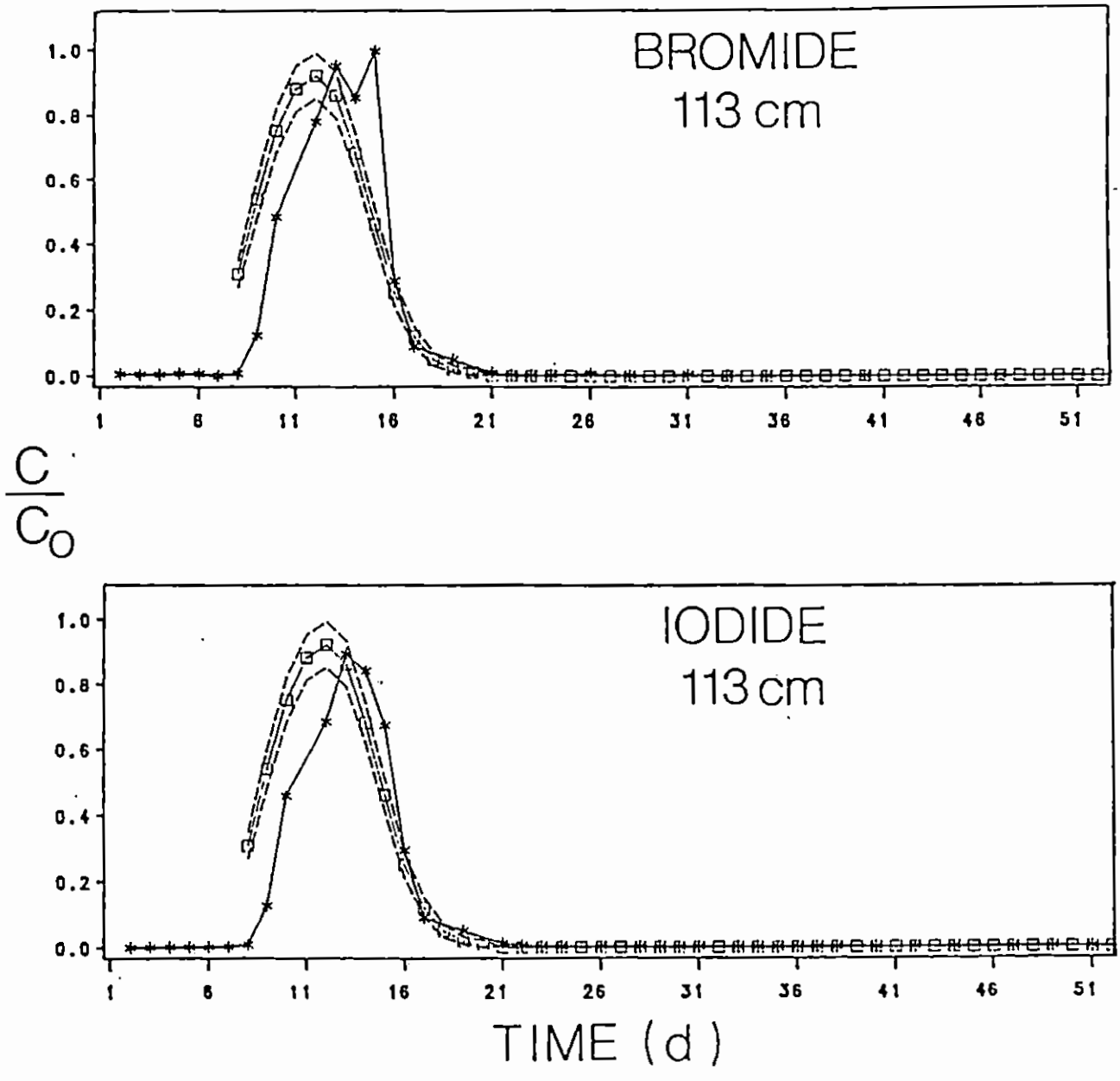

Figure 2. Comparison of measured (*) and predicted (□) bromide and iodide at the 113-cm depth.

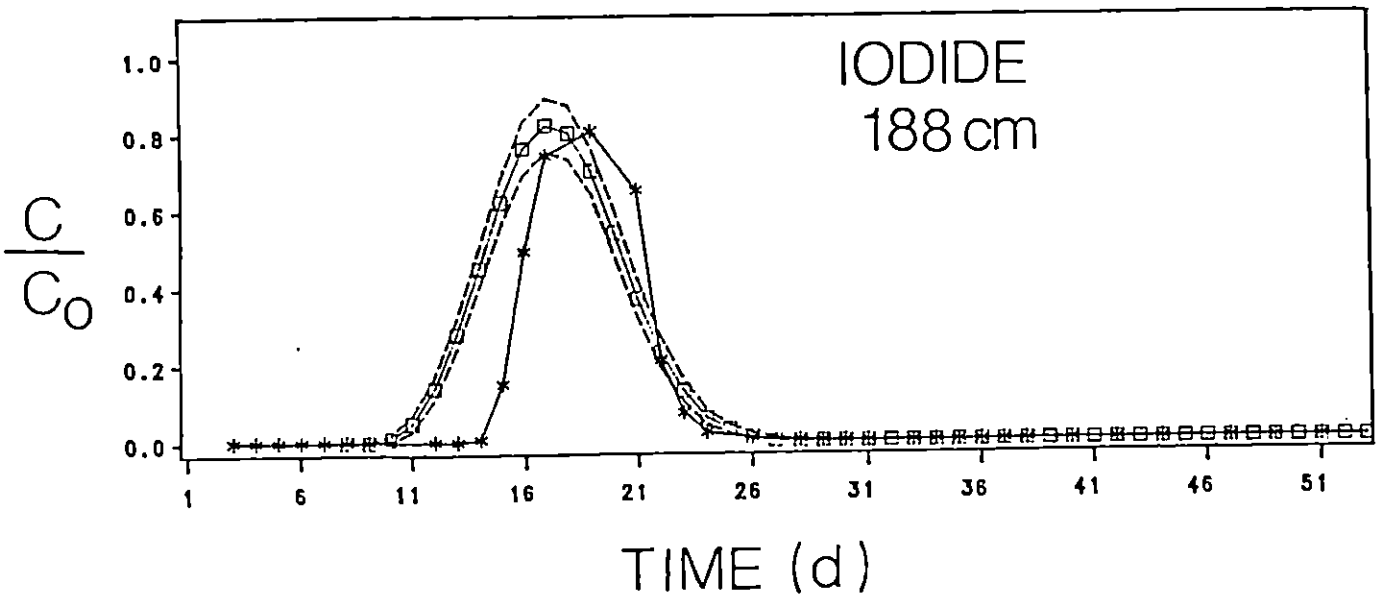

Figure 3. Comparison of measured (*) and predicted (□) iodide at the 188-cm depth. No bromide data available at 188 cm.

between predicted and observed concentrations was in both cases approximately 4 to 5 days. No further divergence of model and measurement was noted as the bromide and iodide traveled from 339 cm to 415 cm.

The CTMP model was unable to describe the bromide or iodide past the 188-cm depth with the average volumetric water flux and constant layer pore volumes, which provided good description of these ions at the first three depths. One reason may be fluctuation in the water flux over the time it took the pulse to travel from the 188-cm depth to the bottom of the caisson. This fluctuation may have resulted in substantially different local fluxes, both greater and less than the average caisson value of 191 cm^3/min. This would produce observed distributions of iodide and bromide that were accelerated (beyond predictions made using 191 cm^3/min) at the upper depths and delayed (behind predictions made using 191 cm^3/min) at the lower depths.

A second possible source of error lies with estimated values of V_i. These were obtained using average measured water contents in a layer of known dimensions. If measured water contents were not representative of conditions

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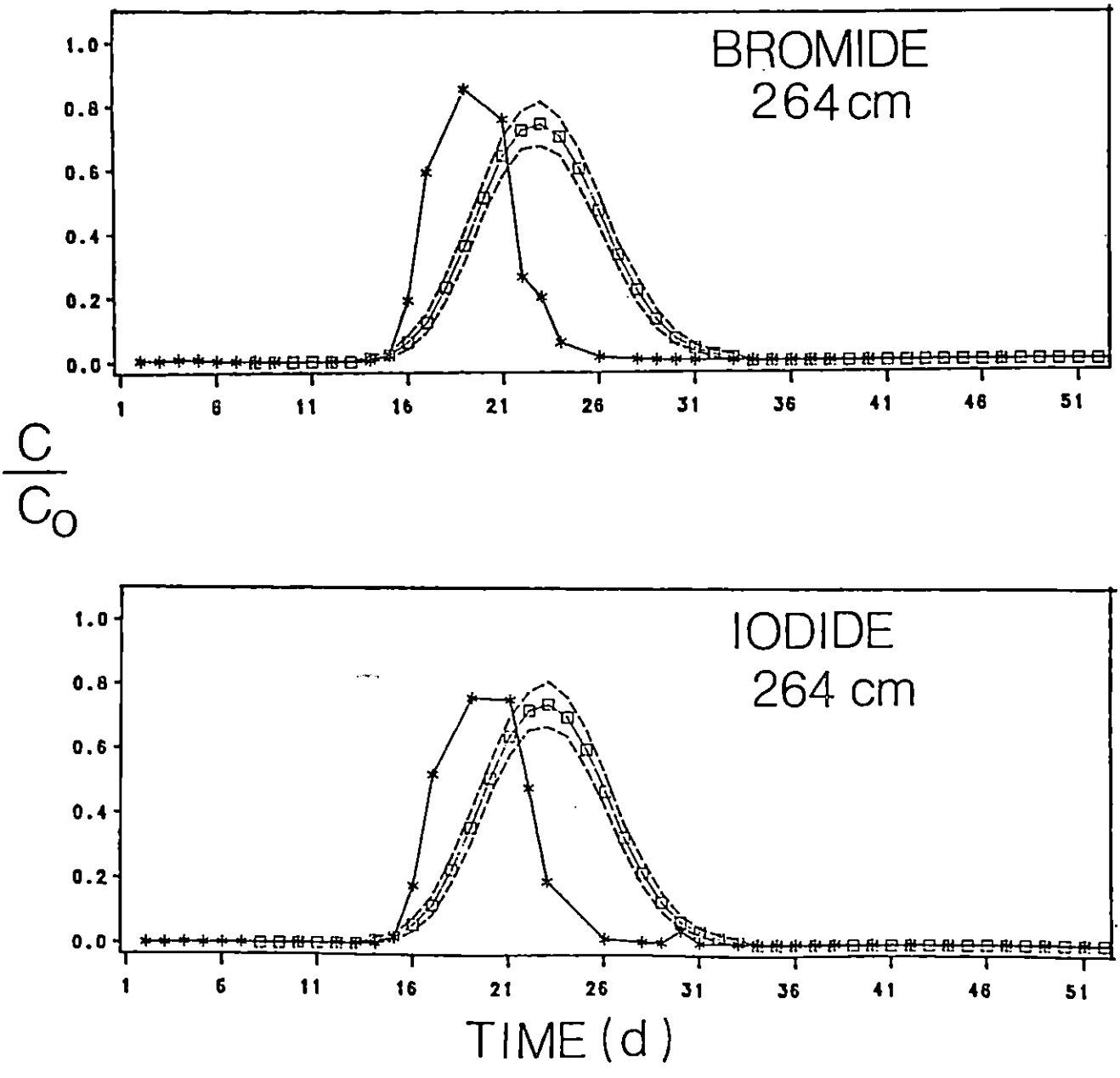

Figure 4. Comparison of measured (*) and predicted (□) bromide and iodide at the 264-cm depth.

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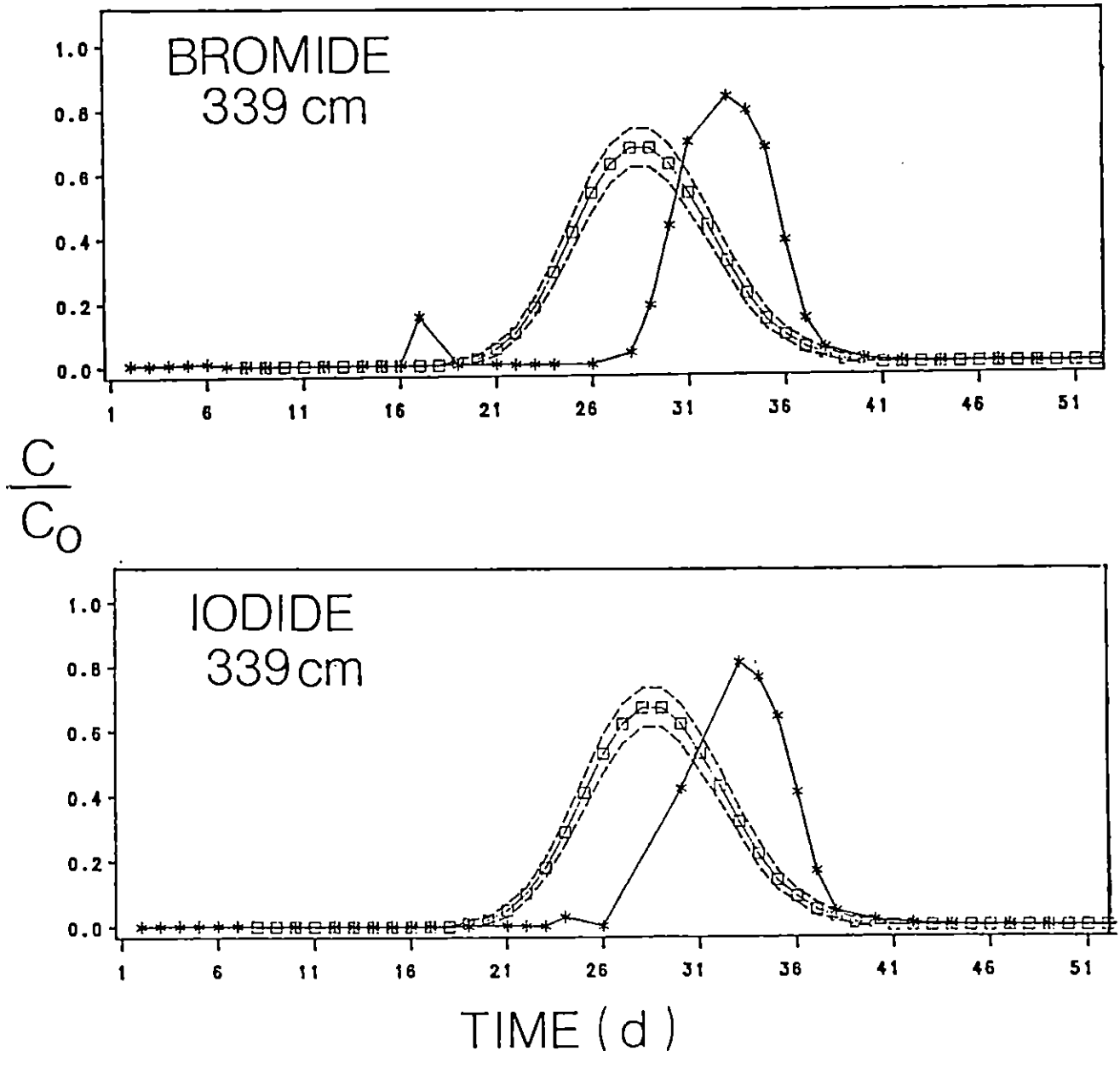

Figure 5. Comparison of measured (*) and predicted (□) bromide and iodide at the 339-cm depth.

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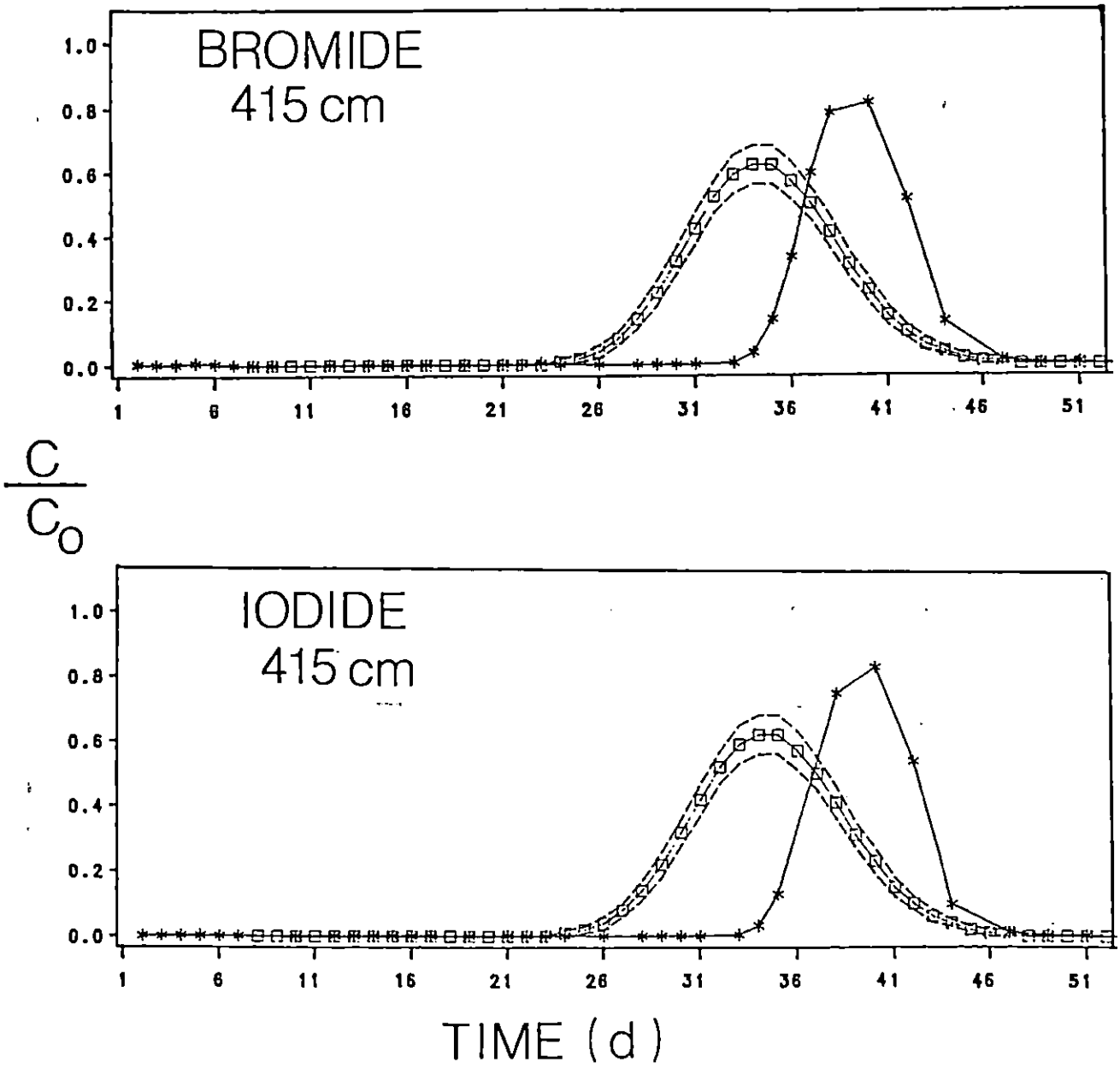

Figure 6. Comparison of measured (*) and predicted (□) bromide and iodide at the 415-cm depth.

within each layer, particularly at unsampled depths between points of measurement, actual water fluxes within the caisson could have varied locally in the manner described above.

Previous comparison of CTMP model predictions with measured bromide concentrations obtained from laboratory soil column leaching experiments conducted under steady state flow (Knighton and Wagenet 1985a) showed good agreement between model and measurements. Additionally, in those studies the approach also agreed quite well with concentrations predicted by the analytic solution to the convection-dispersion equation. This leads us to suspect inconsistencies in the experimental conditions of this study, perhaps in the degree to which steady state water flow was established in the caissons or the degree of uniformity of that flow over the length of the caisson.

Since the CTMP model does not distinguish iodide or bromide, general predicted curves for displacement of nonsorbing solutes can be generated for the conditions of the steady state portion of the experiment. These curves are presented in Figure 7.

Only iodide was measured as an outflow from the column. Measured and predicted effluent concentrations (Figure 8) were only in approximate agreement, perhaps due partially to mixing of eluted iodide in the basal layer of the caisson before exit to the outflow sample collection apparatus. It appears from Figure 7 that the total predicted and measured mass of iodide in the outflow was similar, although the pattern of leaching was only partially described.

Lithium

As with bromide and iodide, lithium was well described with the CTMP model at the three upper depths (Figures 9-10). A K_d value of 0.08-cm^3/g soil

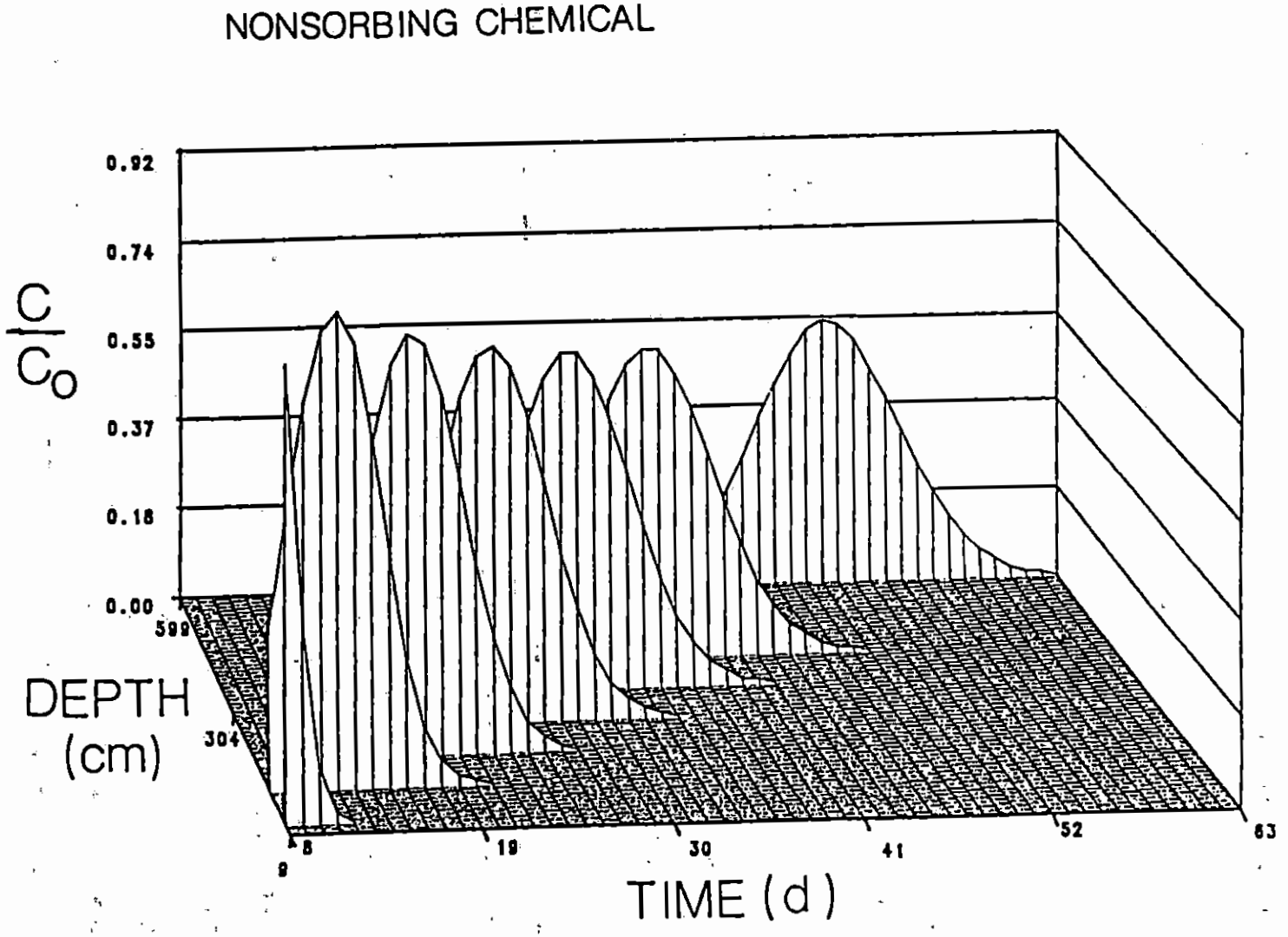

Figure 7. The behavior of a nonsorbing solute under the steady state flow conditions of this study as predicted by the CTMP model.

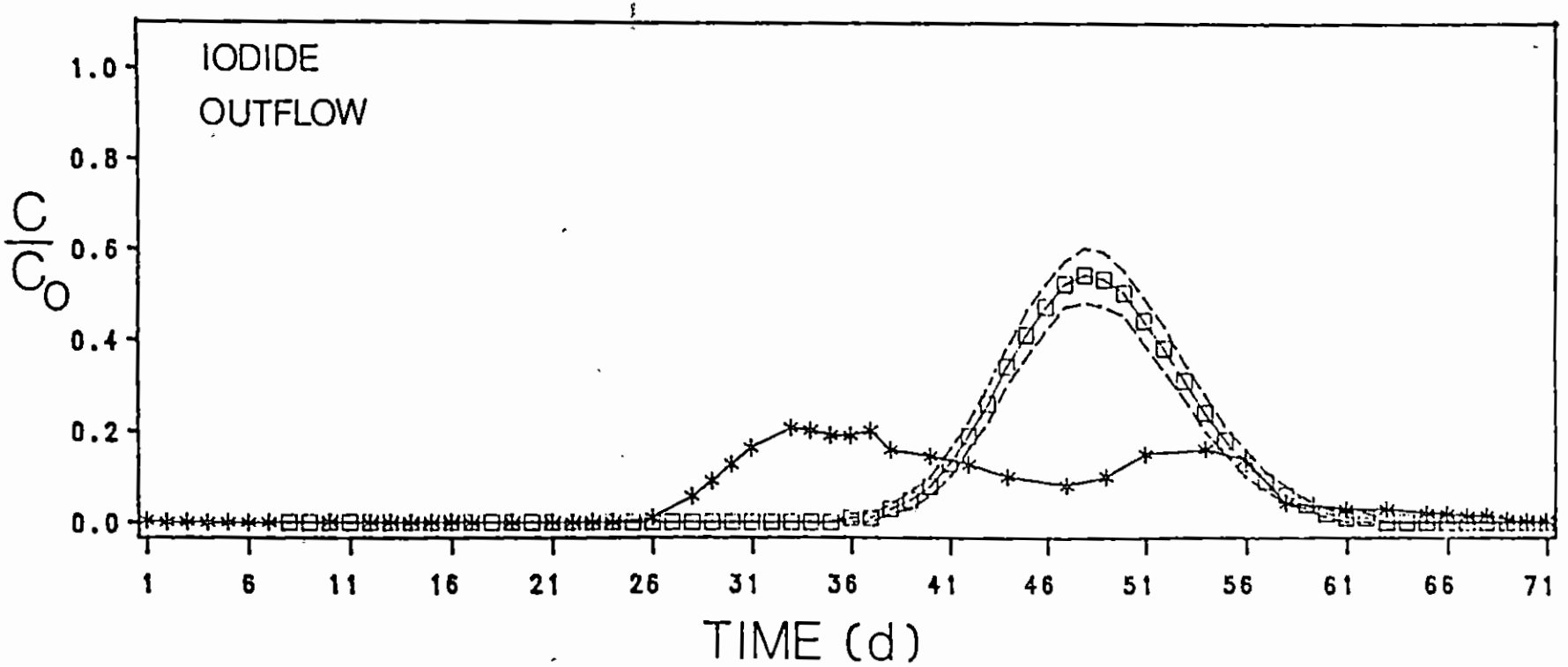

Figure 8. Comparison of measured (*) and predicted (□) iodide in the outflow from the caisson.

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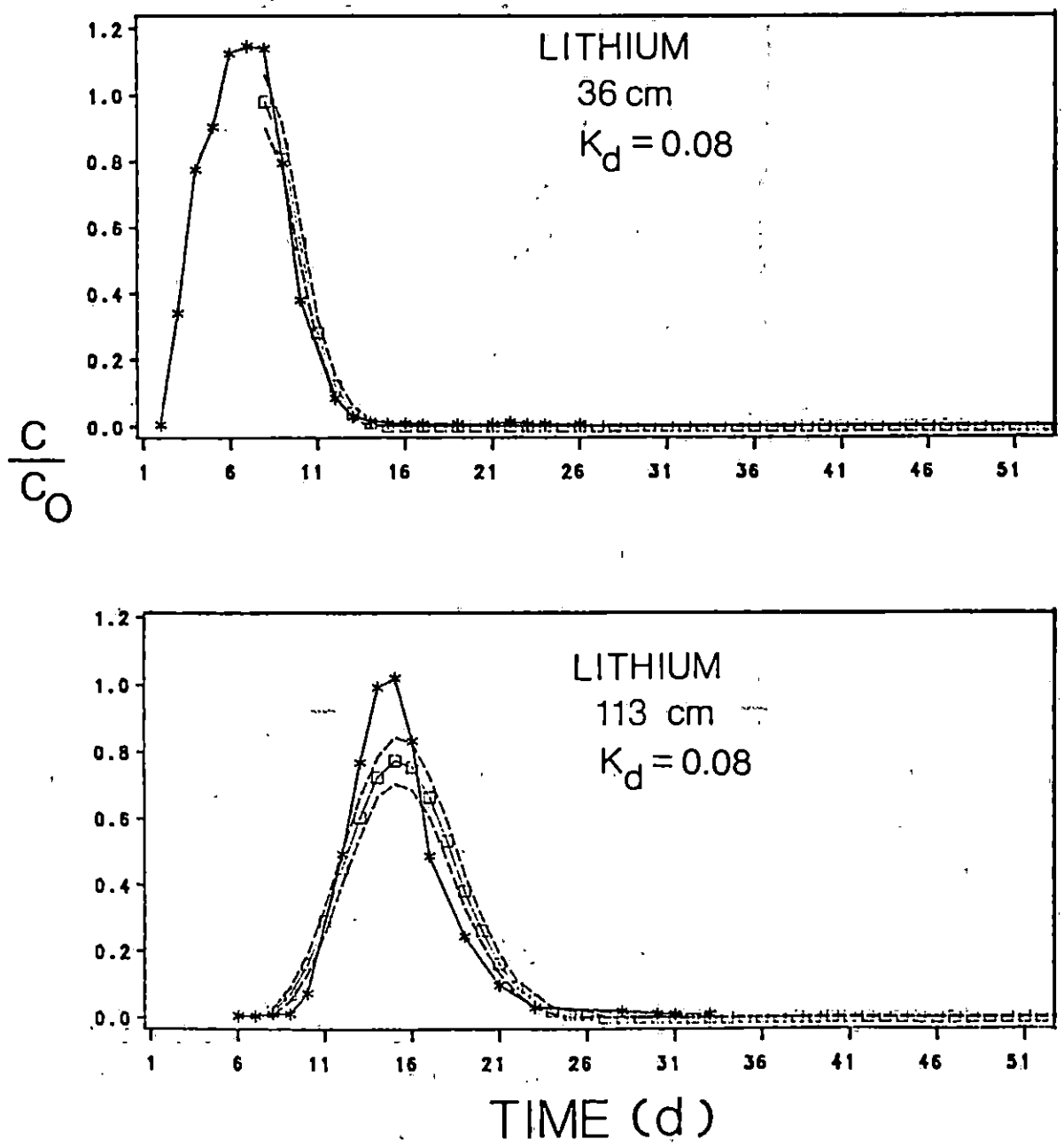

Figure 9. Comparison of measured (*) and predicted (□) lithium at the 36- and 113-cm depths with K_d = 0.08.

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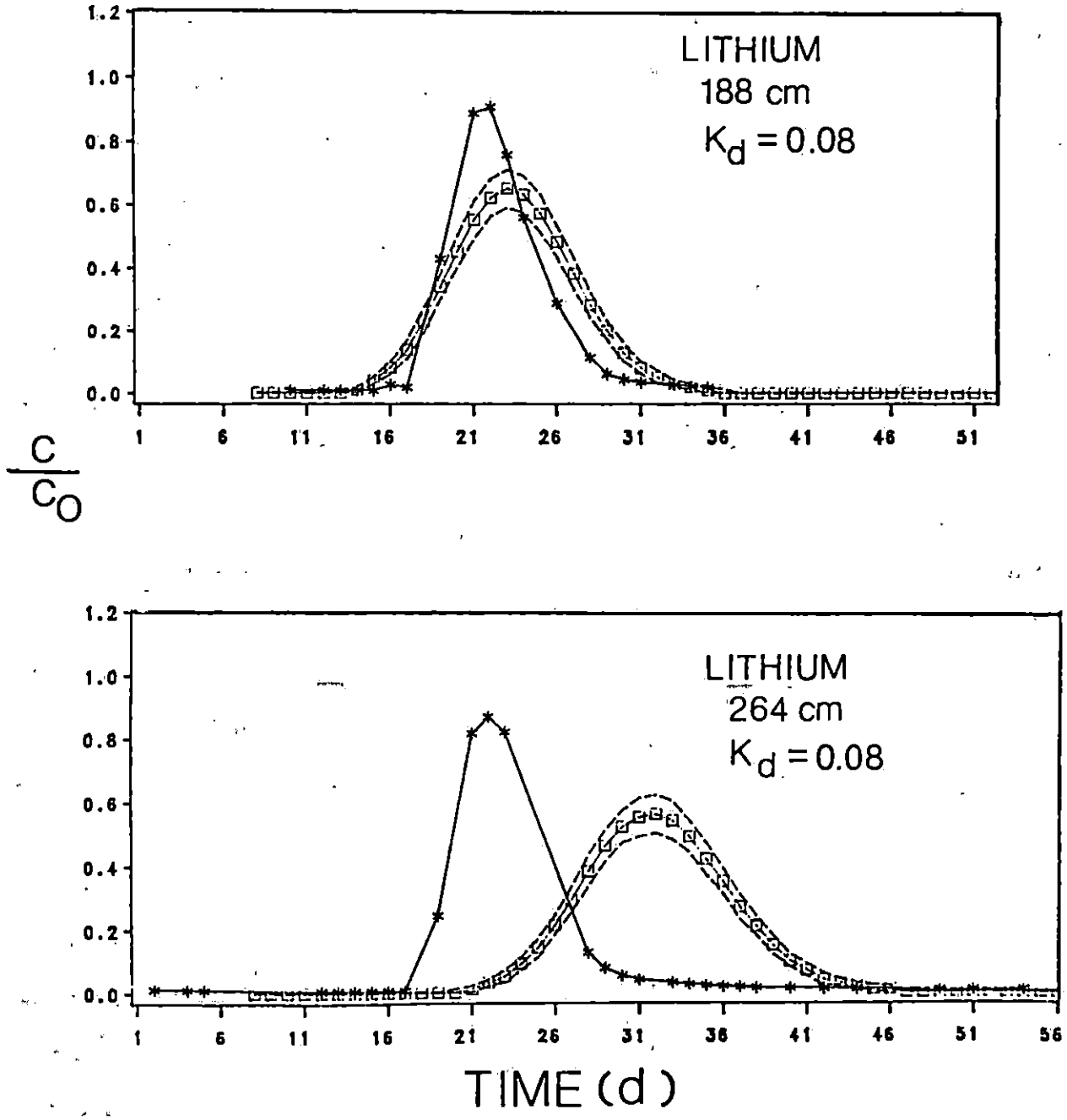

Figure 10. Comparison of measured (*) and predicted (□) at the 188- and 264-cm depths with K_d = 0.08.

was found by a trial-and-error process to provide the best description of the data at these depths. No literature values for lithium distribution coefficients were found to compare with $K_d = 0.08$.

Disagreement between measured and predicted lithium was apparent at the 264-cm sampling depth with more rapid appearance of the measured lithium at that depth than was predicted. This observation was consistent with the comparison of measured and calculated bromide and iodide, as discussed above. It appears that all three ions were similarly affected by some experimental condition not well described by the average water flux and layer pore water volumes used as input to the CTMP model. Agreement at the two deeper depths (339, 415 cm) between measured and predicted lithium (Fig. 11) was somewhat better than for bromide or iodide at those depths. However, the measured peak continued to behave at those depths as if it had been accelerated in the caisson relative to its predicted distribution. This was not the same behavior as observed for the bromide or iodide, which were observed to be delayed at the two deeper depths (compared with the CTMP predictions). If all three ions were subject to the same physical flow conditions postulated as the reason for the bromide and iodide behavior, the difference in lithium transport beyond 264 cm was perhaps related to the interaction of lithium with the soil surface.

It is interesting to note the influence of a K_d value of 0.08-cm^3/g soil. Although this is a relatively small K_d, it does have substantial effect on predicted lithium distribution. Calculation of lithium displacement past the two depths of 188 and 264 cm is presented in Figure 12 for $K_d = 0$. Comparison of Figures 10 and 12 illustrates the difference in predicted time of maximum concentration at each of those depths, with a predicted maximum at 188 cm

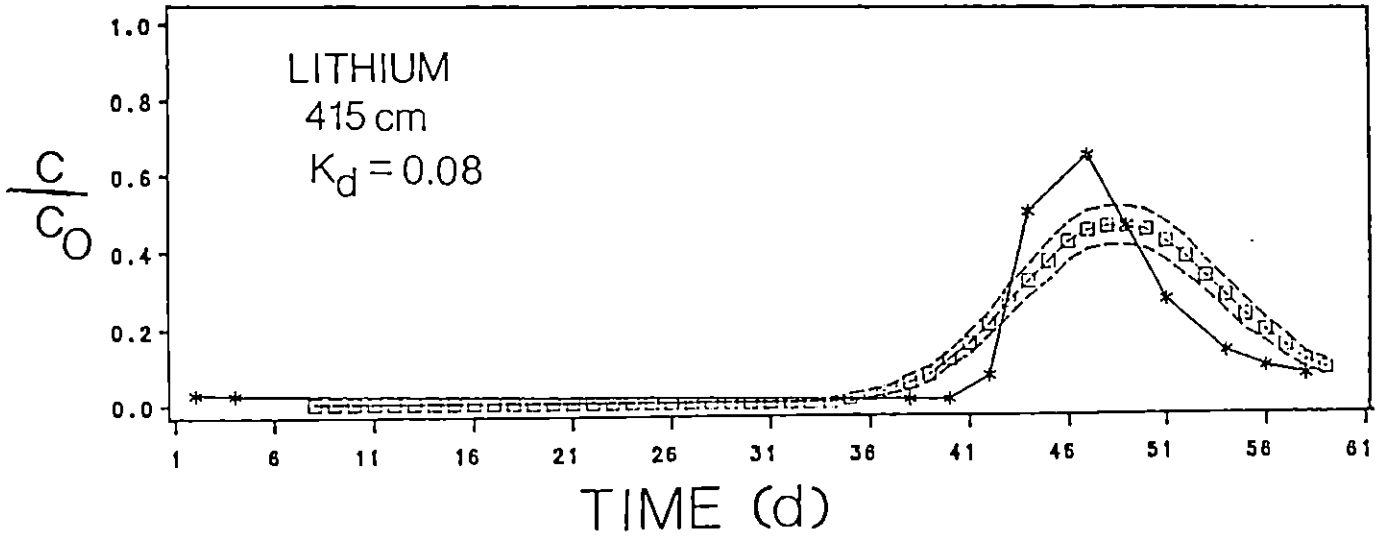

Figure 11. Comparison of measured (*) and predicted (□) lithium at the 415-cm depth with K_d = 0.08. No data available for 339-cm depth.

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after approximately 18 days when K_d = 0, compared with about 23 days when K_d = 0.08. It is also interesting to note that the 264 cm depth was well fitted by CTMP predictions when K_d = 0. This agreement is apparently coincidental given the comparison of measured and predicted values at others depths with K_d = 0.08. Such coincidental fit of measured and predicted concentrations reemphasizes the need for multiple observations of solute behavior with depth and time to gain a reliable estimate of leaching dynamics.

Strontium

The CTMP model was unable to describe the observed strontium data and no comparisons of measured and predicted values are included.

As explained under METHODS, the unsteady volumetric water flux required to predict strontium transport was developed from the measured outflow rates for each time interval between measurements. The interaction of strontium with the soil was described using a K_d = 0.9-cm^3/g soil (Fuentes et al. 1985). Using these values, the CTMP model predicted much more rapid transport of strontium through the caisson than was observed (Polzer et al. 1985). Predicted strontium distributions using the unsteady-state version of the CTMP

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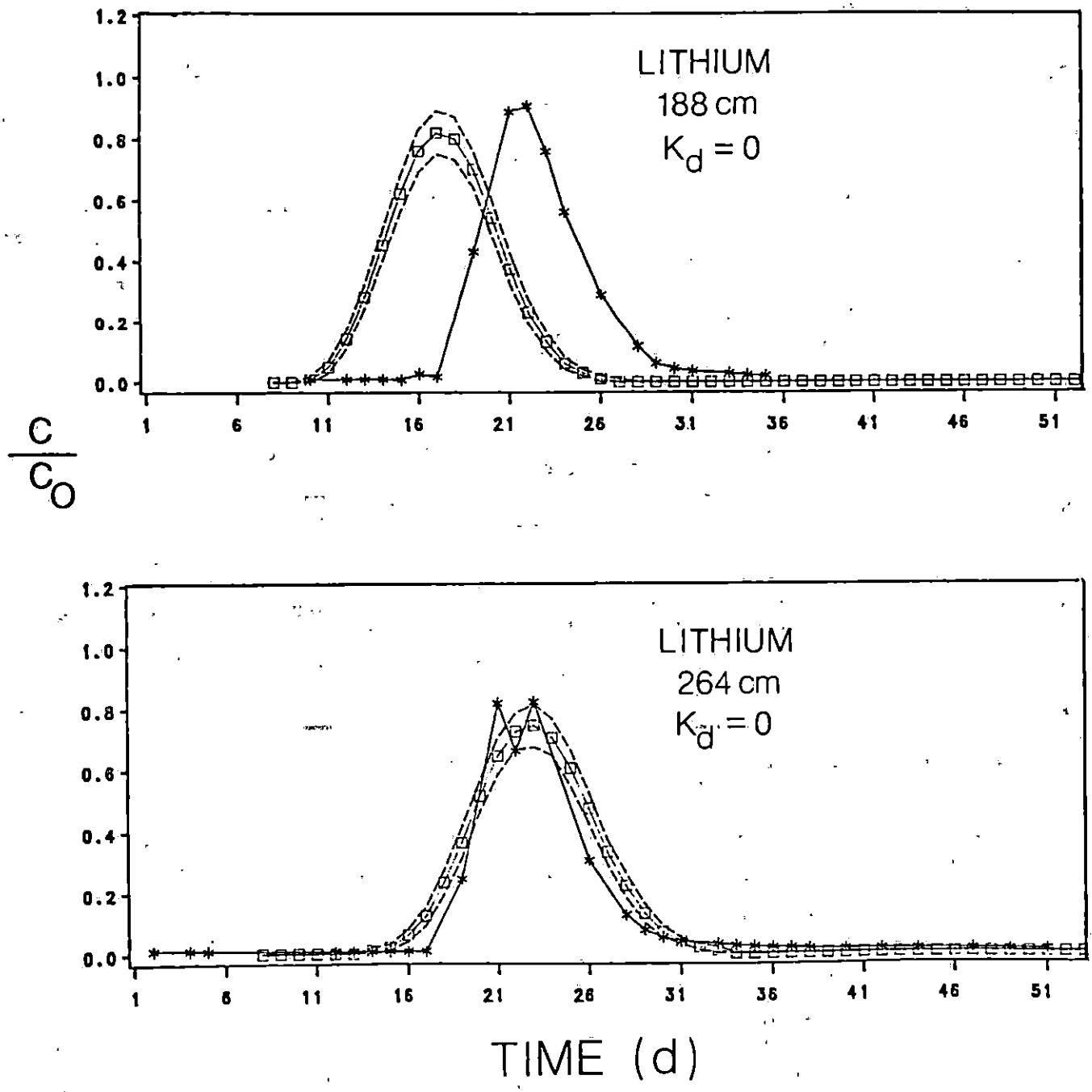

Figure 12. Comparison of measured (*) and predicted (□) lithium at the 188- and 264-cm depths with $K_d = 0$.

model and the measured conditions in the caisson are summarized in Figure 13. The model predicts that all strontium will have passed beyond the 415-cm depth within 42 days after application of the unsteady state pulse. Measured data indicated that the strontium did not reach a maximum concentration at 415 cm until approximately 200 days after application of the pulse. There is clearly a substantial discrepancy between the simulated and measured values.

It was initially thought that disagreement between CTMP predictions and measured strontium concentrations was due to an unreasonably small value of K_d used in the simulations, although a K_d = 0.9-cm^3/g soil was larger than the value reported by Polzer et al. (1985) for strontium. We eliminated this possibility by executing the CTMP model and using a steady state flow rate of 200 cm^3/min over the entire time period. Predicted and measured strontium then agreed much better, although the degree of agreement was not comparable with lithium (Figures 9-10).

It appears that execution of the unsteady state form of the CTMP model for the conditions of the caisson experiment, which is accomplished using multiple incremental additions of water as determined by the measurement schedule, has exposed a possible weakness in the structure of this form of the model. Previous validation of this model has been accomplished using field data of bromide and nitrate leaching (Knighton and Wagenet 1985b). The CTMP predictions of solute distributions with depth and time agreed quite well with measured values. However, in that study the magnitude of volumetric water fluxes was small, and the period of simulation was not as long as in the caisson experiment. Use of the CTMP model to describe the relatively large water fluxes and long times of simulations in the caisson study was not nearly as successful. Given these considerations and the resulting uncertainty

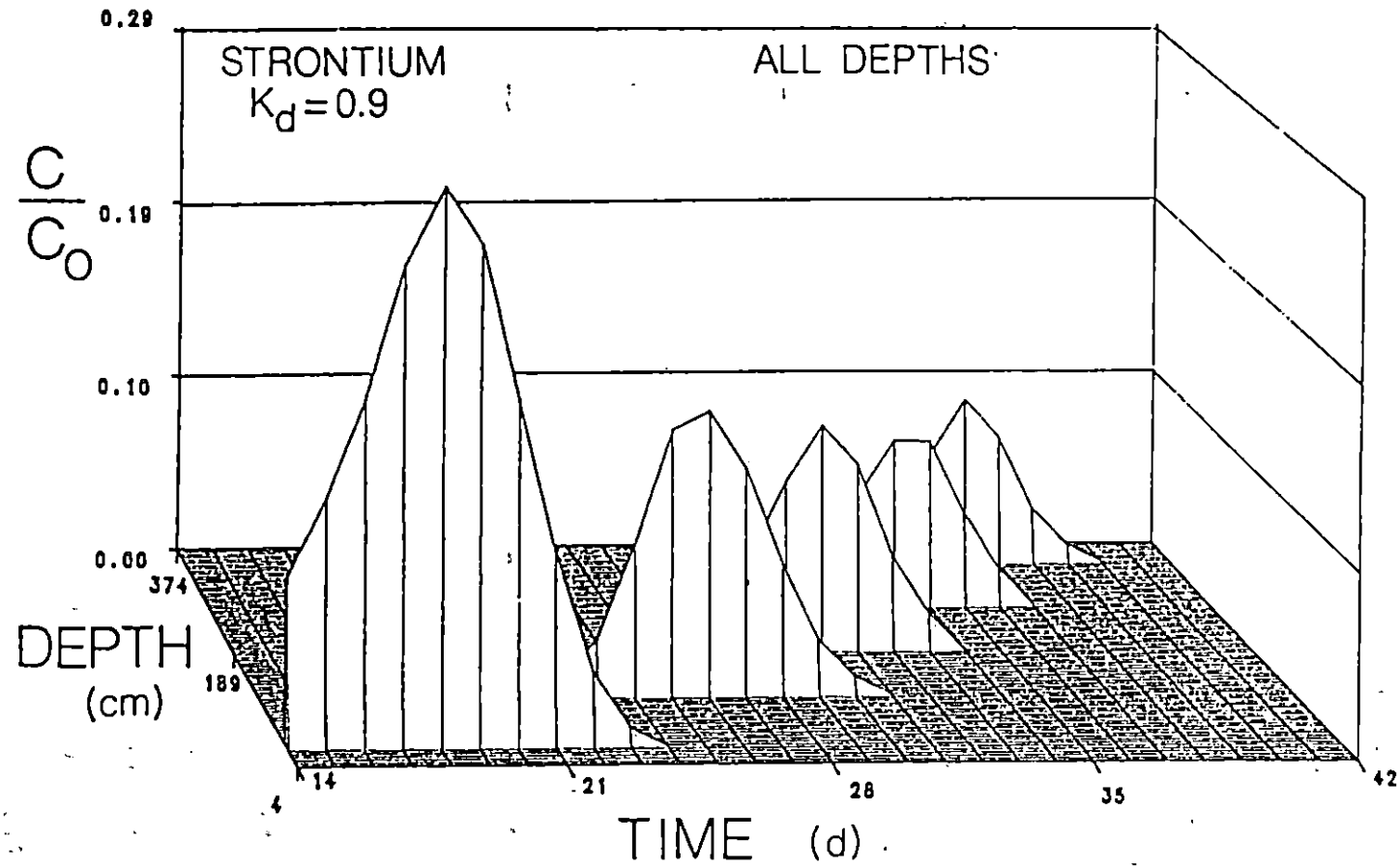

Figure 13. The behavior of strontium as simulated by the CTMP model under the unsteady state conditions in the caisson.

about predicted strontium concentrations, no comparison of measured and predicted strontium is presented.

SUMMARY AND RECOMMENDATIONS

Simulation of solute transport using a continuous-time Markov process is a new approach for modeling chemical movement in soil. CTMP has proved to be a reliable descriptor under steady state laboratory conditions, both here and in studies discussed by Knighton and Wagenet (1985a). CTMP approach was successfully used to describe bromide and nitrate movement under transient field conditions (Knighton and Wagenet 1985b) but it was not able to simulate transient strontium displacement in the current study. Whether this was due to a flaw in the model formulation or was simply a function of the strontium behavior in the caisson is not clear at this point but deserves further attention.

A final point should be considered as the predictive capabilities of the CTMP model are evaluated. As stated above, layer thickness is one of the few input variables required by the model. Previous soil column studies (Knighton and Wagenet 1985a) showed that simulated solute displacement was sensitive to the number of layers used. In those studies, conducted in 1.4-m soil columns and focusing on bromide movement under steady state flow conditions, decreasing the layer thickness from 5.0 cm each to 2.5 cm each (increasing the number of layers) decreased the dispersion about the peak. In those studies, an optimum layer size was selected on the basis of simulations of experiments conducted using homogeneously packed soil columns. A 5.0-cm layer worked well for one soil, while a 3.3-cm layer was found to work best for two other soils. The size of the layers is well within physical reality and corresponds to sample sizes commonly taken in laboratory and field experiments. It is clear that layer size introduces a numerical dispersion, but it appeared from those

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studies that layer width can be related to texture or particle size. More research is necessary to define layer size as a function of texture or some physical process.

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DISCUSSION

C. F. Keller

I noticed that if you use the K_d of .08, you get the timing right but the pulse width is wrong, and if you use a K_d of 0, you get the timing wrong and the pulse width looks fine.

R. E. Knighton

There is basically a dispersion problem. We found in doing the steady state experiments that the dispersion was very much related to the number of layers we used to model the process. What we found from previous experiments was that 5-cm layers worked best for this particular bulk density or void volume process. When we retard the flow, we need to look at the number of layers we use in the model. We're working on other relationships right now to formulate the number of layers we need for a particular pore volume.

W. A. Jury

When you use the model this way with a constant intensity of transition, you get something that is very much like a chromotography model with your dispersion effect built in, and this is tied to the one-dimensional assumption that you make. When you generalize this and develop an intensity of transition that fills the full matrix and get your exponential matrix solution, can you solve it? That is a nice formal solution but mathematically is rather difficult.

R. E. Knighton

I was going to present the numerical solution we use to solve the exponential matrix. I found that it worked quite well. It is a solution which combines an approximation to solve the exponential matrix and a process of scaling and squaring to get the value down within a region where the approximation works well.

W. A. Jury

Another question: are you trying to model these off-diagonal elements and relate them to physical processes in the same way that you did in the diagonal elements by assuming that water flow is to be divided by the pore volume element? Do you have some reason for filling in these off-diagonals?

R. E. Knighton

Physically I don't think there is any reason to because we assume that flow is only occurring between adjacent layers. In the

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transient case of the model, we also considered upward flow. In that case, there would be another term stuck in the matrix so it would become a tri-diagonal matrix. I don't see any reason for putting any more things into the matrix unless you want to consider that there is a probability of transition from layer one to layer three, completely bypassing layer two.

W. A. Jury — I am not ready to concede that yet.

R. E. Knighton — Possibly there is an application to what some people are calling fingering. It may relate to the size of the layer you choose as well as to whether you need to consider some type of bypass flow. The model lends itself quite nicely to that type of application.

H. R. Fuentes — It seems now that at 264 cm we are getting a different effect. I have two questions. The first one is how did you find the 191 mm/min and was that just a simple arithmetic operation for the volumetric flow rate?

R. E. Knighton — I averaged the outflow rates over the simulation time period.

H. R. Fuentes — How sensitive can your prediction be to that estimate?

R. E. Knighton — The prediction would be very sensitive because the outflow rate tells you where the peak should be.

H. R. Fuentes — What is the average percent difference between the observed and predicted values?

R. E. Knighton — That is very difficult to say because I don't think you can really quantify the applied mass from the data set that we were given. Initial concentrations and average inflow rates were used to calculate the mass of applied solute. We made no attempt to try to fit the pulse time with any type of mass balance. We simply don't have those type of numbers.

M. D. Siegel — How thick were the layers that you assumed in your model?

R. E. Knighton — Five centimeters.

M. D. Siegel — Was there any contrast between layers?

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R. E. Knighton — No.

M. D. Siegel — Do you think there may have been some contrast in the properties between the immediate surroundings of the samplers and the samplers? The samplers were inserted in a rock flour and then put into the larger particle matrix. Do you think that could have affected the results?

R. E. Knighton — I am certain that it would affect flow properties. It appears that simulations using average values in the presence of other variabilities aren't too bad.

A. L. Gutjahr — For the modeling in the one-dimensional case that you talked about, doesn't this Markov formulation break down into pure Poisson so that you could really do the whole thing that way?

R. E. Knighton — I am sure you could.

A. L. Gutjahr — I think in the one-dimensional case it does. I think I can see the reason for filling in the whole matrix if you took a slightly different point of view, in fact, where you can look at different materials that are there and you consider different transitions from material to material.

R. E. Knighton — We did try to do that with the strontium data. We looked at volumetric water content changes within each 5-cm increment, which reflected a difference in porosity. These changes didn't seem to make too much differences in the predictions.

D. J. Goode — I am trying to understand the difference between the modeling you have done and an application of the standard advection-dispersion equation. My feeling is that if you use a velocity in the advection-dispersion equation which corresponds to your 191 and you use a dispersion coefficient which corresponds with your 5 cm layers, you are basically going to generate the same results.

R. E. Knighton — In the first place, we are not trying to model any specific kind of mechanisms, although we do use the flux as the intesnity of transition. The advantages are that you can easily incorporate other sources and sinks into the model which are reflected in

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the intensity of transition. In the field case I showed, we actually included plant uptake, microbial degradation, and a few other things. They are very easy to incorporate into the model from the standpoint where you don't have to really think about a mechanism. You can think of it as a stochastic process where you now have coefficients that are determined experimentally. You also get a degree of confidence in your estimate because you are looking at a statistical distribution of the solute. I suppose it can be argued that the convective-dispersive equation can also give you that if you look at what the dispersion coefficient and velocity really mean.

D. J. Goode

It raises another problem though, especially in a more complex situation, in terms of data analysis. You use your model to match a situation where all you get out of it are these transition strengths and you don't get any information on underlying controlling processes, like root uptake or biodegradation, etc.

R. E. Knighton

But by sensitivity analysis you can surmise which one of those properties is having the largest impact on the process though you are not describing the process mechanistically. You can attribute how much of the process is being controlled by each one of those variables.

A. L. Gutjahr

This kind of procedure might also lend itself to more of a residence-type interpretation.

R. E. Knighton

That is what I mentioned before. You can compute residence times from this type of application.

R. J. Wagenet

Concerning the nature of this model compared to the convective-dispersive equation, you might want to distinguish mentally between this type of approach and one that is based on basic mechanism in the sense that we are not trying to use this model to understand or discern basic process. This is more of a management approach in the sense that you are using a minimum of inputs to predict with some level of confidence the distribution of the chemical with depth and time. It is really not designed to study the relationships between pore-water velocity and apparent diffusion coefficient. So you want

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to be careful and distinguish the research-oriented tool from the management one.

J. C. Parker

I would certainly be hesitant to say that there is some mechanistic interpretation to the convective-dispersive equation any more than this approach.

I. P. Murarka

Are probabilities a function of porous media, chemical, and the hydrology or is it strictly defined as a function of the flux at any distance or any xyz location you want to choose in relation to a starting point?

R. E. Knighton

It depends on how you define your basic process.

I. P. Murarka

No basic process -- it is all random with the molecule randomly doing whatever it does and that random event is strictly denoted and represented by a value between 0 and 1.

R. E. Knighton

The basic process is not truly a stochastic process because we have imposed diffusion with linear drift by including the flux, which is deterministic, as the intensity of transition.

I. P. Murarka

But I am trying to go to even more of a starting level than that. On a single-molecule basis, if you introduce one single molecule, there exists the probability that is nonzero for certain distance and may become zero after a while. Now the basic process is strictly based on a molecule introduced in the porous medium will do whatever it does because of physics, chemistry, or anything else going on. We just don't know exactly how it will behave if we knew the physics and chemistry. Therefore, we are going to present that by saying it has a finite nonzero probability of moving from here to there. If we have a bundle of these molecules introduced, we still have the question how to choose a single probability value and is that probability value definable as some function of some physical condition of the environment, as a chemical condition of the chemical of interest and then the process called the transport, the water movement, etc. Unless we go back and forth between that, somewhere down the road we almost have to say it is judgment, i.e., pick a value between 0 and 1.

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R. E. Knighton

That is a real problem, but as we have defined it, the transition probability is derived from flux or plant uptake or whatever terms you put in there.

I. P. Murarka

I just wanted to state that a little differently. You are only worrying about solution molecules, so if there are things coming from different phases in and out of solution, you really don't have the appropriate probability functions defined for them.

R. E. Knighton

Those probabilities can be incorporated quite easily.

I. P. Murarka

You have to define the marginal or joint pdfs, and that can be rather tricky when you are trying to meet the concern of every probability adding to one. It is easy to define but operationally rather difficult to conduct. I noticed that in several of your calculations and predictions the total mass and solutions using the approach is higher than the observed mass under the curves. That is a fundamental problem as I see it.

R. E. Knighton

It relates to the fact that we made no attempt to fit mass with effluent concentration.

I. P. Murarka

Take the observed concentration curve and look at your curve. The area under the curve computed by the method is much larger than the area under the observed curve. The total mass in solution being computed by you is larger based on molecules than the pdf approach. As you are using the transport phenomenon, it seems to me that whatever the assumptions are in computing the probabilities based on flux or water movement, there is something additional going on that is not quite defined by the processes in the model.

J. C. Parker

I think this is an input problem. The problem is that he is assuming that they put in the advertised concentration for the advertised 6-day duration. That is the mass you see under those curves.

R. E. Knighton

For the amount of solution that went in during that time, the mass balance is right on as far as the model in concerned.

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I. P. Murarka

I think the mass balance is much better at the earlier depth, and as you go further, the mass balance is drifting and so it is not an input problem anymore.

R. E. Knighton

Part of the problem is that when solute is moved down into the deeper depths, you no longer have a closed system. You actually have some molecules leaving the system depending on how many layers you choose to model the system with. There now is no way that the probabilities can sum to one and the mass looks different.

I. P. Murarka

I think the assumption about identical and dependent media for each molecule is your problem. I think there are some off-diagonal elements that are nonzero on your transitional probability matrix and therefore you are getting a drift because of that.

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TIME AND FREQUENCY DOMAIN ANALYSIS OF TRACER MIGRATION IN CRUSHED TUFF

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INTRODUCTION

The interpretation of tracer experiments for the estimation of transport parameters has followed a number of strategies. Aris (1958) introduced a spatial and temporal moment estimation approach, where the evolution of mass, center of gravity, and dispersion about the center of gravity are estimated from discrete space or time distributions of the tracer. Valocchi (1985) provides a recent discussion of this approach for the interpretation of column tracer tests, and Freyberg (1985) presents the equations for field-scale tracer analysis by the moment method. One disadvantage of the method, as pointed out by Gangwal et al. (1971), is that noise or errors in the lower moments have a cumulative effect on the estimation of higher moments. Nonetheless, it appears to us that the moment method is presently the preferred method of estimating transport parameters from field data, due to its relative independence of model assumptions and its ease of implementation requiring only a simple integration of the tracer breakthrough.

Another approach to parameter estimation of tracer experiments was proposed by Gangwal et al. (1971) where classical Fourier analysis was applied to the problem. In this case the parameter estimation is done

entirely in the frequency domain by comparison of the theoretical and experimental frequency response functions. The complication of this method is that the experimental breakthrough must be "Fourier transformed"; however, this is done without complication by the fast Fourier transform (Brigham 1974). With regard to the analytic theory, the method has some advantage because closed-form solutions are often easily found in the transform or frequency domain, while time domain solutions may not even exist (i.e., for nonequilibrium adsorption, complex inputs, etc.). Also Gangwal et al. (1971) have shown that in contrast to the moment method where a buildup of errors occur, the "noise" content of a given experiment is more or less constant or evenly distributed over all the harmonics in the experimental frequency response function. In addition, Duffy and Gelhar (1985) have shown that the frequency domain method can be directly extended to situations where the source strength is a nonideal time-varying or stochastic process.

In the present study, we will compare the time moment method as presented by Valocchi (1985) and Himmelbau (1970) with the frequency domain method for transport parameter estimation for the LANL caisson experiments. Parameters for several tracers will be estimated and compared using the time and frequency domain methods to be outlined next. Some speculation is presented regarding the nature of local and macrodispersive effects in the experiment, including some indication concerning the effect of uncertainty in the velocity, source strength, and random measurement errors on the overall interpretation of the experiment.

DESCRIPTION OF THE MODELS

A theory for axial dispersion in a one-dimensional, semi-infinite flow field ($0<x<\infty$) can be expressed as

$$R\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} = D\frac{\partial^2 C}{\partial x^2}, \qquad (1)$$

where u is the velocity of the solute, $D = a_L u$ is the dispersion coefficient, a_L is the dispersivity length scale, and R is the retardation factor for linear equilibrium adsorption. Along with the boundary and initial conditions $C(0,t) = C_o(t)$, $C(\infty,t) = 0$, and $C(x,o) = 0$, the above theory provides the basic framework for the interpretation of the tracer experiments to follow. In this study only linear equilibrium adsorption will be examined. However, more complex theories for physical, chemical, nonequilibrium adsorption, interparticle diffusion, etc., constitute a straightforward extension of this approach.

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PARAMETER ESTIMATION METHODS

The Time Domain Method (Moment Method)

For a soil column subject to a pulse injection $C_o\,\delta(t)$ of tracer (δ is the Dirac delta function), the nth time moment of the concentration distribution at any downstream location can be characterized by

$$M_n = \frac{\int_o^\infty t^n C(x,\ t)\ dt}{\int_o^\infty C(x,t)\ dt} \quad n = 0,\ 1,\ 2,\ 3,\ldots, \qquad (2)$$

where C is concentration, x and t are distance and time respectively, and the integral in the denominator is a measure of the total tracer mass. Himmelbau (1971) showed that the first and second time moments of the concentration breakthrough can be related to the velocity and dispersivity of the system through the following expressions:

$$M_1 = xR/u \quad \text{or} \quad u = xR/M_1 \tag{3}$$

and

$$M_2 = M_1^2 + 2a_L xR^2/u^2 \quad \text{or} \quad a_L = u^2(M_2 - M_1^2)/(2xR^2). \tag{4}$$

Estimation of M_n is accomplished by numerical integration of the experimental solute response by means of Equation (2) for each of the n moments desired. As was mentioned in the introduction, because of the fact that errors in low-order moments produce larger errors in higher-order moments, we generally only compute the n = 1,2 and perhaps n = 3 time moments.

The above analysis depends on being able to represent the tracer injection by a delta function, a mathematical idealization that physically can only be approximated, since a finite amount of tracer must be injected into the column in zero time (Himmelbau 1970). Aris (1959) and, more recently, Valocchi (1985) have described methods that do not require a perfect delta function but rather can accommodate any pulse-like input, as shown in Figure 1.

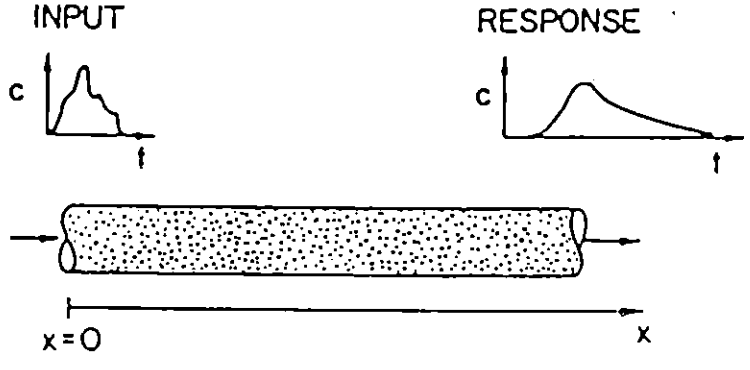

Figure 1. Representation of a nonideal pulse input of tracer (Valocchi 1985).

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For nonideal (i.e., non-Dirac) inputs, it is necessary to apply a correction to the computed moments of the tracer response, which account for the time moments of the source function. For a pure Dirac pulse, the source function is defined as (Kreft and Zuber 1980)

$$C(0,t) = \frac{m}{u\theta}\ \delta(t)\ , \tag{5}$$

while the source function for a non-Dirac pulse is given by

$$C(0,t) = \frac{m}{u\theta}\ F(t)\ , \tag{6}$$

where $F(t)$ has pulse-like shape with $\int_o^\infty F(t)dt = 1$, m = mass per unit cross-sectional area, u is the pore velocity, and θ is the moisture content. To use the moment method for estimation of transport parameters [Equations (3) and (4)] for the nonideal pulse described by (6), Himmelbau (1970) showed that a simple correction to the concentration moments can be made:

$$M_n^{\delta} = M_n^{F} - \upsilon_n\ . \tag{7}$$

where the δ and F superscripts refer to the ideal and nonideal pulse moments, respectively. The correction υ_n is the nth central moment of the tracer source

$$\upsilon_n = \int_o^\infty (t - \hat{v}_1)^n\ F(t)dt,\quad n = 2,3,\ldots, \tag{8}$$

where

$$\hat{v}_1 = \int_0^\infty t\, F(t)dt. \qquad (9)$$

Thus we can simply subtract the effect of the nth moment of the non-Dirac source to produce the desired moments for an ideal pulse.

For the caisson tracer experiments to be examined in this study, a finite-width step input or square wave pulse was used. For a base width of T_o, the mean of F(t) is given by $\hat{v}_1 = T_o/2$, and the variance, $v_2 = T_o^2/12$.

These corrections, along with Equations (3) and (4), were used to estimate the dispersivity, velocity, and retardation coefficient. The moments were estimated using a trapezoidal approximation to the integral in (2).

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Frequency Domain Method

The use of Fourier analysis for the interpretation of column tracer experiments has been examined by Gangwal et al. (1971) and others in the chemical engineering literature. In the field of hydrologic research, Thomann (1972) discusses the use of frequency domain methods for the evaluation of water quality in surface water systems subject to inputs of Fourier series type. Duffy and Gelhar (1985) have extended the analysis of Thomann to include water quality sources that have a stochastic nature. They suggest that identification of transport parameters from water quality signals, which contain a continuous range of frequencies and amplitudes, is most appropriately accomplished in the frequency domain. The upshot is that the method can be applied to any source type including simple deterministic signals, Fourier-type periodic or aperiodic signals and stochastic signals alike, provided the signal has a Fourier representation (i.e., a Fourier series or integral representation). The same basic theory applies in each case.

Although frequency domain analysis is the preferred method for many researchers who deal with extensive data and complex signals (e.g., seismologists, communications engineers, radioastronomers) in hydrology and environmental sciences, the approach has received little attention. In this section we will briefly review the theory behind the frequency domain method for mass transport analysis and the equations necessary for optimal estimation of parameters.

The column experiments to be examined in this study can conveniently be described by the input-output relation known as the convolution or Duhammel integral:

$$C(x,t) = \int_0^\infty h(x,t-\tau)C_o(\tau)\, d\tau \ , \qquad (10)$$

where $h(t)$ is the impulse response of the column, $C_o(\tau)$ is the input source [Equation (6)], and $C(x,t)$ is the output or concentration time series at any point in the column. The impulse response for this case is given by

$$h(x,t) = x(4\pi Dt^3)^{-1/2} \exp\{-(x-ut)^2/4Dt\} \ , \qquad (11)$$

where $D = a_L u$ is the dispersion coefficient. The result in (10) can be extended to the frequency domain by taking the Fourier transform of $h(x,t)$, $C_o(\tau)$, and $C(x,t)$ which leads to

$$C(x,f) = C_o(f)\, H(x,f) \ , \qquad (12)$$

where $C(x,f)$ and $C_o(f)$ are the Fourier transforms of the solute response C and the source $C_o(\tau)$. $H(x,f)$ is the Fourier transform of the impulse

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response or the frequency response function, and f is frequency in cycles/time unit. Equation (12) shows that in the frequency domain the convolution integral (10) is simplified to a multiplication. The theoretical form of the frequency response for (11) is given by

$$H(x,f) = \exp\{ux/2D\ (1 - (1+4i2\pi fD/u^2)^{1/2})\} , \qquad (13)$$

where $i = \sqrt{-1}$. The effect of linear equilibrium adsorption is a simple adjustment of the velocity $u^* = u/R$. The frequency response $H(x,f)$ is a complex quantity that contains information on the transfer function, or amplitude attenuation between input and output frequencies, and the phase, which contains information concerning the lead or lag between frequency components in the input and output time series. The transfer function is defined as

$$|C(x,f)/C_o(F)|^2 = |H(x,f)|^2 \qquad (14)$$

and the phase Φ is defined as

$$\Phi(x,f) = -\tan^{-1}\{\text{Im } H(x,f)/\text{Re } H(x,f)\} , \qquad (15)$$

where Im $H(x,f)$ and Re $H(x,f)$ are the real and imaginary parts of the complex function $H(x,f)$. The theoretical transfer function and phase for the transport model assumed here are shown in Figure 7 of the paper by Duffy and Gelhar (1985).

Estimation in the Frequency Domain

According to Himmelbau (1970), the problem of frequency domain

estimation is used in lieu of time domain methods for three main reasons:

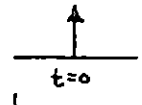
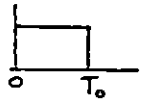
1. The analytical solution of the model may be simpler in the frequency domain than the corresponding solution in the time domain.

2. For some models of solute transport, analytic solutions can be obtained in the frequency domain but not for the time domain response. Or in some cases, the time domain analytic model is in integral form not easily implemented for parameter estimation, such as is the case when the input is a time-varying signal.

3. In situations where large amounts of data are available, the discrete Fourier transform of the time record is a convenient way to efficiently compress and store this information. Frequency domain estimation can be very efficient for large data bases, since time information is grouped and stored according to its discrete frequency content, which effectively compresses the data base.

For parameter estimation from a controlled-source tracer test, the most convenient form of input is the Dirac delta function $\delta(t)$, whose Fourier transform is simply 1. However, any pulse-like input that has a Fourier transform can be used. Table 1 illustrates the pulse and finite step inputs and their transforms.

Table 1. Time and frequency domain representation of the impulse and finite-step responses.

Type of input	x(t)	X(f)
 impulse at t = 0	$\delta(t)$	1
 finite step at t = 0	$U(t) = \begin{cases} 1, & 0<t<T_0 \\ 0, & t>T_0 \end{cases}$	$\frac{2\sin(2\pi f T_0/2)}{2\pi f T_0}$

In the case of a known deterministic input, the estimation problem is reduced to the estimation of parameters, which in our case are the dispersivity, velocity, and retardation coefficient. In the time domain, the least-squares estimation of parameters calls for a minimization of the function

$$\phi = \int_0^\infty \{C^*(x,t) - C(x,t)\}^2 dt \qquad (16)$$

with respect to the model parameters, with $C^*(x,t)$ and $C(x,t)$ the observed and model time responses, respectively. The equivalent function in the frequency domain is given by

$$\phi = \int_0^\infty |C^*(x,f) - C(x,f)|^2 df \ , \qquad (17)$$

where C^* and C are observed and model frequency responses, respectively. Since the source is known in this case, the experimental and theoretical frequency responses can simply be divided by the appropriate source term in Table 1, and (17) become

$$\phi = |H(x,f)^* - H(x,f)|^2 df \ , \qquad (18)$$

where H^* and H are the observed and model frequency responses, respectively. Solution of the estimation problem for a known input amounts to minimization of the above objective function with respect to the parameters. In this case an efficient nonlinear optimization computer package known as MINOS (Murtagh and Saunders 1980) was used. The

algorithm is fast and is not especially sensitive to poor initial guesses on the parameters. However, it does require analytical expressions for the derivatives, which may be a problem for more complex models. The final difficulty is the transformation of the experimental data from the time domain into the frequency domain. The general form of the finite Fourier transform is given by

$$X(t) = T^{-1}\int_0^T x(t)\ e^{-i2\pi f t}dt\ , \qquad (19)$$

where T is the interval of integration. Equation (19) was implemented using a fast Fourier transform (FFT) algorithm described by Brigham (1974), who also gives an excellent account of both practical and theoretical issues regarding the FFT.

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RESULTS AND DISCUSSION

In this section we examine the parameters estimated from the concentration breakthrough data taken from the various sampling ports in the caisson. We consider, the sampling-port data and the resulting parameter estimates to constitute local information, which is not necessarily representative of the total system tracer response of the caisson. In our view the total system response of the caisson can be viewed as a statistical collection of the individual local response functions. We will examine the "local" versus "global" system response subsequently.

Comparison of the Model and Observed Frequency Responses

Figure 2 illustrates typical results of the frequency domain parameter estimation technique described earlier. For interpretation we must first recall that the frequency response H(x,f) has two parts. The transfer

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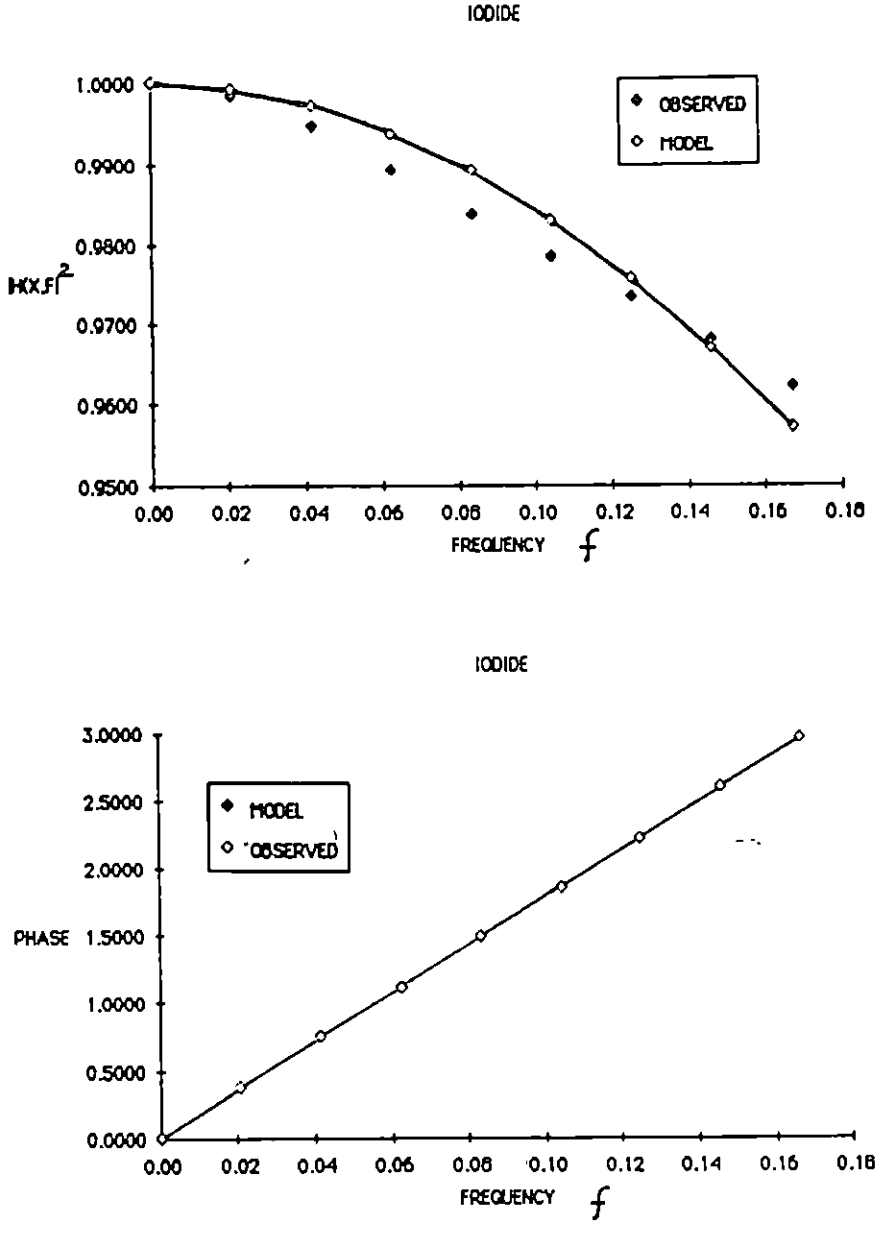

Figure 2. The theoretical and observed transfer function and phase versus frequency for iodide at the 180-cm-depth sampling port.

function describes the amplitude attenuation between source and measured signals as a function of frequency, and the phase measures the time lag as function of frequency. The minimization of the difference between H and H* is entirely equivalent to the time domain approach of fitting the solute breakthrough to the theory. However, in the frequency domain, the measured response $C^*(x,f_i)$ is actually a partitioning or grouping of time information into characteristic frequencies f_i in the data. The observed and model transfer functions and phases in Figure 2 illustrate the distribution of amplitude attenuation and phase lag over the discrete frequencies contained in the time record and its optimal estimator. This comparison results in estimates of the transport parameters to be examined next. A summary of all the estimated transport parameters is given in Table 2.

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Conservation of Mass

In order to see how the local mass of solute passing a point in the caisson compared with the total applied mass at the top of the column, we integrated the concentration breakthrough for each species by using a discrete approximation to the following integral:

$$m_i = Q \int_o^T (C(x_i,t) - C_i)dt \ , \qquad (20)$$

where m_i is the cumulative mass of tracer passing a point x_i, Q is the volumetric flow rate, T is the period of the breakthrough, and C_i is the initial or ambient tracer concentration of the feed solution. The results of the mass calculation for each species and each sampling port are given in Figure 3. The mass at distance zero is the input tracer mass. The iodide tracer shows a 10% to 20% sag in mass in the 113- to 339-cm portion

Table 2. Summary of estimated parameters for the caisson experiment.

Distance	Tracer	Observed Mass (gm)	Time Moment Analysis u	Time Moment Analysis a_L	Time Moment Analysis R	Frequency Domain Analysis u	Frequency Domain Analysis a_L	Frequency Domain Analysis R	No. of Harmonics
0	Iodide	289							
	Bromide	136.72							
	Lithium	11.76							
	Strontium	120.96							
36	Iodide	281.23	13.95	9.66		10.43	2.01	-	8
	Bromide	146.40	13.29	23.89		10.41	1.72	-	8
	Lithium	13.79	12.81	3.97		9.56	1.81	-	8
	Strontium	60.88	(10.43)	7.52	10.82	(10.43)	7.11	11.30	5
113	Iodide	241.11	12.28	3.20		11.20	1.04	-	8
	Bromide	137.11	12.12	4.77		11.12	0.945	-	8
	Lithium	11.72	11.99	7.80		11.16	2.57		8
	Strontium	38.19	(11.20)	3.50	6.115	(11.20)	3.35	6.165	6
188	Iodide	230.86	12.20	1.58		11.53	0.73		8
	Bromide		NA			NA	NA		
	Lithium	11.24	10.42	2.58		9.94	2.10		6
	Strontium	39.03	(11.52)	9.59	5.019	(11.52)	9.44	5.044	8
264	Iodide	224.35	15.59	3.13		14.86	1.32		8
	Bromide	116.12	16.78	5.77		16.04	1.60		6
	Lithium	9.44	13.99	4.17		13.55	2.26		6
	Strontium	24.26	(14.86)	1.95	6.58	(14.86)	1.91	6.64	8
339	Iodide	243.27	11.63	0.72		11.25	0.523		8
	Bromide	131.94	11.86	2.45		11.41	1.73		8
	Lithium								
415	Iodide	259.37	12.77	0.64		12.04	0.517		8
	Bromide	132.97	12.42	0.67		12.06	0.62		6

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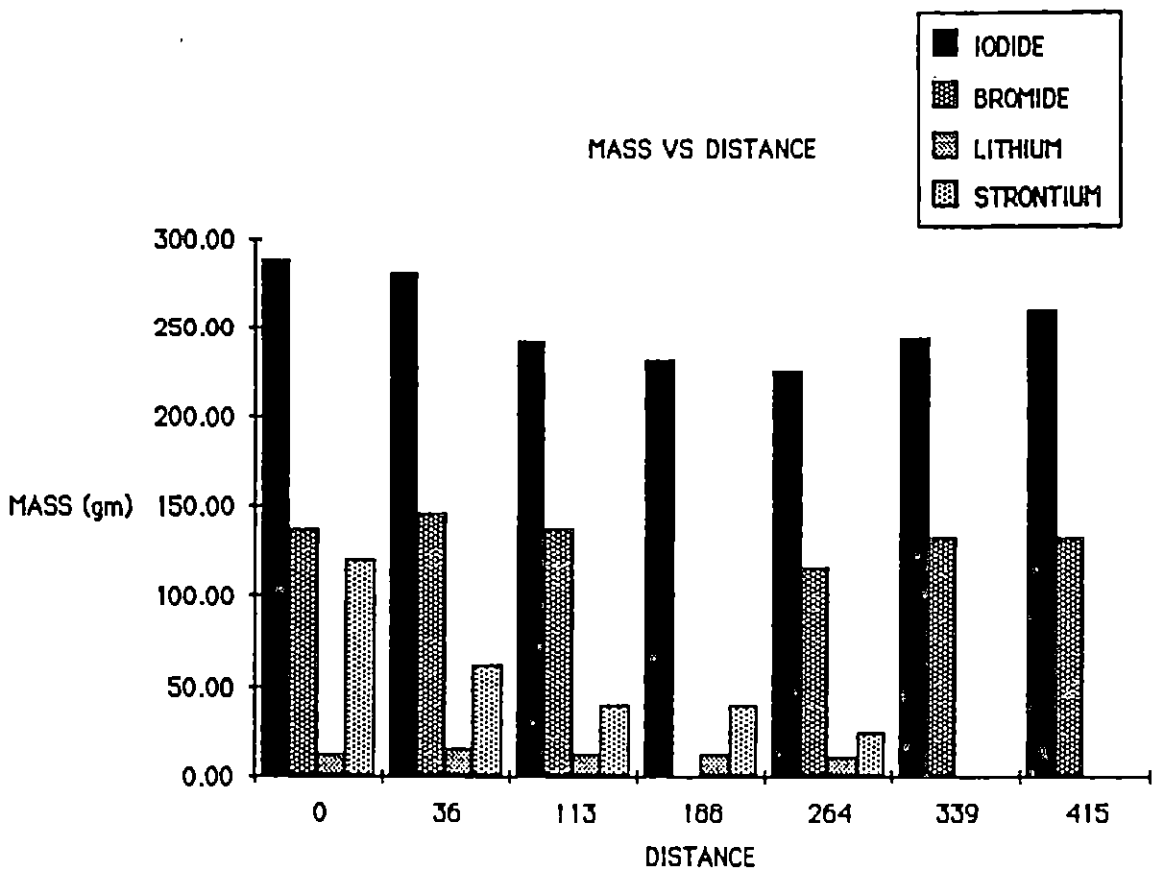

Figure 3. Cumulative tracer mass versus depth in the caisson (distance) for each tracer species.

of the caisson, while bromide and lithium were reasonably consistent throughout. Although there is some potential for lithium adsorption, these results suggest that it must be a minor mass exchange. The expected loss of dissolved mass for strontium with distance is evident in the figure. Overall, the results of these calculations seem to suggest that distribution of the tracer source in the caisson is reasonably uniform. However, since the tracer input was not measured continuously for each species, we cannot really tell if the observed changes in mass within the column are the result of fluctuations in the tracer source or spatial variability effects.

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Tracer Velocity

Both the time domain and the frequency domains methods were used to estimate the iodide and bromide tracer velocities. The estimated velocity in each case is actually an integrated value over the distance from the top of the caisson to the sampling port. Figures 4 and 5 summarize the resulting velocity estimates for bromide and iodide versus sampling depths in the caisson. The first observation is that the time domain or moment method always provides a slightly larger velocity estimate than the frequency domain method. Although the difference is not large for distances greater than 113 cm (1% to 5%), it does indicate that the velocity based on center of gravity (time moment) may not be the same as the fitted value for the frequency domain method at present. We are not able to evaluate this difference; however, it can be surmised that both estimators are consistent measures of the tracer velocity. It is also apparent that a higher velocity zone exists between the 188- and 264-cm level (u = 15-17 cm/d).

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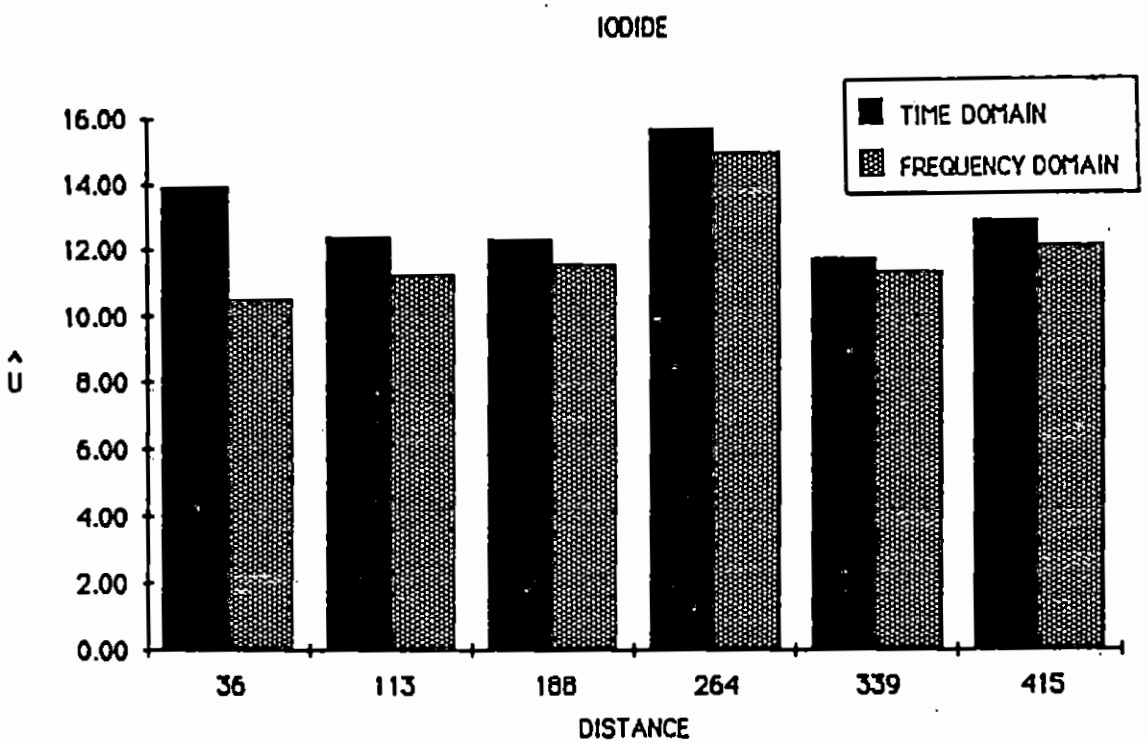

Figure 4. The estimated velocity versus sampling depths (distance) for iodide.

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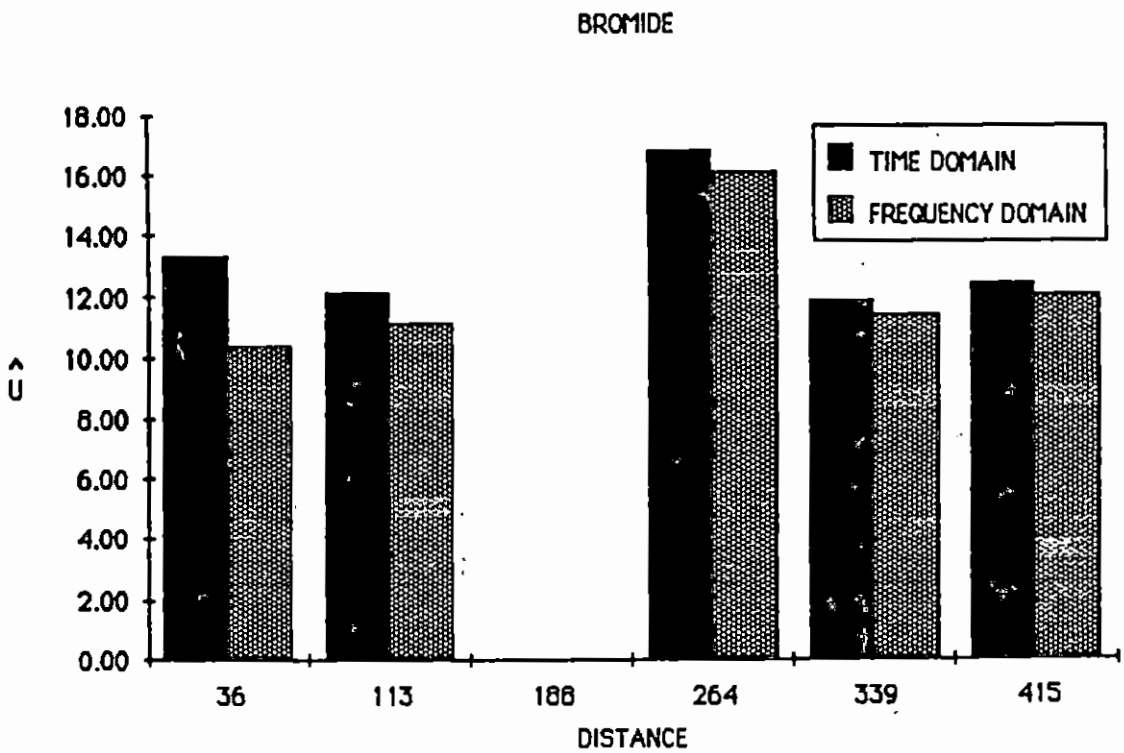

Figure 5. The estimated velocity versus sampling depths (distance) for bromide.

Local Dispersion

The solute response at each of the sampling ports also provides information on local dispersive characteristics of the crushed-tuff material. For the time domain method, the dispersivity length scale a_L is estimated from the minimization of (18). A comparison of the time and frequency domain methods for each of the tracers (iodide, bromide, lithium, and strontium) and all sampling depths in the column is provided in Figures 6, 7, 8, and 9. Beginning with the iodide results, we see that the moment method does not perform particularly well in estimating a_L especially in the upper half of the caisson, while in the lower part of the column the estimator is better behaved and closer to the frequency domain estimate. In general, however, the frequency domain method appears to provide a more consistent estimator. Our interpretation of this difference is that the second moment estimator [n = 2, in Equation (2)] is sensitive to random fluctuations in the tracer response (noise). As proposed by Himmelbau (1970), these fluctuations in the tracer response have a cumulative effect as high moments are estimated (i.e., n = 1,2,...) with less and less precision. Apparently this error diminished because the tracer response became "smoother" in the lower parts of the column. The advantage of the frequency domain method is that errors in the Fourier transform of the tracer response are more or less uniformly distributed over all the frequencies in the record, producing a consistent and stable estimator.

The estimates of a_L for bromide and lithium (Figures 7 and 8) show similar results with a_L in the range of 0.5-24 cm for the moment method. For strontium the estimated a_L from the frequency domain approach is again about 2 cm for the lower sampling ports, while the moment method varies from 2-8 cm. An important feature of the dispersivities estimated from the sampling ports is that there does not appear to be a so-called "scale

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9 2 1 2 4 5 8 0 8 3 4

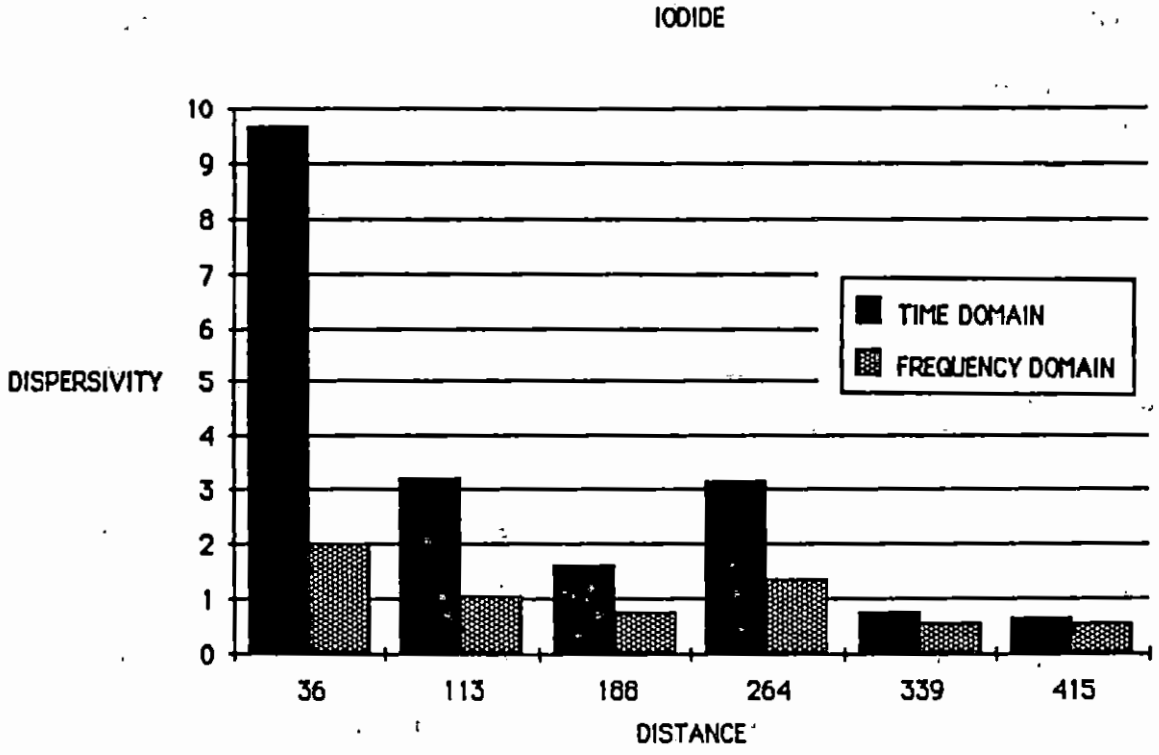

Figure 6. The estimated dispersivity versus sampling depths (distance) for iodide.

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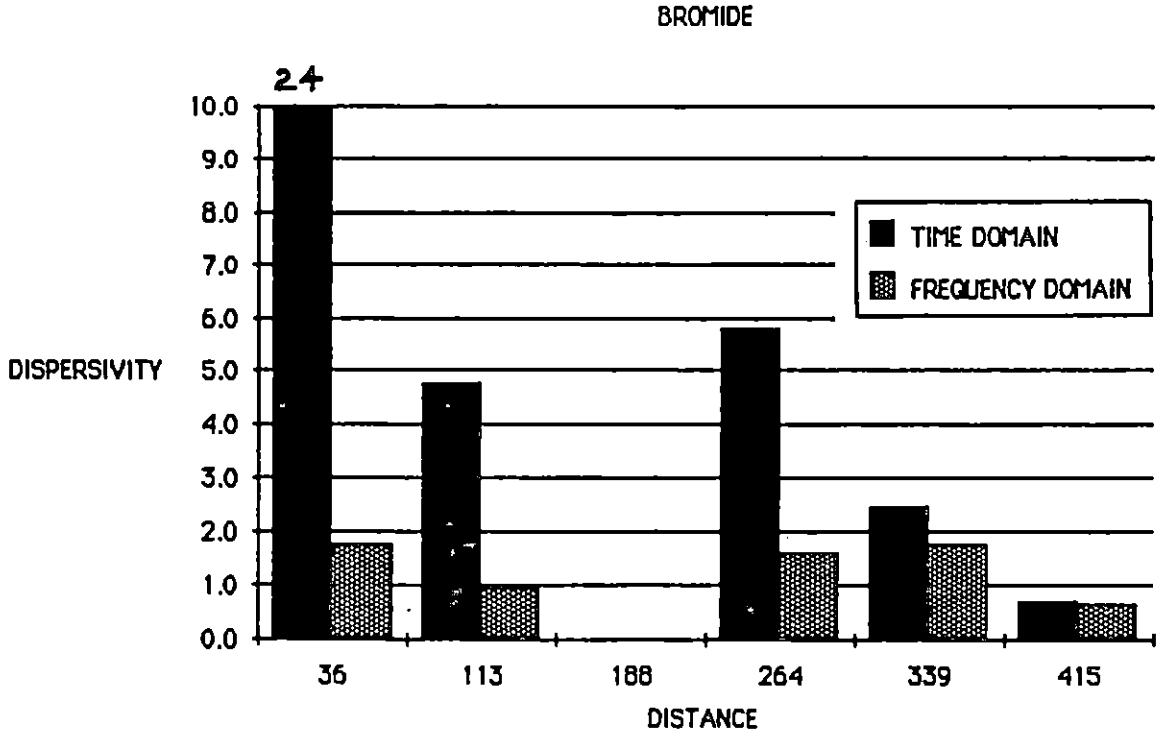

Figure 7. The estimated dispersivity versus sampling depths (distance) for bromide.

9 2 1 2 4 5 8 0 8 3 6

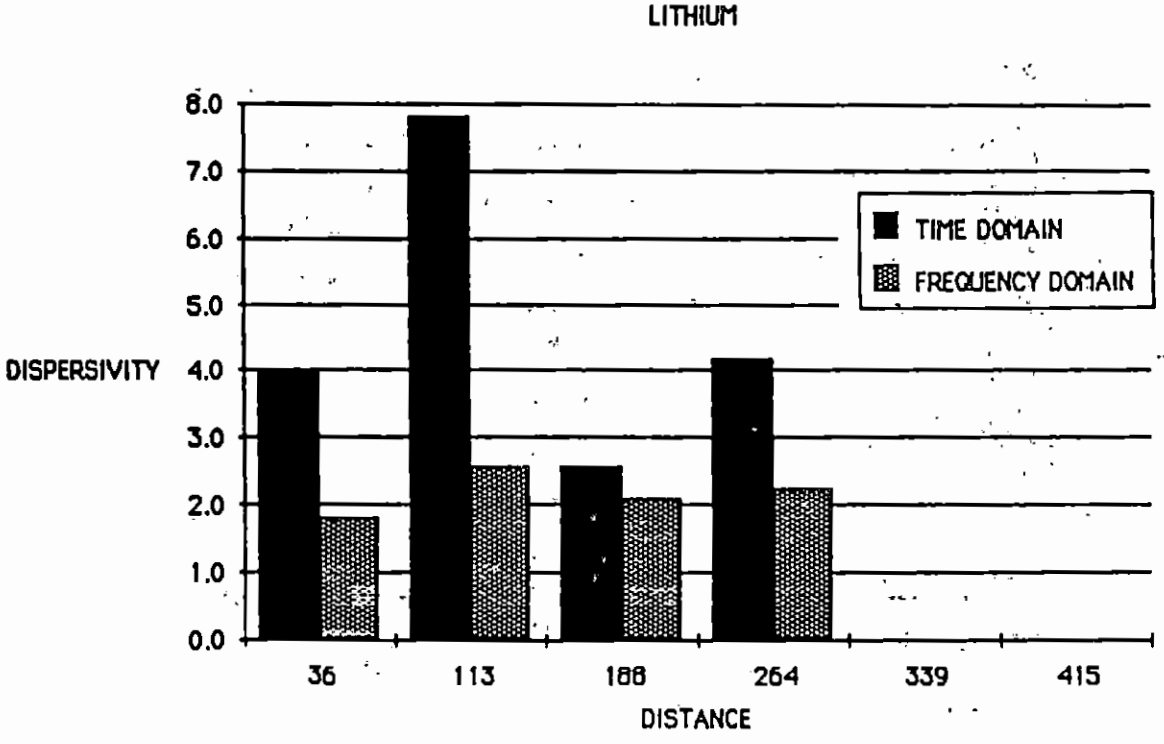

Figure 8. The estimated dispersivity versus sampling depths (distance) for lithium.

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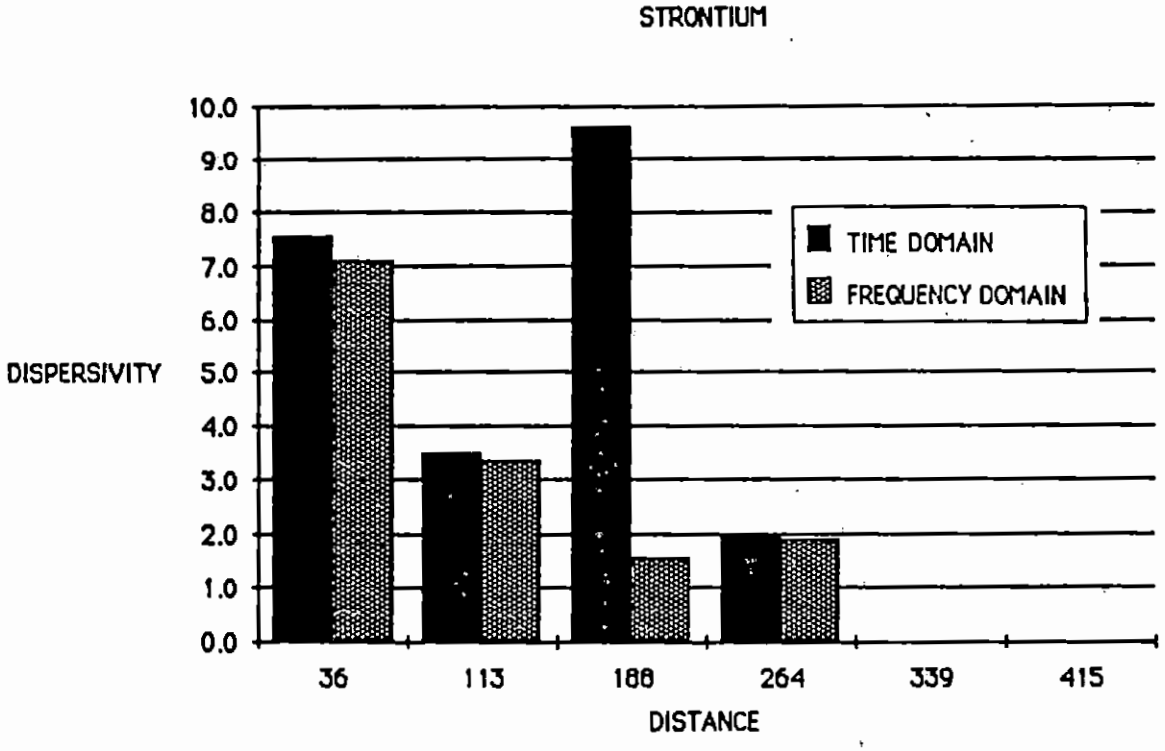

Figure 9. The estimated dispersivity versus sampling depths (distance) for strontium.

effect," or the length scale of dispersion does not appear to grow with distance as is typically observed in field-scale experiments. Another way to examine this is to determine the rate growth of the dispersed zone with depth in the caisson. A measure of width of the dispersed zone is given by

$$d\sigma_t^2/dx = 2a_L/u^2 \quad , \tag{21}$$

where σ_t is the standard deviation of a Gaussian distribution. The growth of σ_t with displacement distance x is then given by

$$\sigma_t = (2a_L x/u^2)^{1/2}. \tag{22}$$

Figure 10 is a plot of σ_t versus x, the sampling depth in the caisson for iodide, bromide, and lithium. A linear relationship seems to be reasonable for iodide and bromide, with the lithium plot inconclusive. A linear growth in the dispersed zone with distance would indicate a_L/u^2 is a constant and the process is reasonably represented as Gaussian.

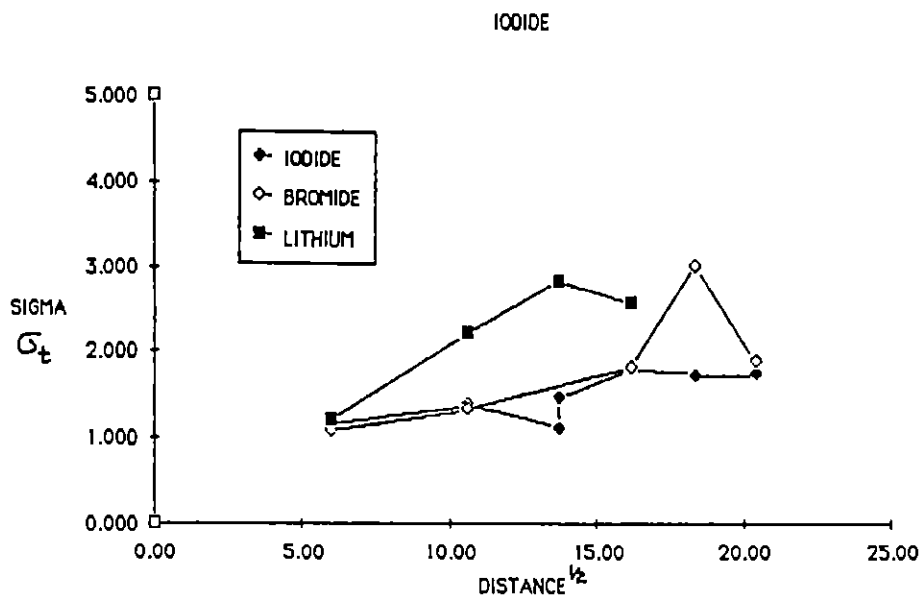

Figure 10. The "rate of growth" of the dispersed zone σ_t versus the square root of distance ($x^{1/2}$) from the source for iodide, bromide, and lithium.

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Linear Equilibrium Adsorption

The sorptive characteristics of the caisson experiment were estimated using the simple linear equilibrium adsorption model as described by Valocchi (1985), where the dimensionless parameter $R = 1 + \rho K_d/\theta$, the retardation coefficient, represents the effect of adsorption on the mass transport process, with ρ the bulk density, K_d the distribution coefficient, and θ the moisture content. Because of time constraints, it was not possible to explore other models of the sorption process, such as physical and chemical nonequilibrium models. However, it is our intention to pursue this in the future, since it is for these more complex theories that the frequency domain approach can provide a simplification over time domain methods allowing closed-form solutions. For the moment method, the parameter R was estimated from the ratio

$$u_i/u_i^* = R \ , \tag{23}$$

where u_i is the fluid velocity or velocity of a conservative tracer, and u_i^* is the solute velocity for the adsorbing tracer. For the frequency domain method R is estimated directly by means of the nonlinear least-squares approach and Equations (13) and (18), where u_i^* is substituted for u_i. The coefficient R for strontium versus distance along the caisson is shown in Figure 11. In this case the moment method works well, since R is calculated from the first moment or center of gravity of the breakthrough and, as in the case of the velocity estimation, shows only small differences with the frequency domain method. Without the 36-cm level, the average is R = 5.95 for the frequency domain method and R = 5.90 for the time domain method.

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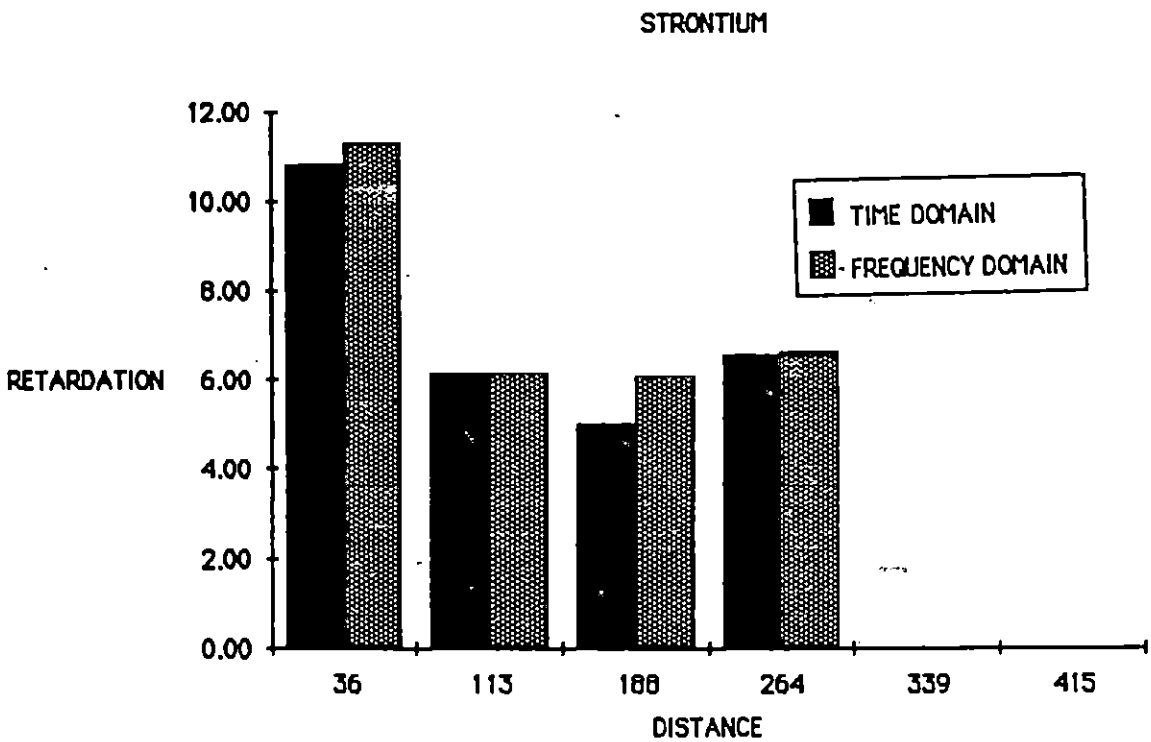

Figure 11. The retardation factor R versus sampling depths (distance) for strontium.

A Systems Approach to Uncertainty in Caisson Effluent

Up to this point, we have confined the analysis to "local" transport behavior, as measured at individual sampling ports along the caisson. From an engineering point of view, it is also critical to make an assessment of the overall or "global" system performance, as measured by the caisson effluent. In order to demonstrate the distinction between local and global system performance, we can compare the iodide breakthrough for the effluent concentration with the breakthrough at the 339-cm level as is shown in Figure 12. The data are plotted versus (x-ut)/u. The first characteristic of the effluent is that, although it has roughly the same mass or area under the curve, it is much more spread out or dispersed than the 339-cm sampling port. Secondly, the effluent breakthrough appears to have at least two peaks, while the 339-cm breakthrough is quite smooth with a Gaussian shape.

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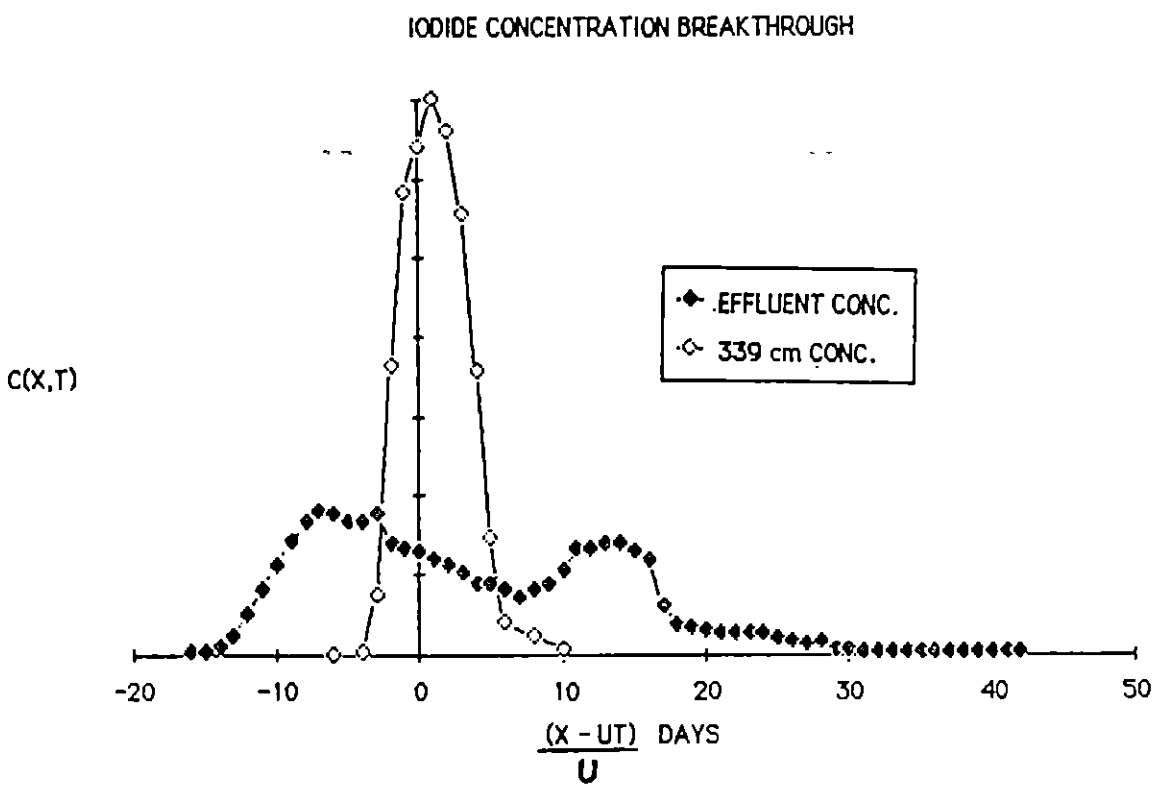

Figure 12. The iodide concentration breakthrough for the 339-cm sampling depth and in the effluent versus (x-ut)/u.

As a first cut, we applied the time domain moment method and determined the dispersivity for the effluent to be a_L = 18.91 cm and the velocity to be u = 15.29 cm/d. For the frequency domain method, we found a_L = 18.61 cm and u = 14.88 cm/d. The values are 5 to 10 times greater than the dispersivities estimated from the sampling ports. This inconsistently suggests the need for an alternative explanation.

From a systems point of view, we might examine this problem as a discrete collection of random pathways, or a parallel combination of independent linear filters, with each filter associated with an unknown random velocity. In some sense this approach is similar to the stratified aquifer problem of Gelhar et al. (1979) and Molz et al. (1983) and the transfer function model of Jury (1982). In any case the system to be explored here is a linear combination of n linear filters as shown in Figure 13. Each of the n filters is described by Equation (1) with the frequency response, transfer function, and phase given by Equations (13) through (15). The system of equations in the frequency domain are expressed as

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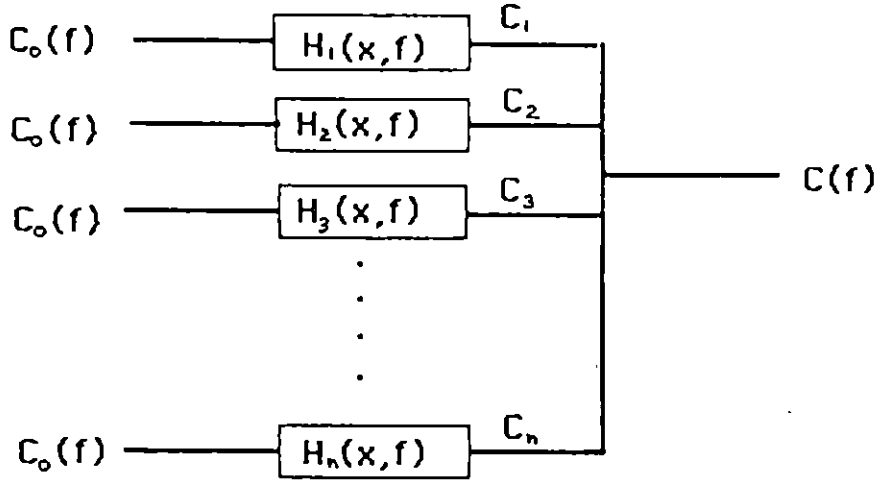

Figure 13. A parallel arrangement of linear filters.

$$C_i(f) = H_i(x,f:u_i)\, C_o(f), \quad i = 1,2,3,\ldots n \tag{24}$$

and

$$C(L,f) = \sum_{i=1}^{n} \alpha_i C_i(x,f), \quad 0<\alpha_i<1 \ , \tag{25}$$

where α_i is the weight of each cell or pathway. Equation (24) describes the frequency characteristics of the individual cells $C_i(f)$, and (25) describes the effect of mixing individual pathways in the effluent $C(L,f)$. The capital letters indicate Fourier transform.

The nonlinear estimation approach described earlier [Equations (14), (15), and (18)] was used to estimated the velocity distribution necessary to describe the effluent concentration in Figure 12 for various numbers of paths n. The dispersivity was held constant in each case (a_L = 1.5 cm) at the mean local value calculated for the sampling ports, and the weighting parameter was taken to be uniform ($\alpha_i = 1/n$). Figure (14) illustrates the velocity values estimated for n = 5, and Figure (15) is for n = 10. Although this is only a preliminary effort at applying systems analysis methods to tracer test studies, it does illustrate an alternative discrete approach to the problem of advective mixing effects, where classical "Fickian" dispersion is inappropriate. Future work will expand on these ideas including the problem of deconvolution and source strength identification in the frequency domain.

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9 2 1 2 4 5 8 0 8 4 4

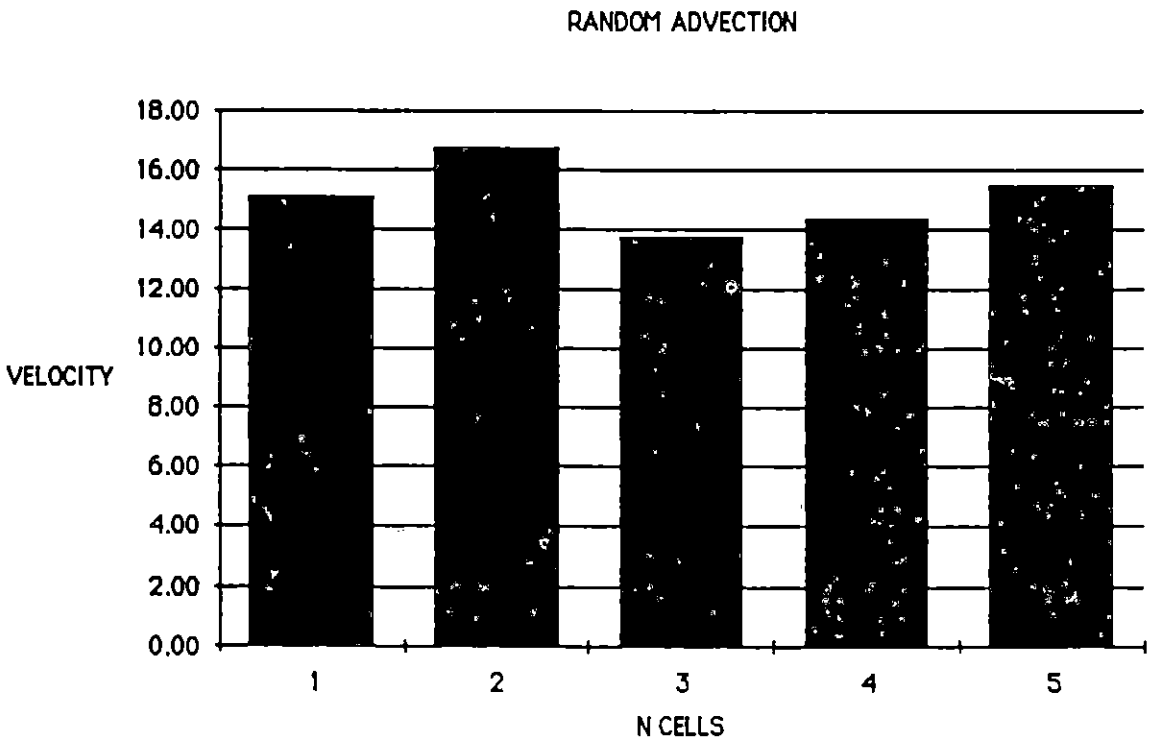

Figure 14. Individual cell velocities estimated for the parallel combination of linear filters (n = 5).

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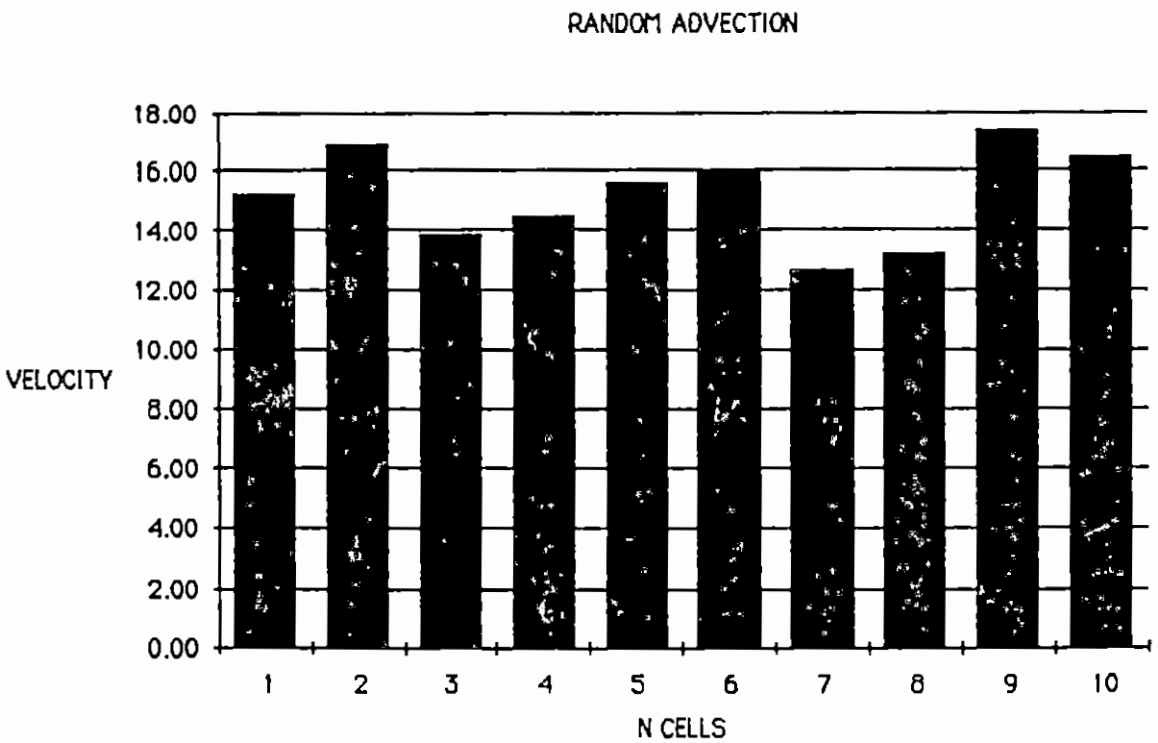

Figure 15. Individual cell velocities estimated for the parallel combination of linear filters (n = 10).

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DISCUSSION

J. C. Parker — I am curious about the relative constancy of dispersivities estimated in the frequency domain. Did you redo those analyses trying to subtract out noise? Do you think the apparent constancy in those dispersivities reflects constancy in the noise, and if you took out the noise, you would see more variation?

C. J. Duffy — We estimated them directly without subtracting out any of the noise. Noise definitely has something to do with our ability to estimate the dispersivity. The noise in the data prevented us from making reliable estimates of a_L using the moment method due to propagation of errors in higher moments. Because these errors are uniformly distributed over frequency (white noise), the frequency domain approach provides a much more stable estimator. Reducing the noise by filtering would serve to improve the moment approach and also lead to a stable estimation.

I. P. Murarka — Why should dispersivity be a function or related to velocity?

C. J. Duffy — It is not. It is a constant; that is what I was showing. I am saying that there is an independence there. Jack used the dispersion coefficient. Once you take the velocity out of the analysis, dispersivity is a constant on the local scale, and it does appear to range between 0.5 to 2 cm for the frequency domain method.

I. P. Murarka — That is a factor of 4.

C. J. Duffy — That is not much compared to the other uncertainties present.

I. P. Murarka — Our prediction abilities are within 50%, and if the individual parameters going into the prediction are 400% off, then there is something strange going on. The parameter uncertainty should not be larger than the prediction uncertainty.

C. J. Duffy — True, but I don't know how that scales. It doesn't scale linearly. The point is that the moment method gives a dispersivity range of 0.5-24.0 cm, which of course is totally

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unreliable. Dispersivities have been reported in the literature anywhere from 10^{-2} - 10^{3} m, so a 0.5-2 cm range doesn't appear to bad.

D. J. Goode

One of the approaches that we are starting to take with a lot of problems is looking at more chronic long-term health effects. Dispersivity isn't all that important. I realize that is what we are spending a lot of time talking about, but I think that the uncertainty in prediction of health effects or doses of 50 percent are not going to be affected by a factor of 4 in dispersion terms.

C. J. Duffy

Dispersion is an attenuation phenomenon. If you are looking for conservatism in predictions, it seems to me that these large dispersion coefficients are not useful. A conservative approach suggests that we be very careful when using large dispersivities.

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W. A. Jury

In the application of the frequency domain method for evaluating parameters, the main limitation I have found with it is when you are using field data it is by no means clear that the convection-dispersion equation is even a good starting hypothesis. What one would like to do is to evaluate the impulse response function deconvoluted from the input signal. Using this approach, one can get the frequency space solution easily, but the numerical inversion of that in general is an unsolved problem. What do you see, other than working with restricted parameterizations of model impulse response functions, that would allow this technique to be used as an investigative tool for developing candidate model strategies from scratch?

C. J. Duffy

There are many difficulties inherent to deconvolution for empirical response estimation, such as nonlinear systems, unknown source strength, numerical instability, etc. However, I think there have been real improvements in several areas as in the fast Fourier transform business and in the area of what is known as maximum entropy spectral estimation. This approach preserves peaks better, and you can get better resolution. So I am not pessimistic about the empirical approach that you are talking about. As far as nonlinear systems, that remains a real question.

A. L. Gutjahr

In a sense what you did is modeled the effluent if you look at the number of cells and the kind of velocity variation you would get from the number of cells. Did you consider using the fact that you did observe a number of velocities on an individual basis and sample cells and see what that effluent concentration would be?

C. J. Duffy

That idea would be to consider the hydraulic information or velocity field as known and then go after the transport parameters such as dispersivity or retardation coefficient. This can be done, but a much more extensive analysis would be necessary to evaluate the details of the velocity field.

A. L. Gutjahr

That way you could use your data that was taken at the various levels to try and make some predictions about the effluent and then compare the two.

H. R. Fuentes

In your analysis, did you assume a finite step function?

C. J. Duffy

Yes. We used the data as provided.

H. R. Fuentes

In regard to the same approach, did you try it with the two lowest depths at 415?

C. J. Duffy

The dispersivities at the bottom of the caisson came out to be approximately 0.5 cm and were the lowest values. From the frequency domain method, the dispersivities for crushed tuff appeared to be in the range of $0.5 < a_L < 2.0$ cm.

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FINITE ELEMENT SIMULATION OF MOISTURE MOVEMENT AND SOLUTE TRANSPORT IN A LARGE CAISSON

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INTRODUCTION

Recent concern regarding the necessity to provide effective means for disposal of low-level radioactive wastes has led the Department of Energy (DOE) and Nuclear Regulatory Commission (NRC) to sponsor performance assessment studies of shallow land burial site disposal. A number of such studies have recently been performed by Los Alamos National Laboratory (LANL). Site integrity is affected by environmental processes such as subsidence, erosion, and overburden breaching, as well as migration of water and contaminants in site media. Active investigations include field experiments designed to provide data to develop the capability to predict solute transport under variably saturated conditions in soils. These experiments were conducted to assist DOE and NRC in improving the understanding of leaching and transport of water and contaminants in porous materials beneath the shallow land burial trench cap. Data from one series of experiments performed on crushed Bandelier Tuff are being made available from LANL to selected investigators to help assess current modeling capabilities. Preliminary analysis using different simulation approaches

can provide a basis for discussion of future need in this area of research. Under the direction of the Environmental Science Group (HSE-12) of LANL, various modeling teams have recently performed simulations of a common experiment using an existing data base developed under DOE and NRC funding.

The purpose of this paper is to simulate and analyze results of the solute transport experiments performed on compacted, crushed Bandelier Tuff in caisson B of the experimental cluster described by DePoorter (1981). Both one- and three-dimensional simulations of solute transport have been performed using two selected finite element codes. The conditions of the experiment and measured data were supplied by HSE-12 of LANL in a work group meeting on January 27, 1986. Results of bromide and iodide tracer experiments conducted during near-steady flow conditions have been analyzed for pulse additions made on December 6, 1984, and followed over a period of up to 60 days. In addition, a pulse addition of nonconservative strontium tracer on September 28, 1984, during questionably steady flow conditions has been analyzed over a period of 240 days. One-dimensional finite element flow and transport simulations were carried out assuming the porous medium to be homogeneous and the injection source uniformly distributed. To evaluate effects of the nonuniform source distribution and also to investigate effects of inhomogeneous porous medium properties, three-dimensional finite element analyses of transport were carried out. Implications of the three-dimensional effects for the design and analysis of future tracer studies are discussed herein.

MODEL DESCRIPTIONS

For this study two different but related codes have been utilized. SATURN, a two-dimensional, finite element code capable of simulating water flow and associated solute transport in variably saturated porous media,

has been used for one-dimensional flow and transport analyses. FLAMINCO, an enhanced three-dimensional extension of the SATURN code, has been used for the three-dimensional transport analysis. Details on the SATURN code and its formulations are available in Huyakorn et al. (1984, 1985, 1986) and a description of the FLAMINCO code can be found in Huyakorn and Wadsworth (1985).

Both codes are similar in design and solve the governing flow and transport equations using Galerkin finite element techniques. The SATURN code treats the nonlinearity of the variably saturated flow equations using either a Picard or Newton-Raphson iterative technique whereas, at this time, FLAMINCO has only the Picard option. Although both codes contain an automatic procedure to update the value of the underrelaxation factor (adapted from Cooley 1983), the Newton-Raphson option in SATURN has been observed to be extremely important in effectively solving simulations reflecting the highly nonlinear flow characteristics of the material in caisson B. Coincident with this project, both codes have been modified to accept the extended functional form of the relative permeability-saturation relationship described by Kool et al. (1986) for caisson A data and, in addition, the codes now include a nonlinear Freundlich isotherm as well as a linear equilibrium isotherm. SATURN and FLAMINCO contain both flow and single-species solute transport models. The codes can perform two types of flow analysis: (1) variably saturated analysis using pressure head as the dependent variable and (2) fully saturated, confined or unconfined, ground-water flow analysis using hydraulic head as the dependent variable. Major assumptions of the flow model are as follows:

- Flow of the water phase is considered isothermal and governed by Darcy's law. Flow of the air phase is neglected.

o The fluid considered is slightly compressible and homogeneous.

Major assumptions of the solute transport model are as follows:

o Transport in the porous medium system is governed by Fick's law. The hydrodynamic dispersion coefficient is defined as the sum of the coefficients of mechanical dispersion and molecular diffusion. The medium dispersivity is assumed to correspond to that of an isotropic porous medium and hence related to two constants, α_L and α_T, which are the longitudinal and transverse dispersivities, respectively.

o Adsorption and decay of the solute may be described by either a linear equilibrium isotherm or Freundlich nonlinear equilibrium isotherm and a first-order decay constant.

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METHODS OF ANALYSIS

One-Dimensional Flow Simulations

Soil hydraulic properties for crushed Bandelier Tuff in caisson A, which is in the same experimental cluster as caisson B, have been reported by Abeele (1979, 1984) and van Genuchten et al. (1986) for monotonic drainage from a saturated condition. The soil moisture properties are described by the relations

$$k_{rw} = S_e^{\ell} [1-(1-S^{1/\gamma})^{\gamma}]^2 \qquad (1)$$

and

$$S_e = (1+|\alpha\psi|^{\beta})^{-\gamma} , \qquad (2)$$

where k_{rw} is the relative permeability; ψ is the pressure head; α, β, γ, and ℓ are functional parameters; and S_e is effective saturation defined as

$$S_e = \frac{S_w - S_{wr}}{1 - S_{wr}} , \qquad (3)$$

in which S_w is the water saturation and S_{wr} is the residual saturation. Equation (1) is known as the Mualem relation (Mualem 1976). For $k_{rw}(S_e)$, we also use the following equation:

$$k_{rw} = S_e^N , \qquad (4)$$

where N is an empirical parameter. The parameters in Equations (1) and (4) were obtained by adjusting the results of van Genuchten et al. (1986) to account for the apparent differences in hydraulic properties between caissons A and B so as to provide consistency with water contents and pressure heads measured in caisson B during the tracer experiments. One-dimensional steady flow simulations were carried out using the SATURN code. The boundary conditions imposed were a specified Darcy flux of 4.07 cm/d at the upper soil surface (z = 0) and a specified zero value of pressure head at the bottom of the caisson (z = 550 cm).

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One-Dimensional Transport Simulations

One-dimensional solute transport simulations were performed using SATURN for the steady flow regime. The longitudinal dispersion coefficient was assumed to be described by

$$D_L = \alpha_L |V| , \qquad (5)$$

where α_L is the longitudinal dispersivity and V is the Darcy velocity which was assumed equal to the fluid application rate of 4.07 cm/d. Simulations were carried out for bromide and iodide by assuming no adsorption (R = 1)

and with longitudinal dispersivity, pore water velocity distributions, and pulse durations specified in two different ways.

Case 1: The pore water velocity distribution corresponds to the measured Darcy velocity of 4.07 cm/d with the water content distribution given by the solution to the one-dimensional steady state unsaturated flow problem as described in the preceding section. The longitudinal dispersivity was assumed to be 2.5 cm. This is approximately five times larger than the value used by van Genuchten et al. (1986). The duration of the tracer application was assumed to be 6 days as prescribed in the Los Alamos description of the experiment.

Case 2: In this case, we employed a longitudinal dispersivity value of 0.5 cm corresponding approximately to that determined by van Genuchten et al. (1986). (Note that van Genuchten et al. discuss the dispersion coefficient in terms of pore water velocity, whereas in Equation (5) we use the Darcy velocity.) In addition, we assumed a Darcy velocity of 3.22 cm/d, which in conjunction with water content distribution obtained from the flow simulation, produces a mean pore water velocity in the caisson equal to that used by van Genuchten et al. The duration of the tracer application was assumed to be that fitted by van Genuchten et al. -- 5.43 days.

Simulations of strontium movement were carried out using the same values of dispersivity and pore water velocity as for case 2 above and with nonlinear partitioning described by the following Freundlich isotherm:

$$s = kC^{\eta} , \tag{6}$$

where s is the sorbed concentration (MM^{-1}), C is the solution concentration

(ML^{-3}), and k and η are empirical parameters. The retardation factor for equilibrium adsorption is then given by

$$R = 1 + \rho_B k \eta C^{\eta-1} / \phi S_w \ , \qquad (7)$$

where ρ_B is the soil bulk density (1.60 g/cm^3). Parameters for the Freundlich isotherm are taken from van Genuchten et al. (1986) as k = 1.486 (for units consistent with C in mg/ℓ and s in mg/g) and η = 0.835.

Three-Dimensional Transport Simulations

Simulations of iodide and strontium transport were performed in three dimensions using the FLAMINCO code. FLAMINCO allows examination of the potential three-dimensional transport effects of discrete point application of tracer, as well as possible heterogeneities in the Bandelier Tuff material. The assumptions and parameters considered in the current simulations are described below. Flow in the caisson was assumed to be steady state. Darcy velocity was regarded as constant and set equal to 4.07 cm/d throughout the entire region. Water saturations were assumed to be vertically uniform as generally suggested by radially averaged observed values and one-dimensional flow simulation results (presented in Figure 1).

To assess the effect of material heterogeneity, we partitioned the caisson into two zones. These zones are differentiated in the input to the FLAMINCO code by differing water saturations, but their difference can also be viewed with respect to seepage velocity. As seepage velocity is a function of saturation, the more highly saturated zone is a slow zone and the less-saturated zone is a fast zone. Alternatively, the slow zone, with higher value of water saturation, can be viewed as the zone of lower

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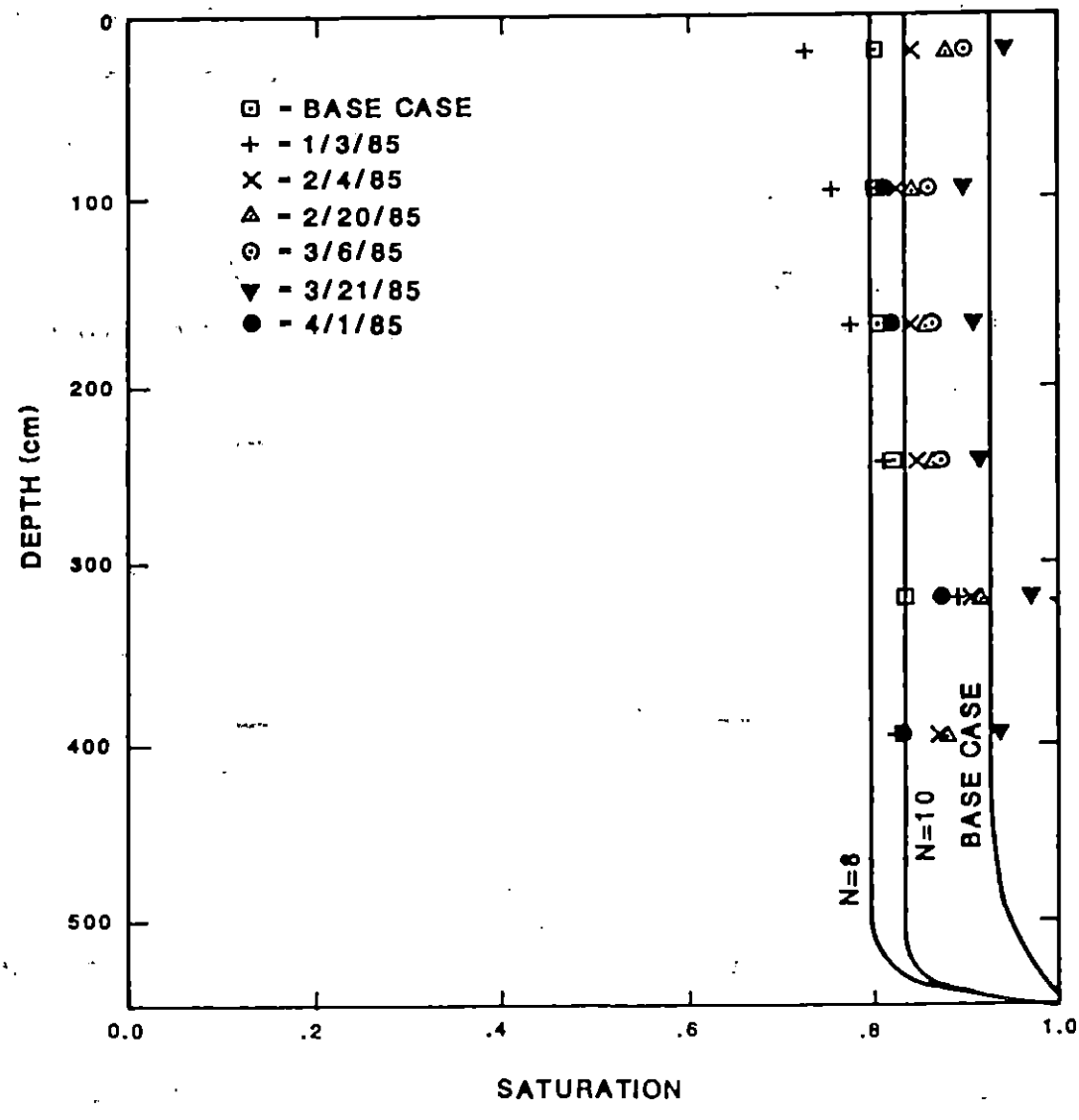

Figure 1. Vertical profiles of simulated and observed water saturation.

hydraulic conductivity. Mixing from zones of differing hydraulic conductivity has been suggested by van Genuchten et al. (1986) to explain the multiple peak concentrations apparent in the observed effluent concentration curve for iodide. Radially heterogeneous water saturation is particularly suggested by the variations in the observed water content data, where higher values are consistently observed toward the middle of the caisson. In the three-dimensional transport simulations for both iodide and strontium, water saturations were prescribed such that they areally average to the water saturations calculated in the one-dimensional flow simulation (0.834). Iodide was treated as conservative (no adsorption), whereas strontium sorption was described by the Freundlich isotherm presented in Equation (6). Longitudinal and lateral dispersivity values, together with the values of other physical parameters, are given in Table 1.

Advantage has been taken of the symmetry of the problem, and just one-quarter of the caisson cylinder was discretized. Only the tuff layer was considered (i.e., the underlying thin layers of coarse sand and gravels were neglected). This quarter-segment of the caisson was discretized into 51 horizontal layers, each consisting of 117 nodes. Thus, the entire grid consists of 5967 nodes and 4700 rectangular prism elements. The time stepping, initial conditions, and prescribed boundary conditions are given in Table 2. Note that for both iodide and strontium the prescribed concentration c_o at the injection nodes was computed using the following mass balance equation:

$$c_o = \sum_{I=1}^{n} Q_I = QC^* \quad , \tag{8}$$

Table 1. Physical parameter values used in three-dimensional simulation of transport of iodide and strontium.

Darcy velocity, V	= 4.07 cm/d	
Effective porosity, ϕ	= 0.331 cm	
Longitudinal dispersivity, α_L	= 2.5 cm	
Lateral dispersivity, α_T	= 2.5 cm	
Inner Zone		Outer Zone
Saturation, S_w = 1.0, which corresponds to a seepage velocity, v = 12.3 cm/d		Saturation, S_w = 0.716, which corresponds to a seepage velocity, v = 17.2 cm/d
For Iodide		
Retardation coefficient, R	=	1
Decay constant, λ	=	0 d^{-1}
For Strontium		
Freundlich coefficient, k	=	1.486 $(cm^3 g)^{**}0.835$
Freundlich exponent, η	=	0.835
Decay constant, λ	=	0 d^{-1}

where Q is the total volumetric flux of water (200 cm^3/min), C* is the measured concentrations of the tracer solution at the points of injection, Q_I is the volumetric flux of water at the solute injection nodes. The nodal volumetric water flux Q_I can be determined as the effective nodal surface area (see shaded area in Figure 13) multiplied by the water flux density (i.e., Q/surface area of caisson). This necessary approach to the injection node boundaries is a result of the one-dimensional flow

assumption used to calculate the Darcy velocity Q,which is applied across the entire surface of the caisson. When transport simulations are combined with discrete multiple injection points, the flow assumption leads to the prescription of artificially high concentrations to conserve mass. The three-dimensional flow effects are not expected to be important at the caisson sample depths associated with the observation nodes.

Table 2. Boundary, initial, and time-stepping specifications used in three-dimensional simulation of transport of iodide and strontium.

Boundary Conditions

Concentrations at the solute injection nodes, marked on top nodal layer shown in Figure 13 with a triangular symbol, were prescribed as follows (see text):

For iodide, $C = c_o$ = 696 mg/ℓ, t≤6d,

= 0 mg/ℓ, t>6d.

For strontium, $C = c_o$ = 286.8 mg/ℓ t≤6d,

= 0 mg/ℓ, t>6d.

The remaining top nodes were treated as zero-concentration nodes at all times for both species.

Initial Conditions

For both species, C = 0.2 mg/ℓ for all but the top nodes, at t = 0.

Time Stepping

For iodide, Δt_k = 1d, k = 1 to 60.

For strontium, Δt_k = 2d, k = 1 to 120.

---

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RESULTS AND DISCUSSION

One-Dimensional Flow Simulations

Flow simulations were first carried out using method 1 parameters of van Genuchten et al. (1986) for which the soil parameters in Equations (1) and (2) are given as follows: $\alpha = 0.014$ cm^{-1}, $\beta = 1.51$, $\gamma = 0.338$, $S_{wr} = 0.0$, $\phi = 0.331$, $\ell = 0.5$. The saturated hydraulic conductivity is $K_s = 25$ cm/d. Simulated steady state water content and pressure head distributions denoted as the "base case" are compared with measured water contents averaged in the horizontal plane at various times during the study and with measured pressure heads temporally averaged at two port depths in Figures 1 and 2, respectively. Although truly steady state conditions were evidently not obtained, it is observed that the simulated water content tends to overpredict the observed values while pressure heads are underpredicted.

Comparison of observed and predicted relationships of saturation versus pressure head (Figure 3) indicate that observed time-averaged saturations are less than those for the base case parameters obtained from the caisson A drainage experiment. The apparent discrepancy between caisson A and caisson B hydraulic properties may be due to hysteretic effects since caisson A parameters were obtained for monotonic drainage, while caisson B studies entailed a more complex saturation history. To obtain a more suitable representation of the caisson B properties, we first consider modification of the parameters for the $S_w(\psi)$ function. Kool et al. (1986) have shown that adjusting α in Equation (2) will provide a suitable correction to describe the main wetting and drying hysteresis loops of $S_w(\psi)$. Therefore, we adjust α to obtain a satisfactory correspondence with the measured data. The curve for $\alpha = 0.08$ cm^{-1} is seen to give a reasonable representation of the observed data (Figure 3).

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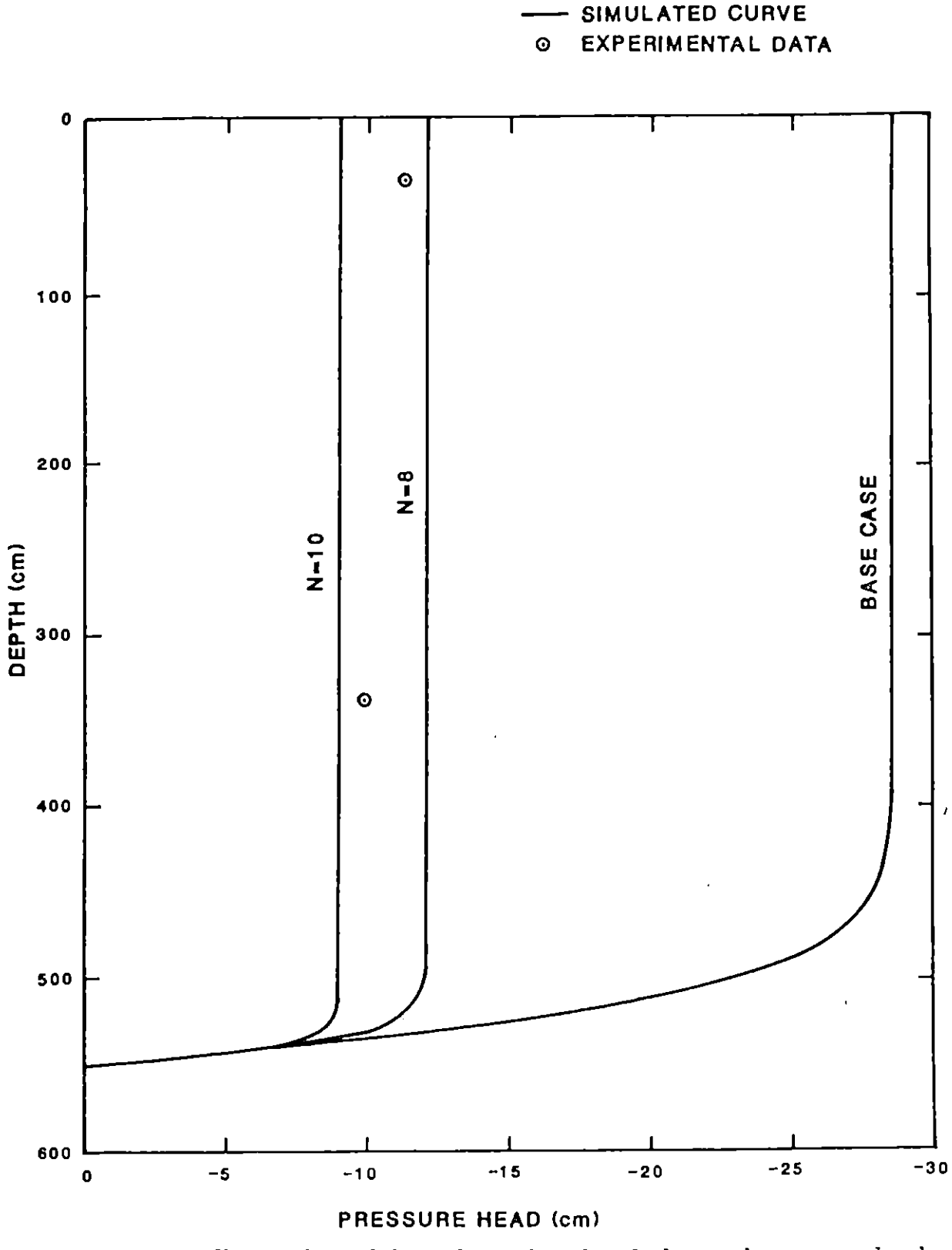

Figure 2. Vertical profiles of simulated and observed pressure head.

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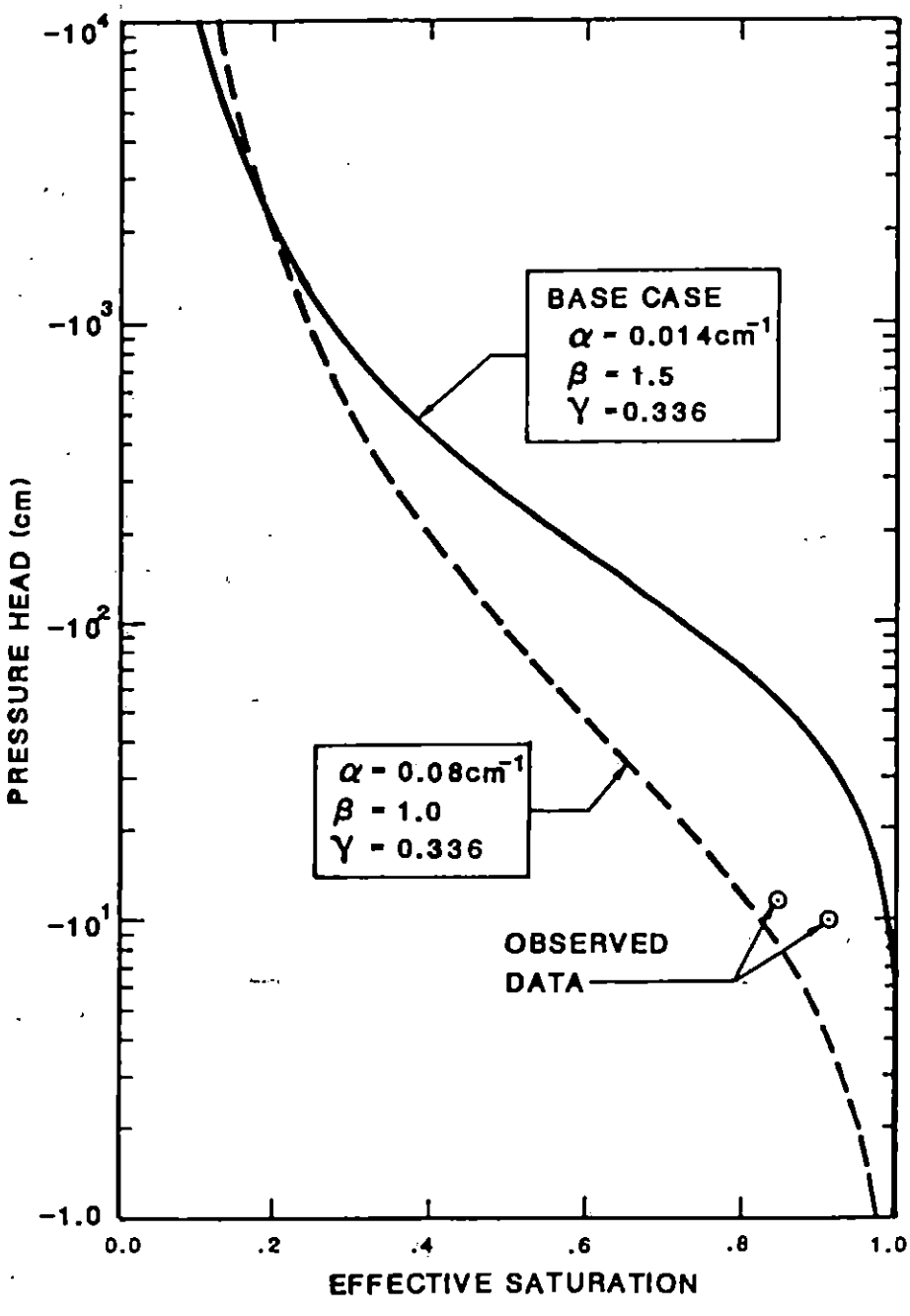

Figure 3. Pressure head versus effective saturation relationships used in the one-dimensional flow simulations.

Adjusting $k_{rw}(S_w)$ improved the $\psi(z)$ predictions but had very little effect on $S_w(z)$ at steady state. Hence, we altered the $k_{rw}(S_w)$ function by employing Equation (4) and adjusting N. The effect of N on the relative permeability k_{rw} is shown in Figure 4. The effects of N on water saturation and pressure head profiles are shown in Figures 1 and 5 and in Figures 2 and 6, respectively, when the steady state flow problem is solved using Equation (4) for $k_{rw}(S_w)$ and $S_w(\psi)$ described by the $\alpha = 0.08$ cm^{-1} curve of Figure 3. From these results we conclude that N = 10 provides a reasonable representation of the steady state flow regime in caisson B during the tracer experiments. In subsequent analyses, we utilized N = 10 in Equation 4 and $\alpha = 0.08$ cm^{-1} with other parameters as previously discussed.

Since N strongly affects the nonlinearity of the flow problem, it may be anticipated that convergence of nonlinear iterations will be hampered by increasing N. This is evident in Table 3, which shows the rate of convergence for the single-step steady state solution using Picard and Newton-Raphson iterative methods. It is observed that for the highly nonlinear cases, Picard iteration cannot be efficiently employed, whereas the Newton-Raphson method still yields a convergent solution without excessive increases in the number of iterations.

To evaluate the optimal mesh spacing for an accurate and stable solution of the flow problem, steady state simulations were carried out for element lengths (Δz) of 5, 10, and 25 cm. The results (Figure 7) indicate that oscillations in the solution occur near the water table where k_{rw} changes abruptly if $\Delta z = 25$ cm but are absent for $\Delta z = 10$ cm. Further reductions in Δz have a negligible effect on the solution indicating $\Delta z = 10$ cm is a satisfactory mesh spacing for this problem.

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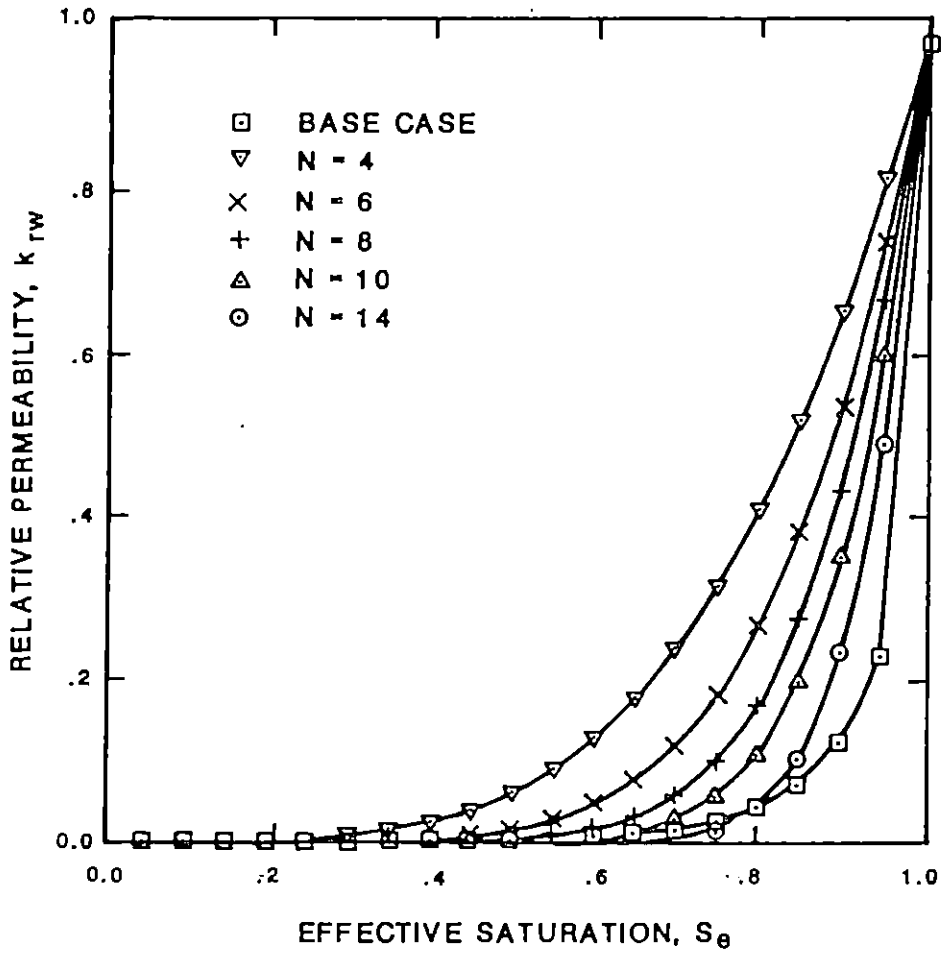

Figure 4. Relative permeability versus effective saturation relationships used in the one-dimensional flow simulations.

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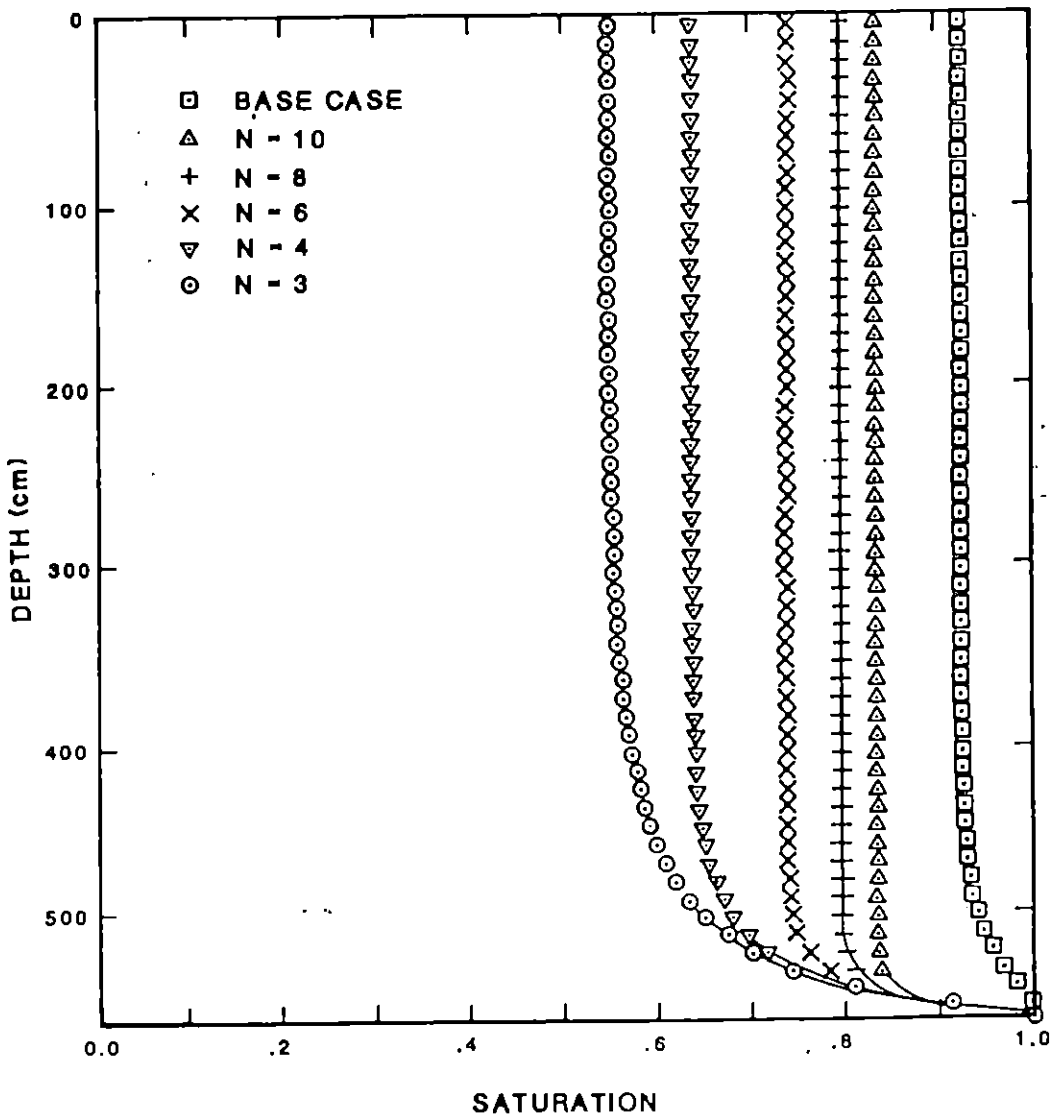

Figure 5. Vertical profiles of simulated water saturations showing the effect of parameter N and a comparison with the base case.

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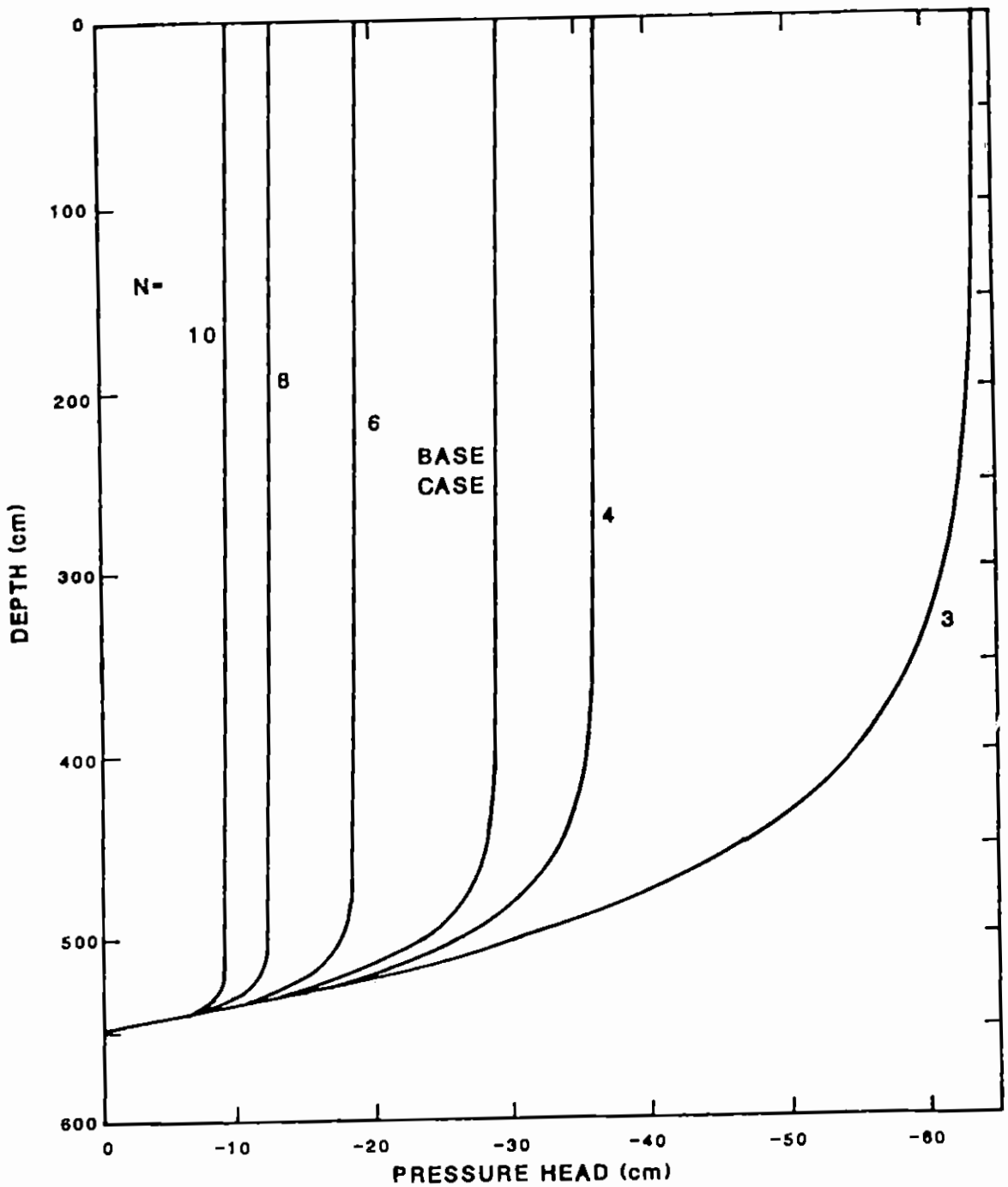

Figure 6. Vertical profiles of simulated pressure head showing the effect of parameter N and a comparison with the base case.

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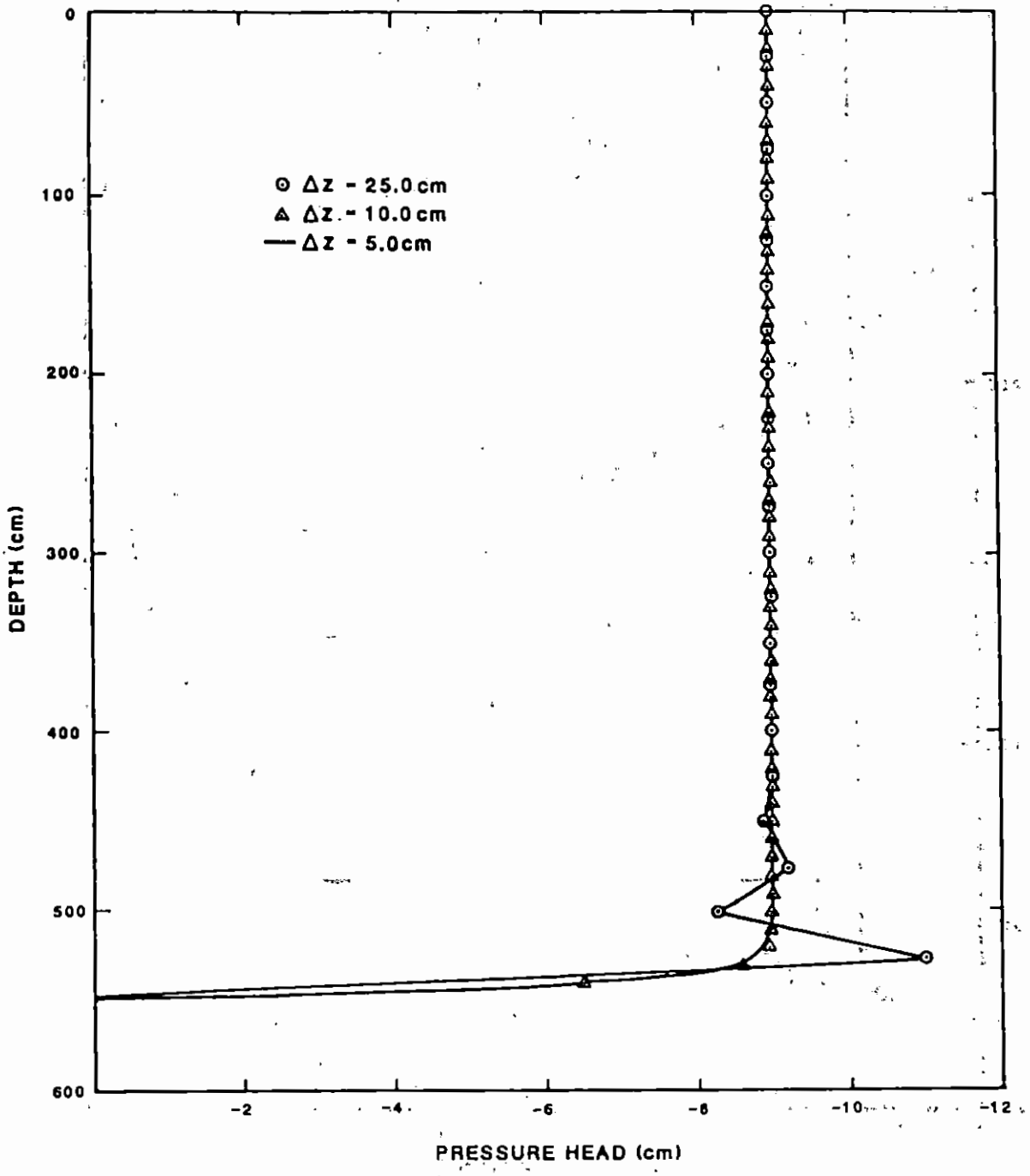


Figure 7. Vertical profiles of pressure head showing the effects of grid spacing on the numerical solutions.

Table 3. Iterative procedure performance comparison.

Case	Number of Nonlinear Iterations: Newton Raphson	Picard
Base case	30	n.c.[a]
N = 3	12	33
N = 4	13	56
N = 6	19	n.c.
N = 8	27	n.c.
N = 10	31	n.c.

[a]No convergence. Head tolerance = 0.0001 cm. Grid spacing = 10 cm.

9 2 1 2 4 5 8 0 8 6 9

One-Dimensional Transport Simulation

Observed iodide breakthrough data measured with hollow fiber samplers at depths of 36, 113, 188, 264, 339, and 415 cm and in the caisson effluent were compared with simulated curves using case 1 and case 2 parameter values in Figures 8 and 9, respectively. A summary of the parameter values used in the simulations are given in Table 4. As can be seen in Figure 9, case 2 parameters closely fit the data for all depths except 264 cm and, to a lesser extent, 188 cm. As noted by van Genuchten et al. (1986), it appears that a faster velocity zone occurs in part of the caisson, which intersects the 264-cm depth sampler and results in a double peak in the effluent breakthrough curve.

Case 2 parameter values selectively fit the slow flow zone results and hence closely predict the travel time for effluent through the slow zone but not the earlier peak from the fast zone.

Close correspondence between case 2 results and the analytical results of van Genuchten et al. (1986) verify the accuracy of the numerical

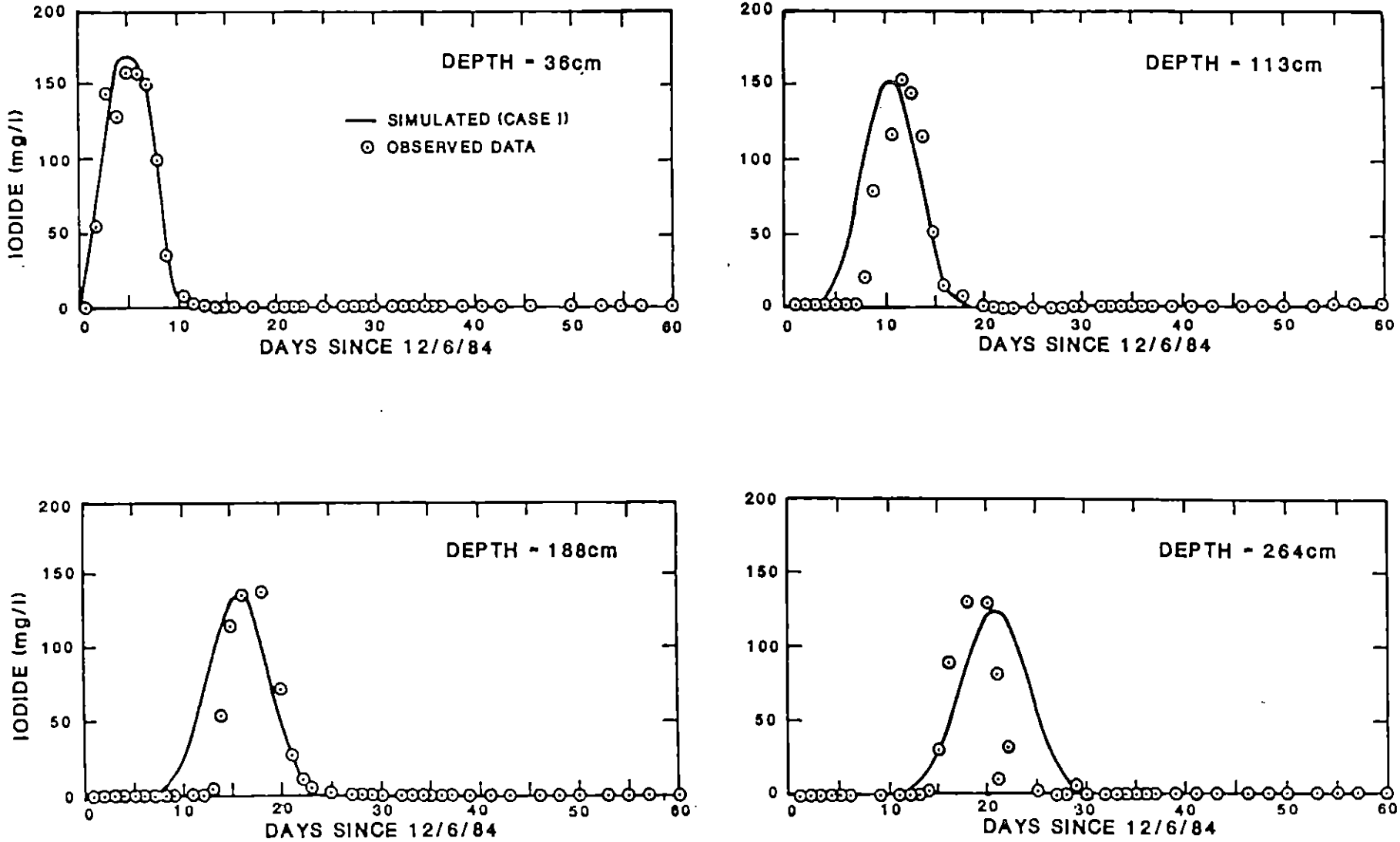
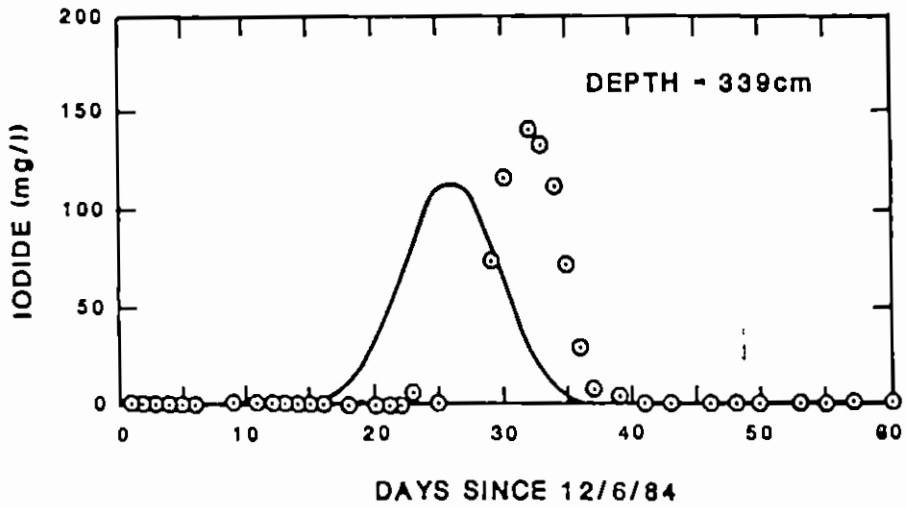
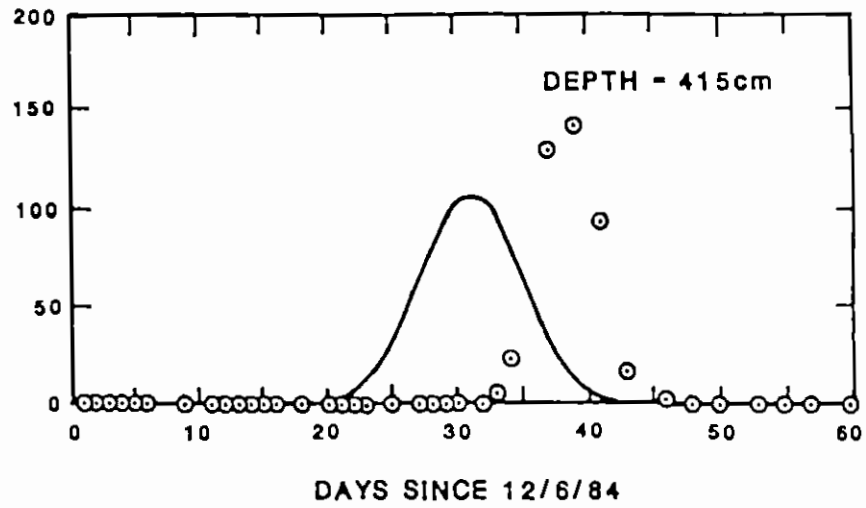


Figure 8. Iodide breakthrough data measured at various depths in hollow fiber samplers and predicted curves obtained from one-dimensional transport simulation (case 1).





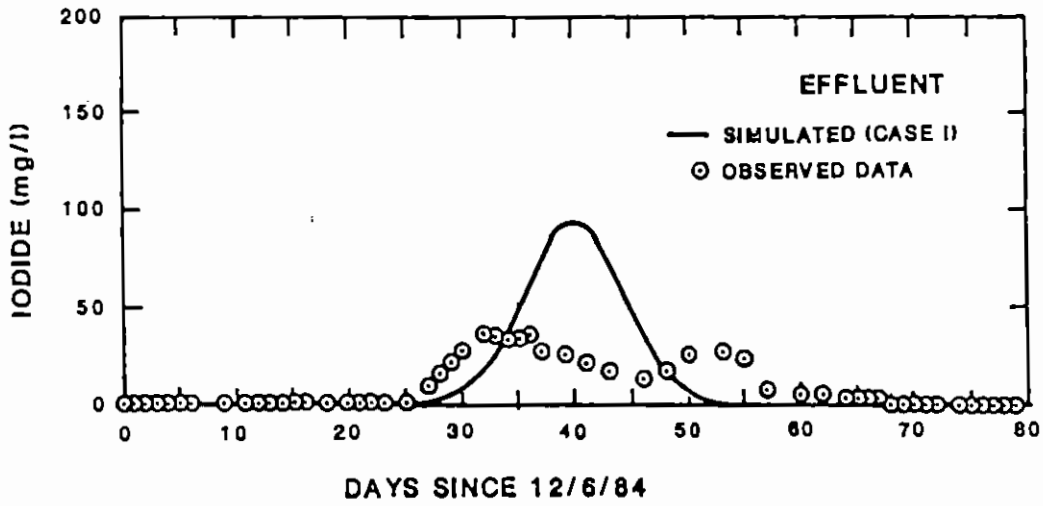


Figure 8. (continued)

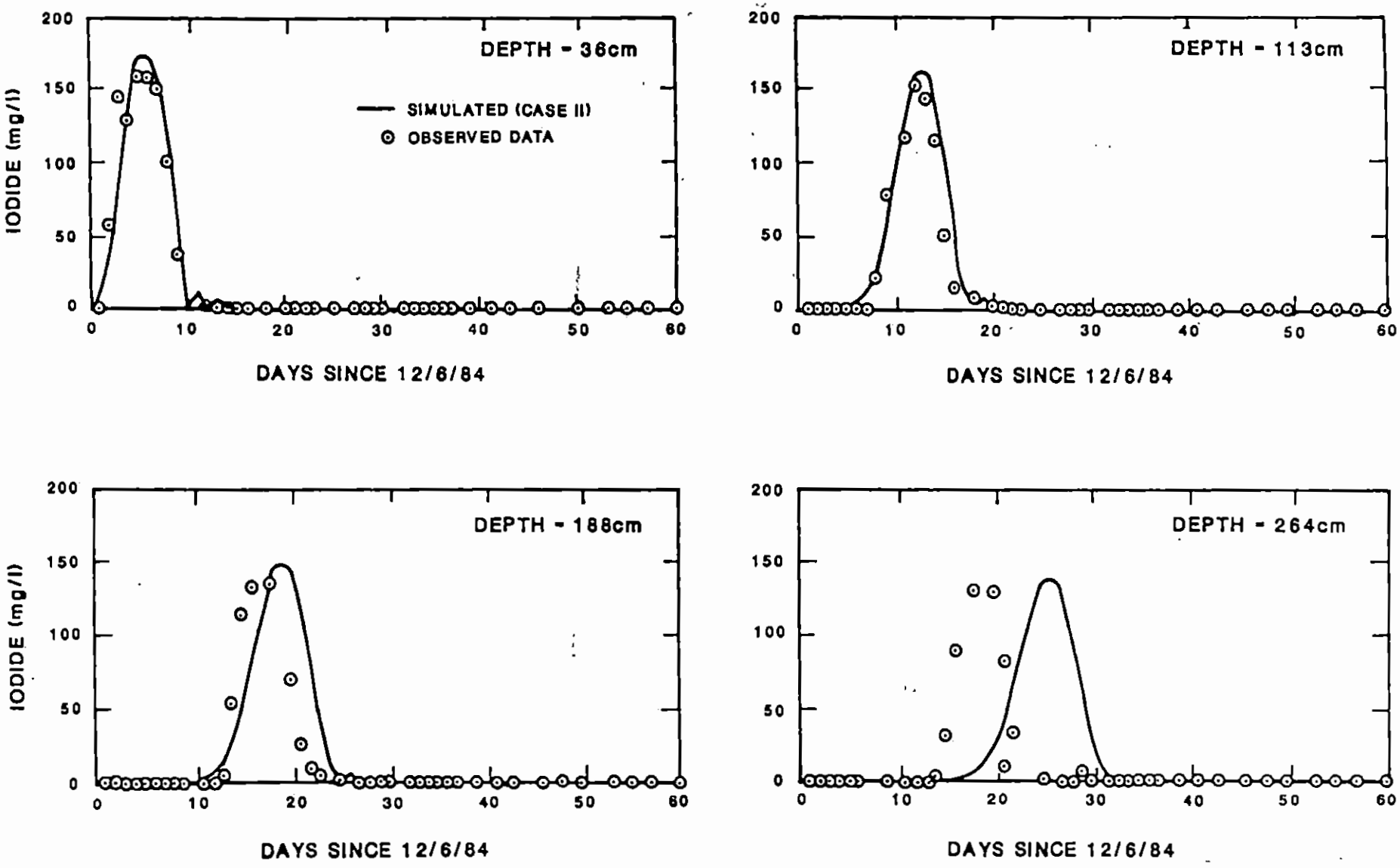


Figure 9. Iodide breakthrough data measured at various depths in hollow fiber samplers and predicted curves obtained from one-dimensional transport simulation (case 2).

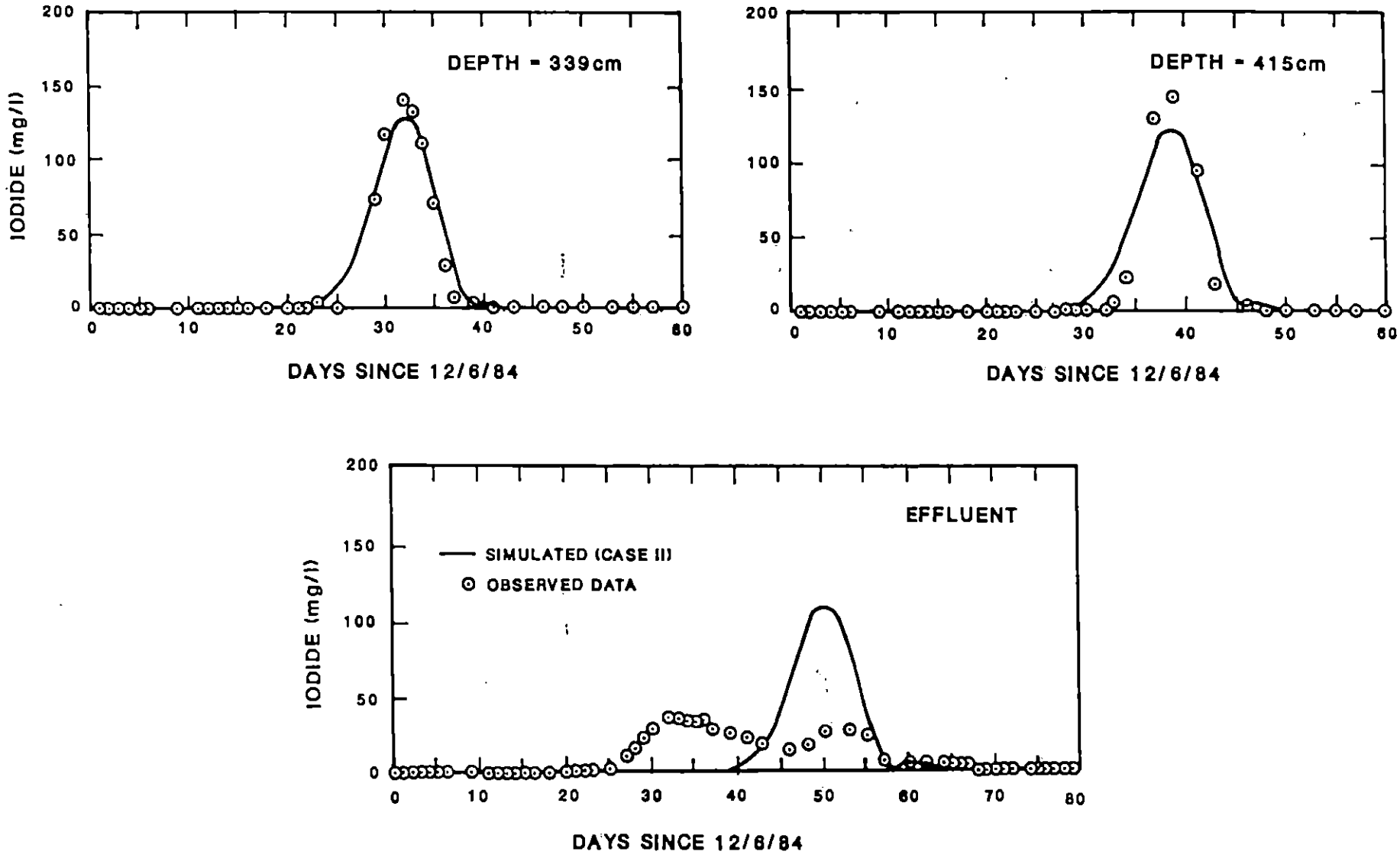


Figure 9. (continued)

Table 4. Summary of parameter values for one-dimensional transport of iodide, bromide, and strontium.

Effective porosity, ϕ	=	0.331
Water saturation, S_w	=	0.834
Soil bulk density, ρ_B	=	1.60 g/cm^3
Freundlich coefficient, k	=	1.486 (cm^3/g**0.835)
Freundlich exponent, η	=	0.835
Injection concentration, c*	=	170 mg/ℓ I, 78 mg/ℓ Br, 70 mg/ℓ Sr
Background concentration, c_o	=	0.2 mg/ℓ I, 0.0 mg/ℓ Br, 0.2 mg/ℓ Sr
Case 1		
Darcy velocity, V	=	4.07 cm/d
Longitudinal dispersivity, α_L	=	2.5 cm
Pulse duration, T_o	=	6.0 d
Case 2		
Darcy velocity, V	=	3.22 cm/d
Longitudinal dispersivity, α_L	=	0.50 cm
Pulse duration, T_o	=	5.43 d

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analysis used in the present study. The results also indicate that the nonuniform water content distributions (hence, nonuniform pore water velocities) have a negligible effect on transport, subject at least to the validity of the one-dimensional approximation for the problem. When the parameters representative of the average behavior in the entire caisson, and not just the slow flow zone, are employed for the simulations (i.e., case 1 rather than case 2 parameters), deviations between observed and predicted results for the fast zone sampler at 264-cm depth diminish.

However, at other depths, predicted peaks tend to be earlier than those observed. For the effluent data, the predicted peak lies intermediately between the observed doublet.

Similar results to those for iodide are obtained for bromide (Figures 10 and 11). Again, case 2 parameters provide a close representation of data from samplers in the slow zone but overpredict the time for breakthrough at the 264-cm depth. With case 1 parameters, better correspondence between observed and simulated results at 264 cm are obtained at the expense of poorer representation at other depths. The results clearly indicate that distinct differences in pore water velocities occur in various zones within the caisson. A primary objective of the three-dimensional simulations will be to investigate means of explicitly describing the effects of this heterogeneity on solute transport.

Finally, before turning to an evaluation of the three-dimensional simulation results, we consider the one-dimensional analysis for strontium movement, which is subject to nonlinear sorption. The results using transport parameters essentially identical to those of van Genuchten et al. (1986) are in good agreement with the results of those authors. This provides a check on the accuracy of the present method for solving the nonlinear transport problem (Figure 12). It may be observed that significant tailing in the strontium breakthrough curves is predicted because of isotherm nonlinearity. Poor apparent mass balance arises at many sampling depths. Van Genuchten et al. (1986) attribute this to precipitation of $SrCO_3$.

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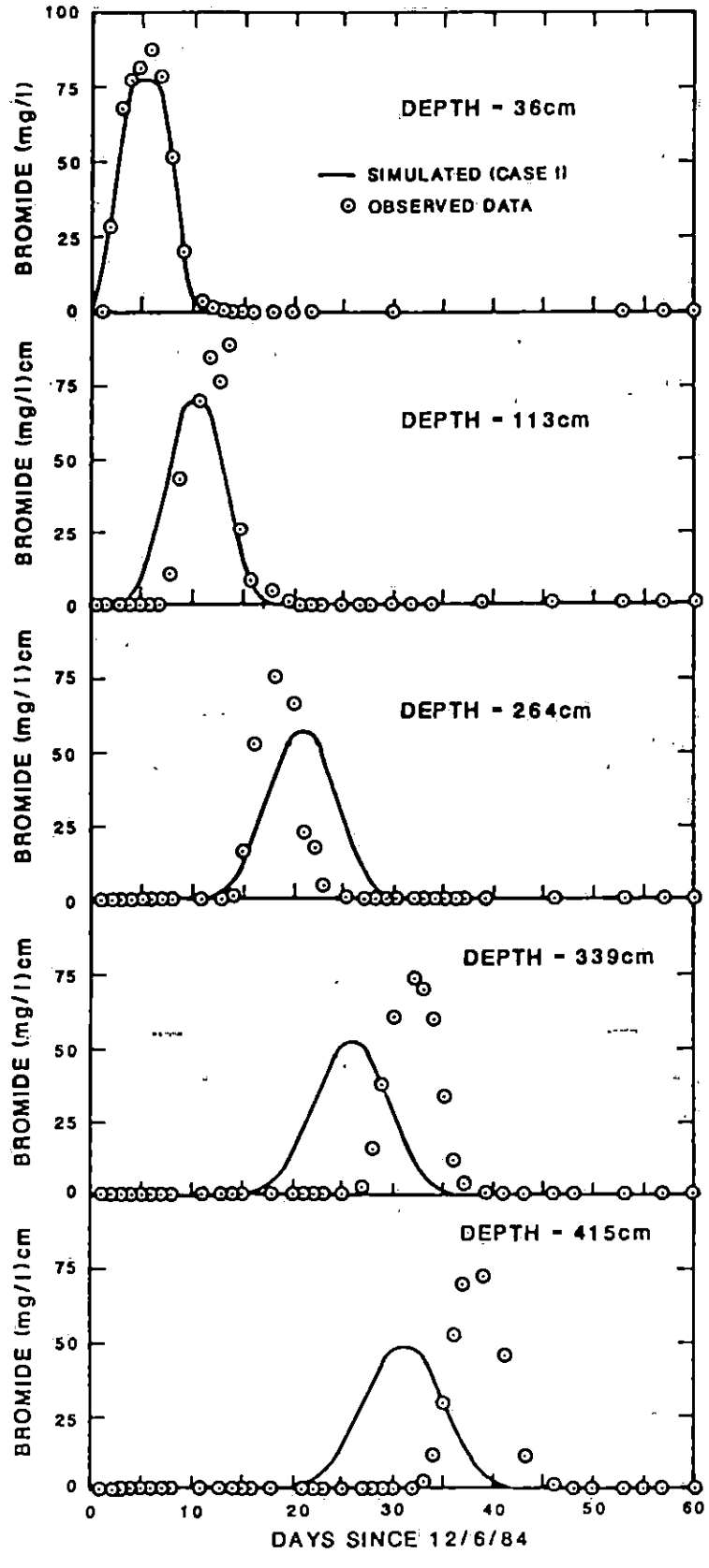

Figure 10. Bromide breakthrough data measured at various depths in hollow fiber samplers and predicted curves obtained from one-dimensional transport simulation (case 1).

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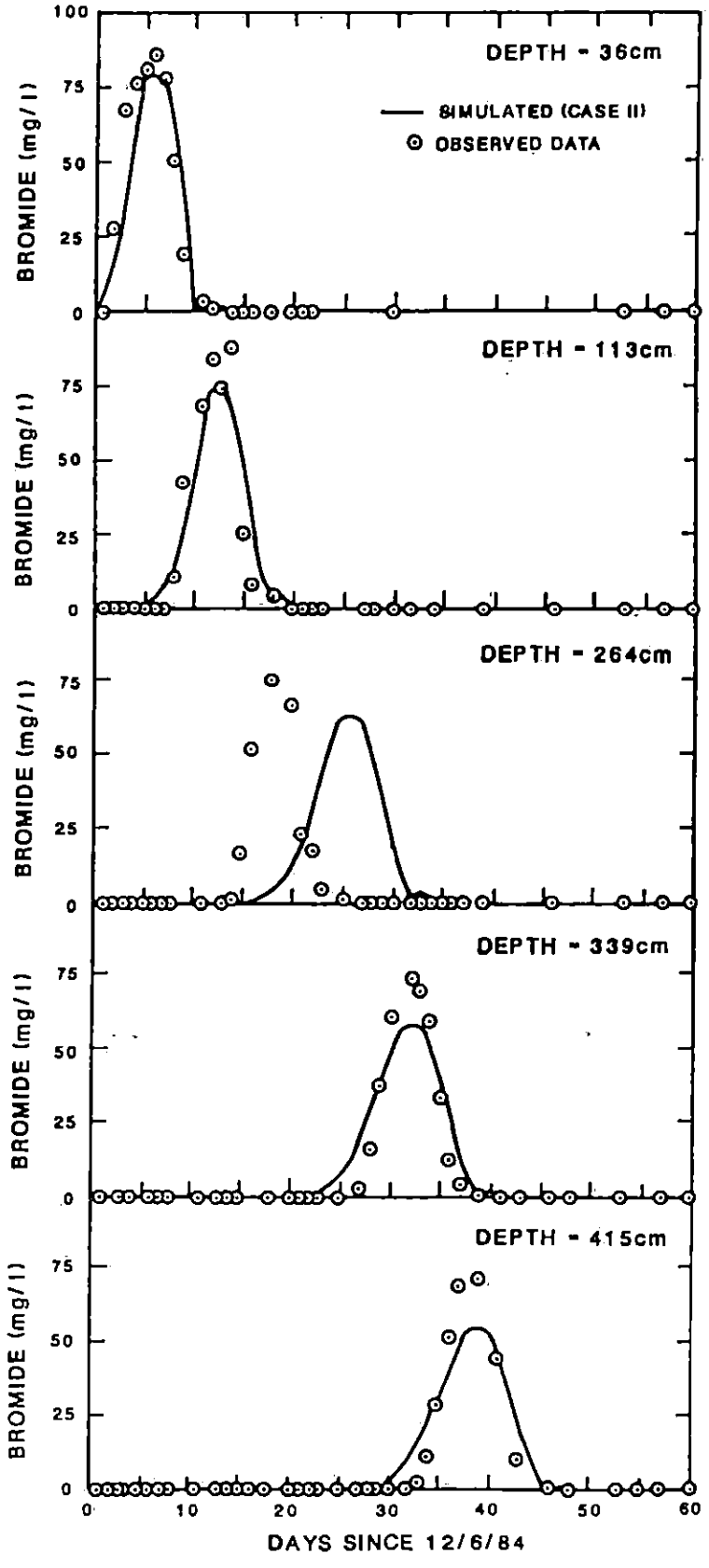

Figure 11. Bromide breakthrough data measured at various depths in hollow fiber samplers and predicted curves obtained from one-dimensional transport simulation.

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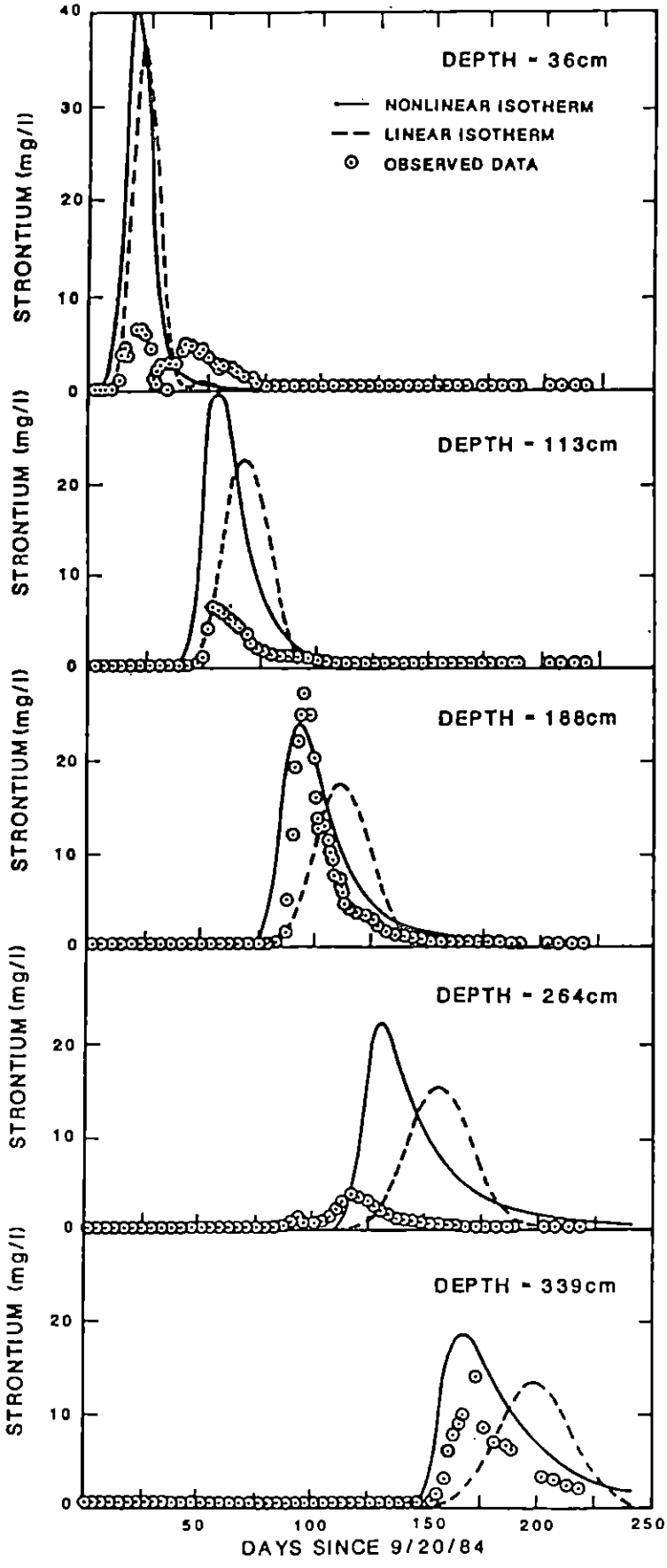

Figure 12. Strontium breakthrough data measured at various depths and predicted curves obtained from one-dimensional simulations using linear and Freundlich isotherms.

Three-Dimensional Transport Simulations

Before running the simulations described in the next section, we performed a three-dimensional re-creation of the one-dimensional results to check both the three-dimensional representation of the caisson and the recently added Freundlich isotherm. The 5967 node grid, referred to in Figure 13, was checked by using the one-dimensional iodide case 1 parameters with uniform injection represented by consistently prescribed concentrations at each top layer node. The Freundlich isotherm incorporated in FLAMINCO was verified by creating an abbreviated three-dimensional grid and effectively rerunning the one-dimensional strontium transport problem. For both test cases, the three-dimensional results were essentially identical to the one-dimensional results.

The results of the truly three-dimensional simulations of interest defined below have been processed to create breakthrough curves at observation nodes comparable with the observed data and one-dimensional transport results. In addition, effluent breakthrough curves have been derived by taking flow-weighted averages of the nodal concentrations at the bottom plane of the caisson grid. To demonstrate the three-dimensional effects of the two zones and discrete point tracer application, concentration contours have been plotted for selected layers corresponding to sampling depths at selected times.

Iodide Simulation Results

Simulated breakthrough curves are compared in Figure 14 with the observed data at sample depths of 36, 113, 188, 264, 339, and 415 cm. The simulated concentration values are seen to be nearly identical for the three nearby observation nodes located in the slow zone (zone 1) considered at each depth. Only at 36-cm depth, where three-dimensional effects due to

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9 2 1 2 4 5 8 0 8 8 0

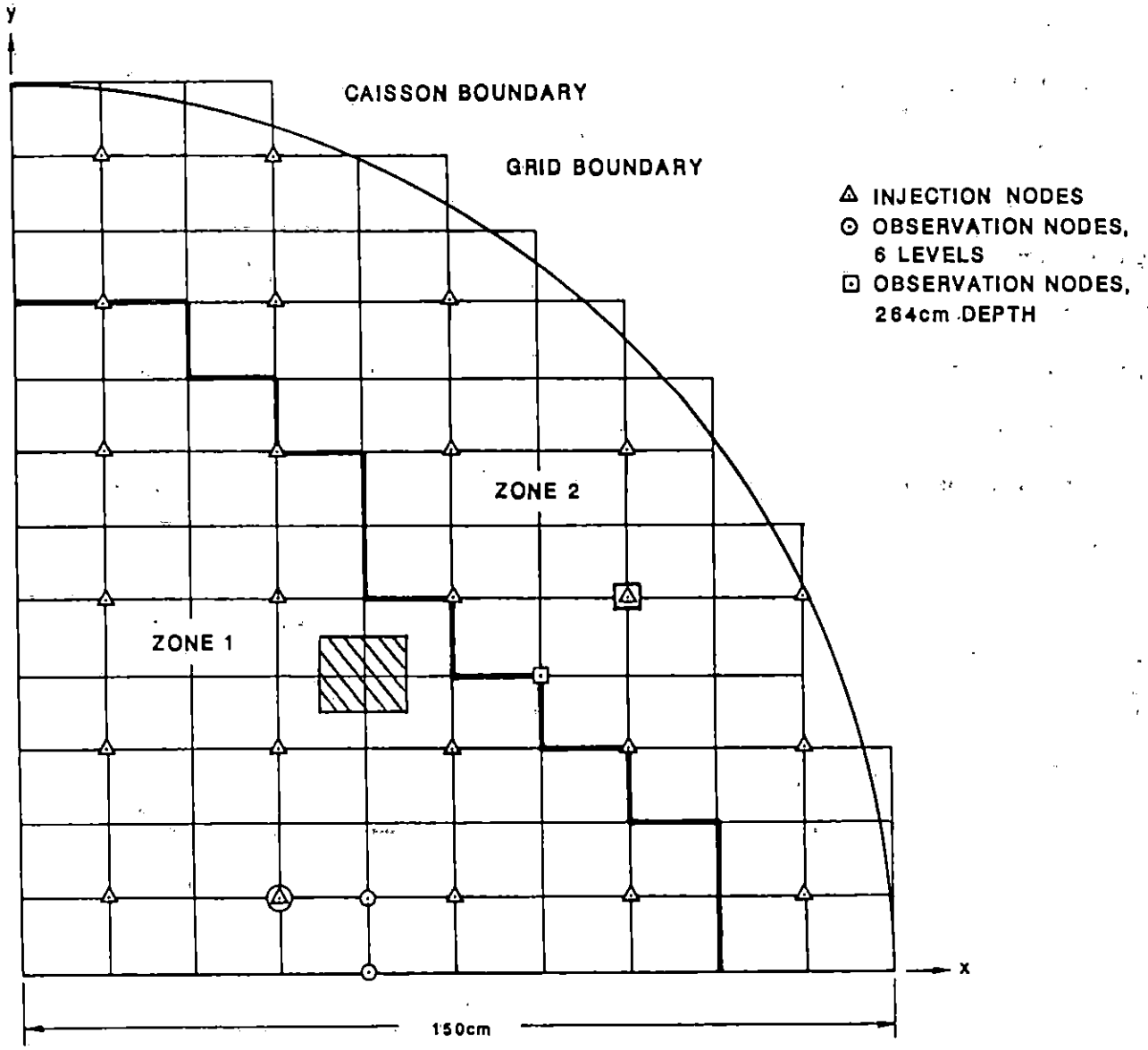


Figure 13. Top plan view of three-dimensional finite element grid used in transport simulations.

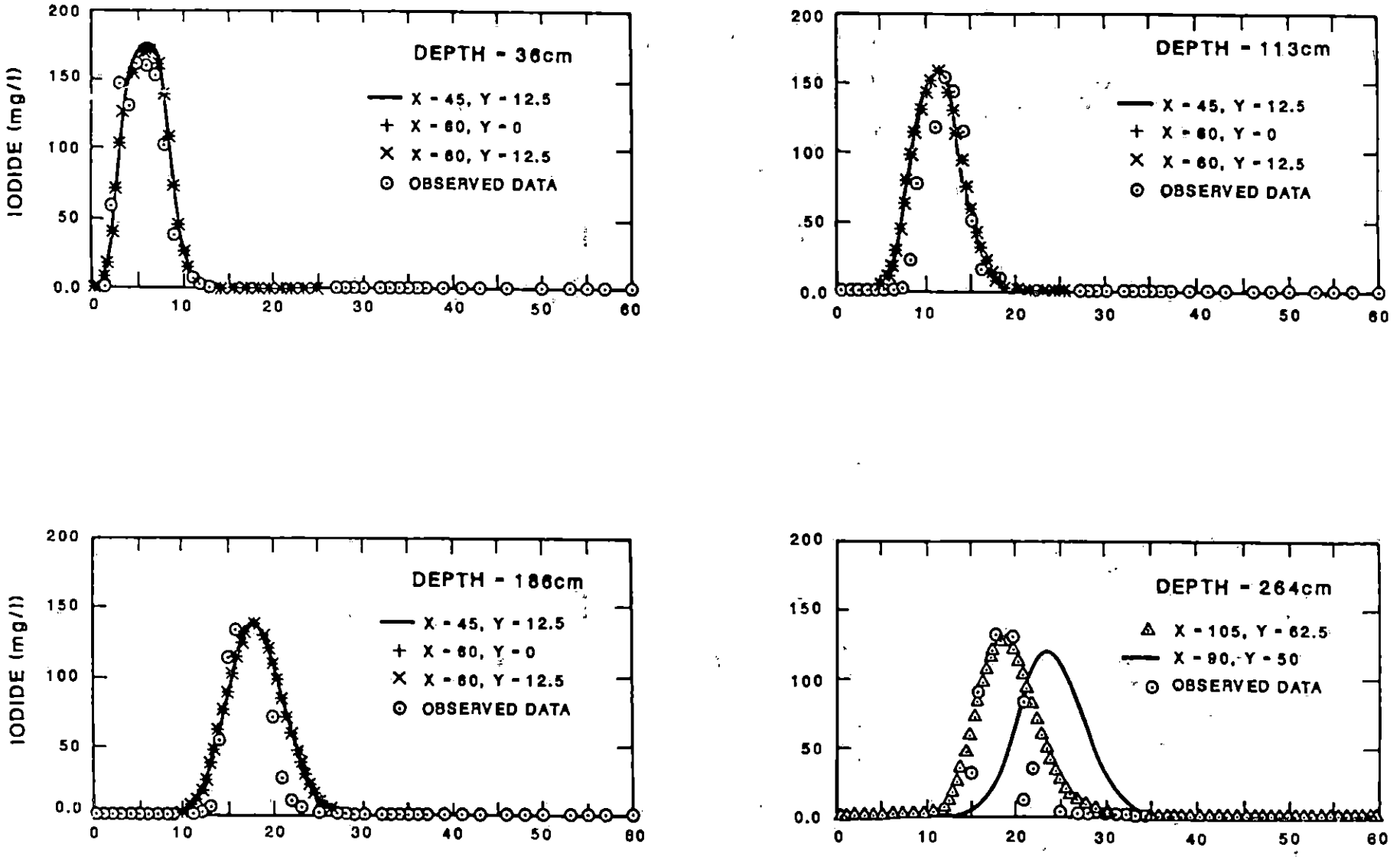
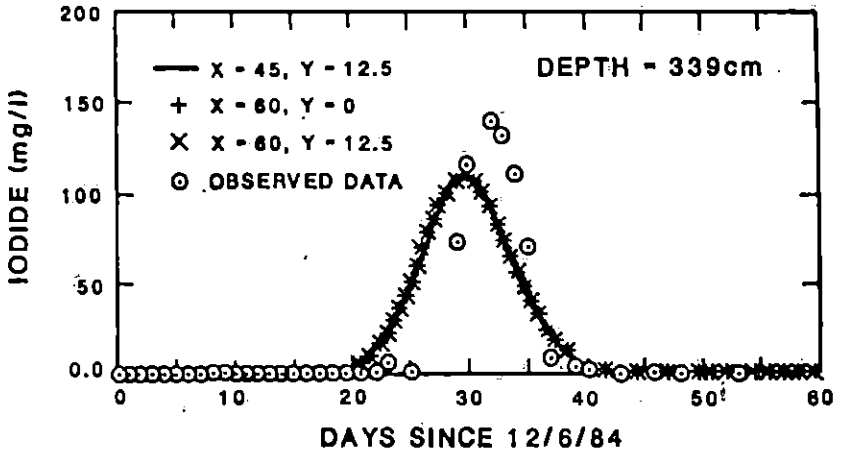
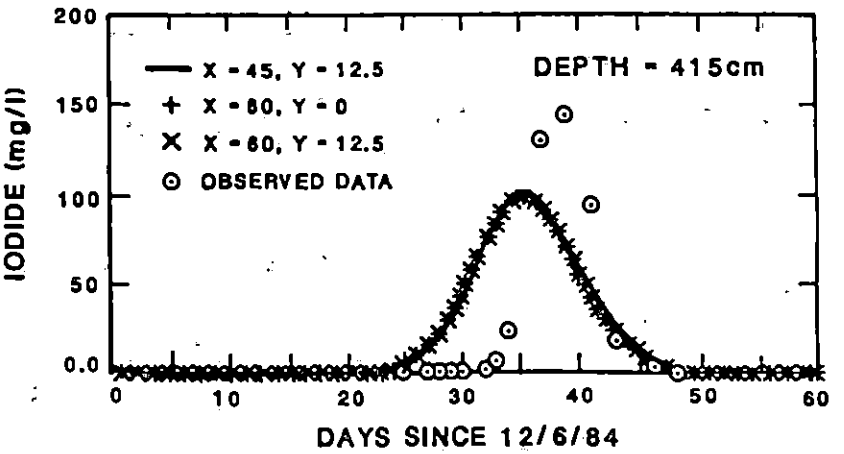


Figure 14. Iodide breakthrough data measured at various and predicted curves obtained from three-dimensional transport simulation.





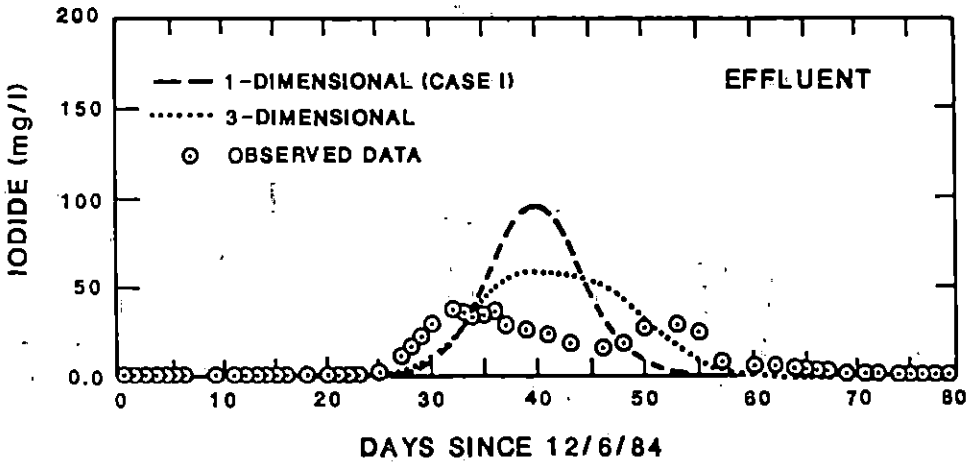


Figure 14. (continued)

discrete point injection would be expected to be greatest, is there a discernible difference between these three nodal values. The plot for the 264 cm depth includes two additional breakthrough curves corresponding to two selected nodes (see Figure 13) in the fast zone (zone 2) and shows the expected earlier breakthrough in this zone. The simulated and observed effluent concentrations over time are also presented, together with the results for the case 1 one-dimensional simulation.

Comparison of the simulated and observed data indicates reasonable agreement at the top three observation depths: 36, 113, and 188 cm. At the 264-cm depth, the data are better matched by the curves associated with the fast zone. This implies that the fast zone at 264 cm may be more extensive than the fast zone in other layers and may include the sample point. Such a possibility is consistent with discrepancies observed in the one-dimensional transport simulation and with observations made by van Genuchten et al. (1986). The simulated breakthrough curves for the 339- and 415-cm depths show significantly lower and earlier peaks and broader shapes than would be suggested by the observed data. This was not seen in the one-dimensional transport analysis (case 2) and was probably caused by lateral mixing of solutes from the slow and fast zones. Simulated and observed effluent concentrations are compared in the last frame of Figure 14. The results of the three-dimensional analysis fit the observed data better than the one-dimensional results. The concentration curve for the three-dimensional analysis exhibits a more sustained peak and a lower maximum value than the one-dimensional concentration curve. This is apparently due to the dispersion-like mixing of solute from the two zones. The better fitting three-dimensional concentration curve does not have a double peak like the observed data, indicating the two-zone heterogeneity

simulated may be more simplistic than the true heterogeneities in the caisson.

Contour plots of iodide concentration distributions at six levels corresponding to the sampling depths 36, 113, 188, 264, 339, and 415 cm are shown in Figures 15 to 20, respectively. These plots consistently show the three-dimensional influence of the fast and slow zones. At each depth, the concentration plume exhibits a gradual transition of concentration values corresponding to the interface between the two modeled zones. The transition becomes more gradual between the two zones at greater time and at greater sampling depths. This is the result of lateral dispersion; its effects would be expected to be more noticeable with greater time and distance from the pulse source. The iodide pulse breaks through into the faster outer zone first and then correspondingly is flushed from the outer zone first. The contrast between concentrations simulated in the two zones is typically quite marked at a given time. Often the outer zone concentrations are decreasing from flushing at the same time the inner zone concentrations are increasing because of breakthrough. The only direct evidence of the three-dimensional effects of the discrete point tracer application are the closed contour anomalies observed at the earlier plotted time at the 36-cm depth. These correspond to regions of less concentration resulting from the uneven tracer application.

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Strontium Simulation Results

In Figure 21 the breakthrough curves for the three-dimensional simulation of strontium tracer movement are presented with observed data from five levels corresponding to sampled depths of 36, 113, 188, 264, 339, and 415 cm, respectively. Similar to observations for iodide, the simulated concentration values at the three nearby observation nodes in the

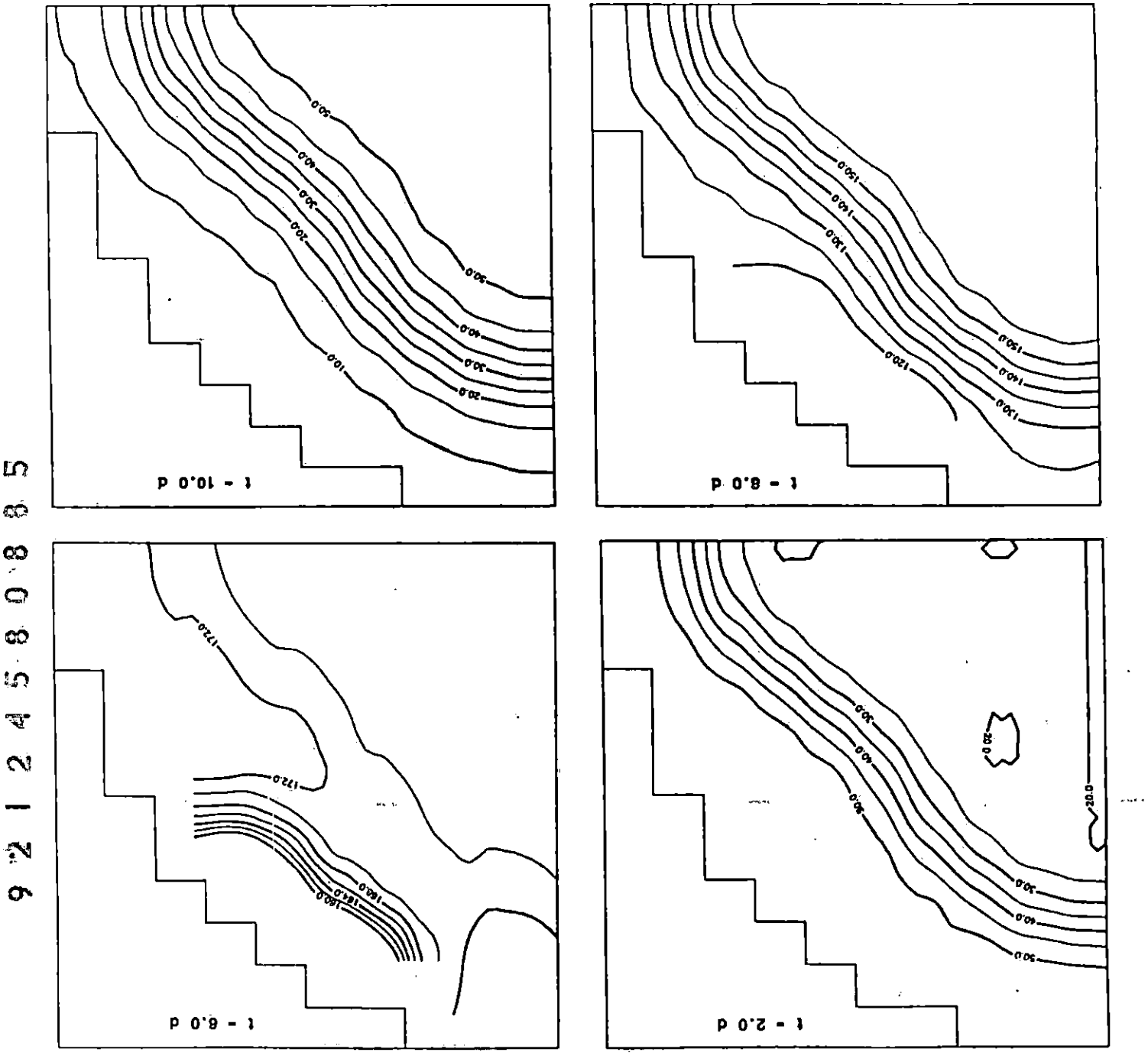


Figure 15. Contour plots of iodide concentration distribution in the horizontal plane at the 36-cm depth.

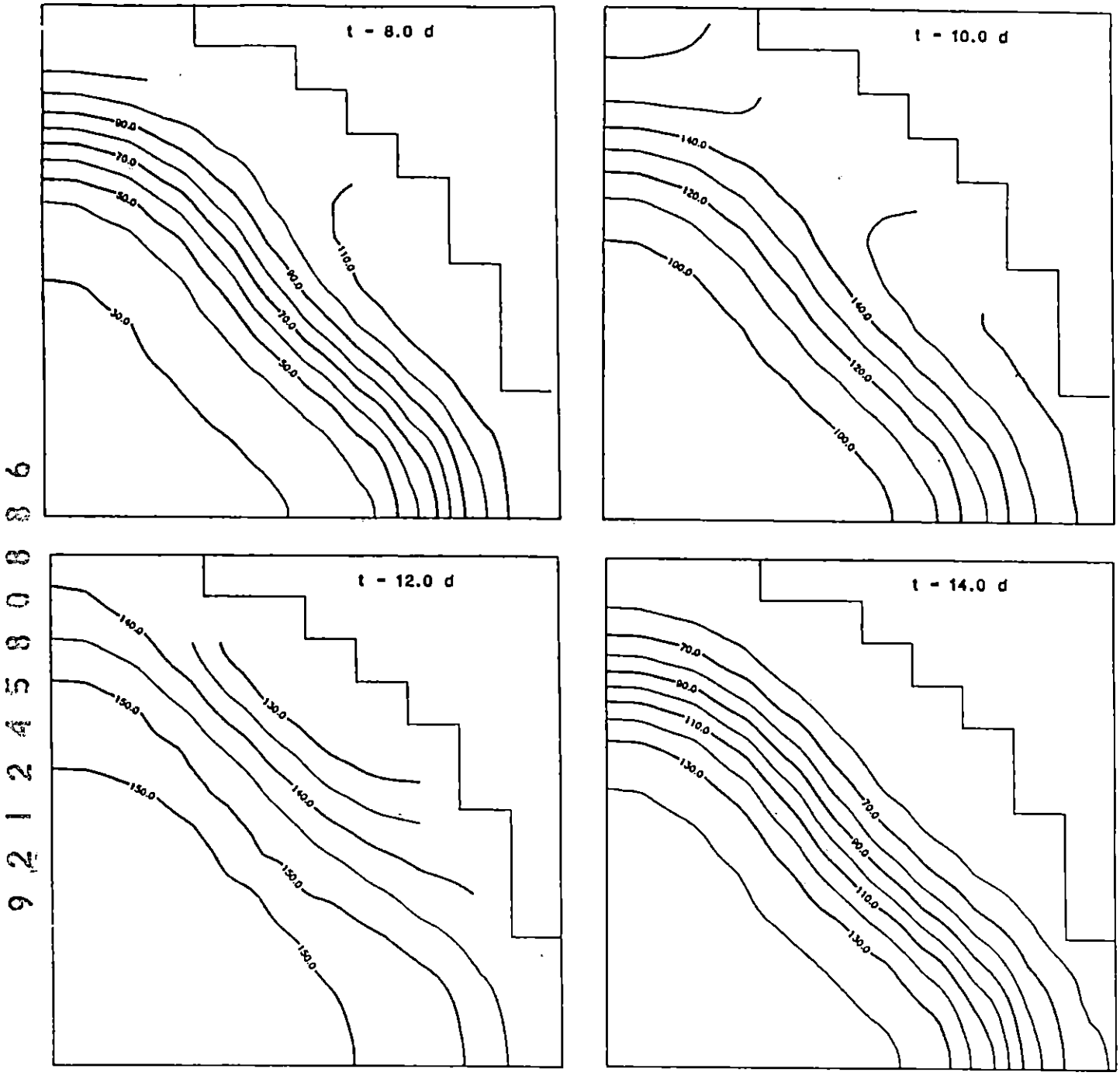


Figure 16. Contour plots of iodide concentration distribution in the horizontal plane at 113-cm depth.

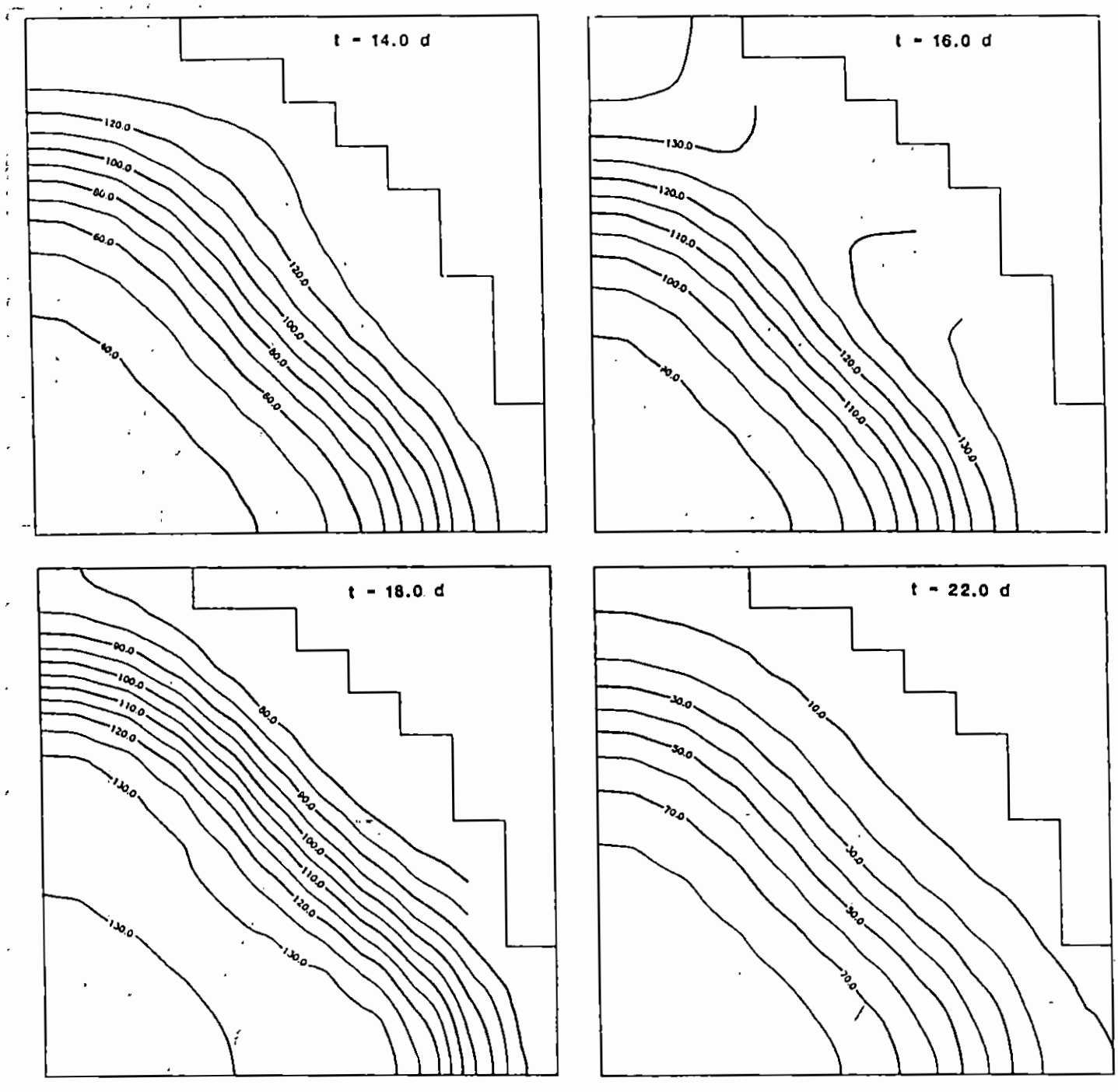


Figure 17. Contour plots of iodide concentration distribution in the horizontal plane at 188-cm depth.

9 2 1 2 4 5 8 0 8 8 9

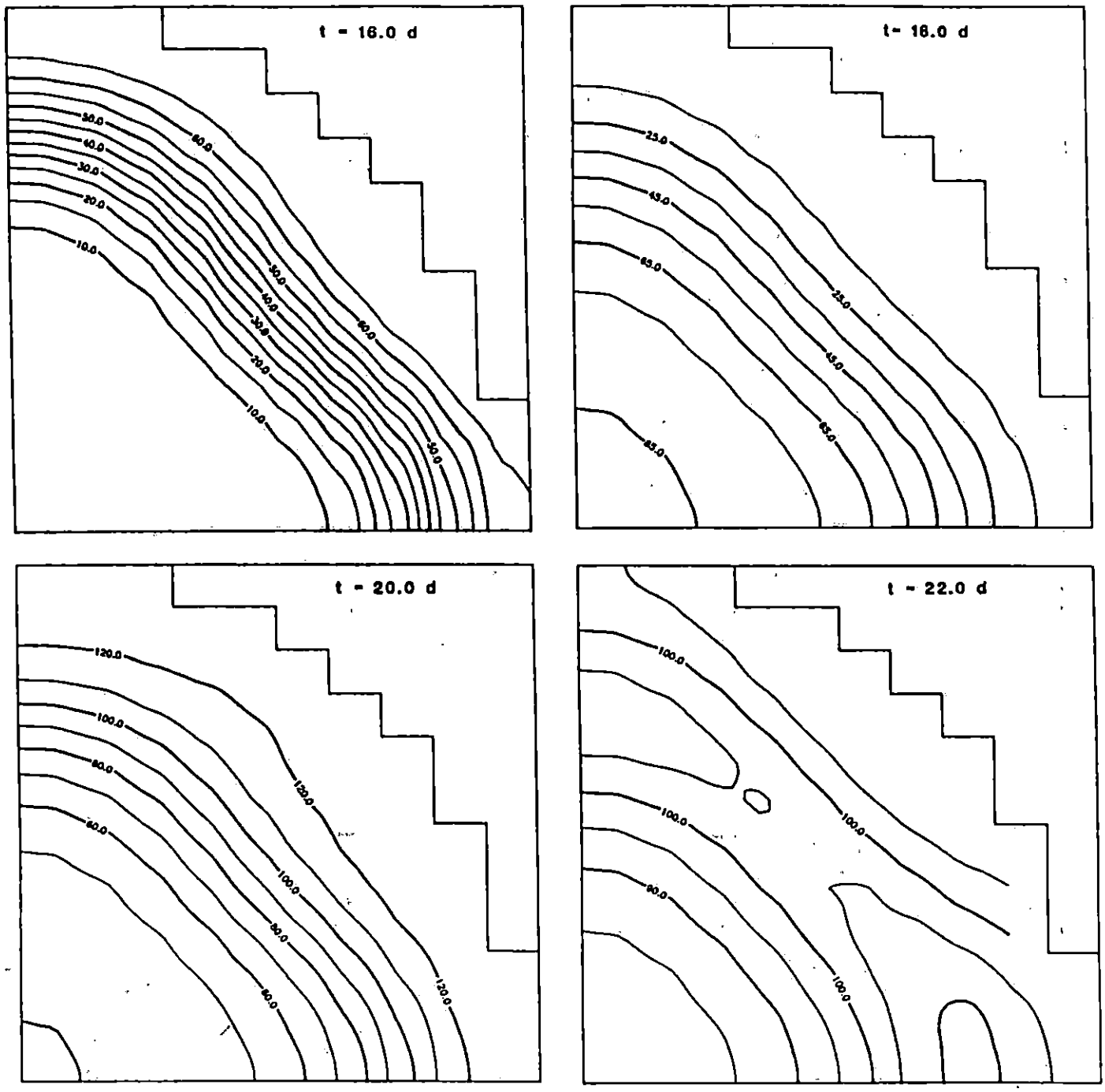


Figure 18. Contour plots of iodide concentration distribution in the horizontal plane at 264-cm depth.

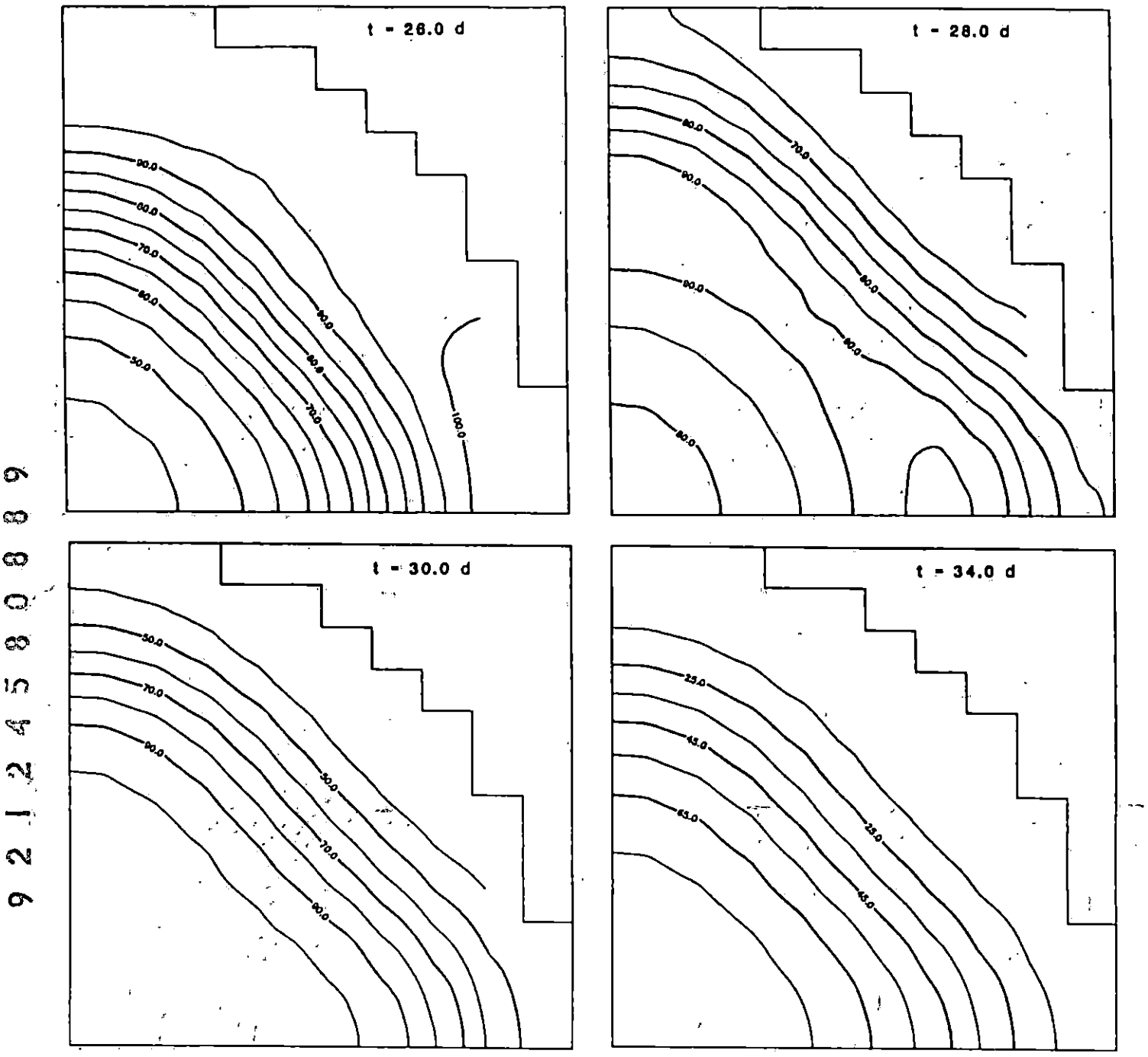


Figure 19. Contour plots of iodide concentration distribution in the horizontal plane at 339-cm depth.

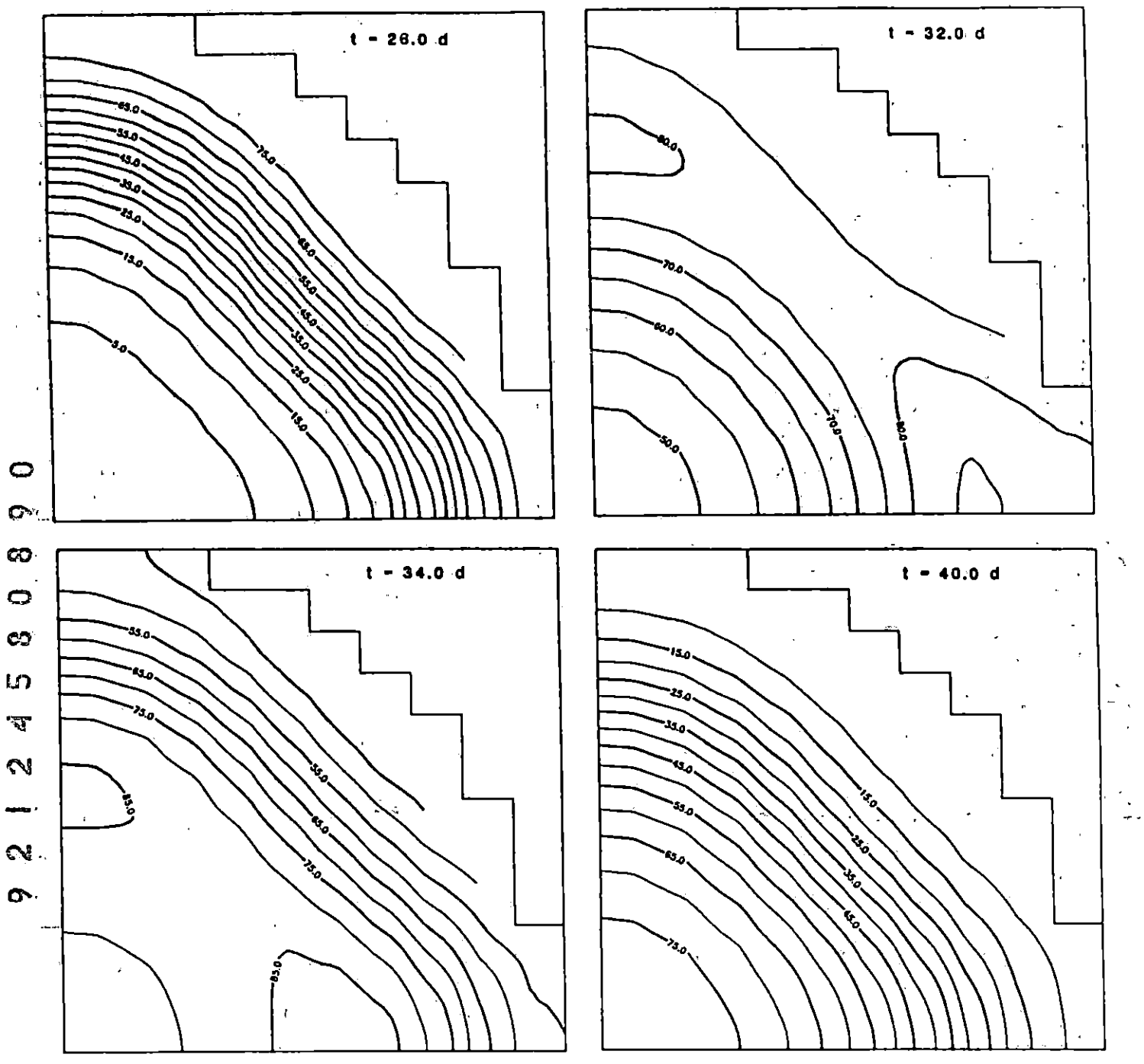


Figure 20. Contour plots of iodide concentration distribution in the horizontal plane at 415-cm depth.

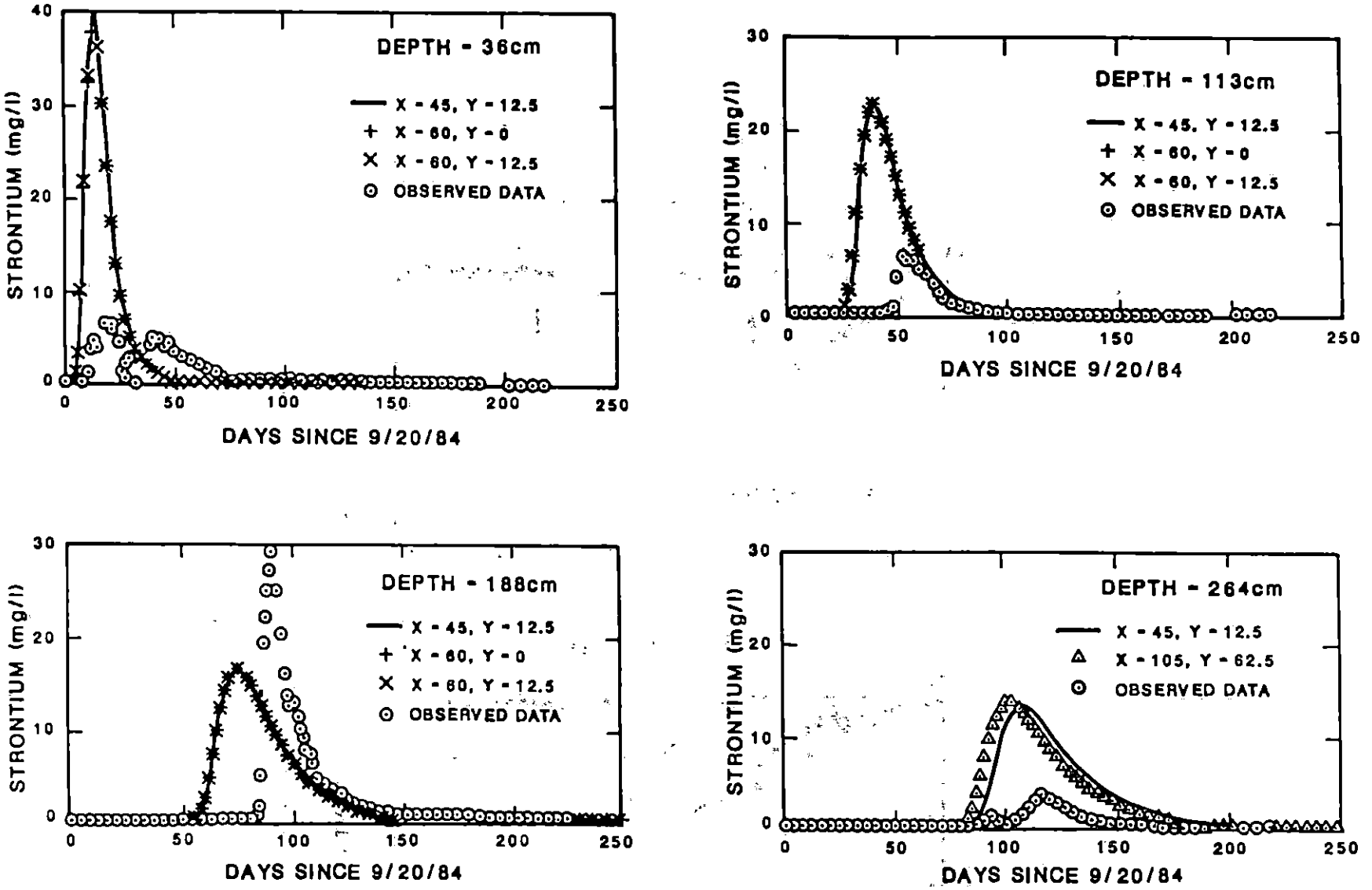
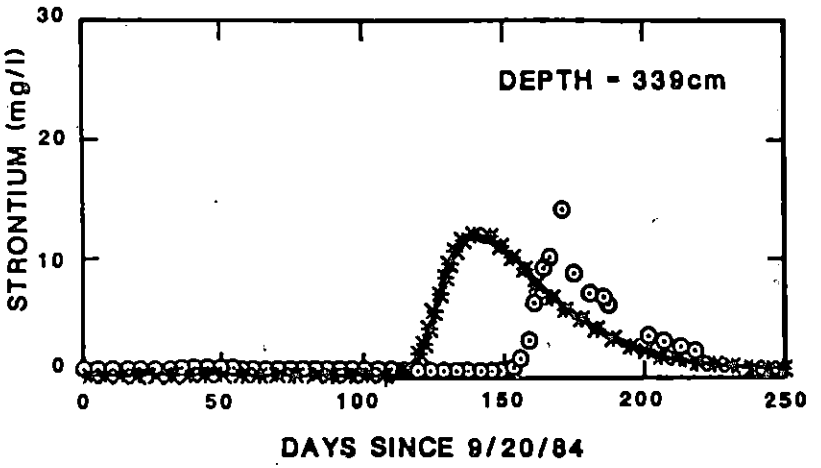


Figure 21. Strontium breakthrough data measured at various depths and predicted curves obtained from the three-dimensional simulation using Freundlich isotherm.



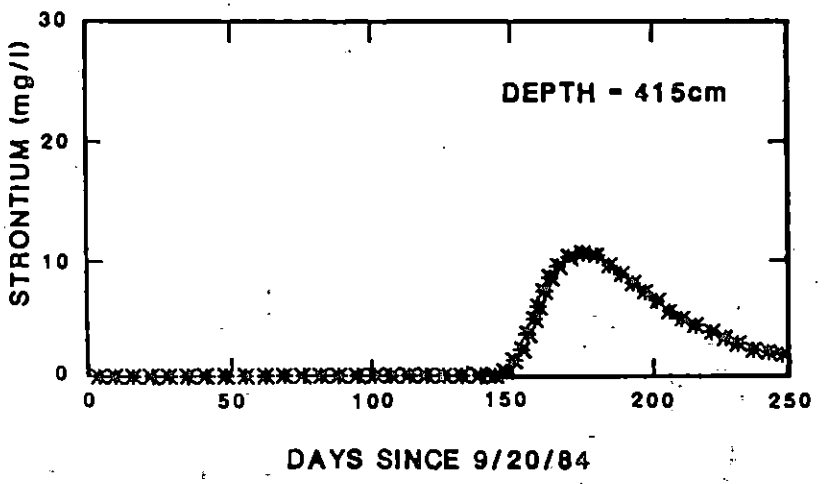


Figure 21. (continued)

slow zone are nearly identical at all depth levels considered. Only at the 36-cm depth is there a barely discernible difference. The plot for the 264-cm depth shows a breakthrough curve for an observation node in the fast zone just ahead of a breakthrough curve for an observation node in the slow zone. The effluent curve is not presented as there are no observed data available for comparison.

The asymmetric shape of the concentration versus time data is duplicated by the nonlinear simulation curves. However, the positions and heights of the concentration peaks do not agree well with the experimental data. For the sampling depths of 36 and 264 cm, the simulated peak arrival times are in reasonable agreement with the observed. At the remaining sampling depths, the first arrival times and the peak arrival times simulated are earlier than those observed. Differences in the comparison of simulated to observed data at the 264-cm sampling depth have been noted previously for both iodide and strontium.

The results of the three-dimensional simulation are less in agreement with the experimental data than the one-dimensional simulation results. This is caused by differences in the parameter values used and by the increased complexities of nonlinear transport in three dimensions. The one-dimensional transport simulation used flow parameters estimated by van Genuchten et al. (1986), whereas the three-dimensional transport simulation used flow parameters estimated by the calibration of the one-dimensional flow model. This indicates that the set of flow and transport parameters that were selected based on one-dimensional model calibration may not be valid for strontium. There are several additional factors contributing to the complexities of the strontium transport: (1) the consideration of nonlinear adsorption in a heterogeneous medium and the imposition of a

three-dimensional solute flux boundary in a flow field presumed one-dimensional involve uncertain interactions possibly affecting solute transport, (2) the flow conditions during early time in the strontium experiment have been determined as unsteady by variations in effluent quantities, (3) temperature and effluent monitoring indicate the caisson was at or near freezing at later time during the experiment, and (4) strontium concentrations may be affected by geochemical reactions associated with dissolution of the volcanic material or complexing with the calcium chloride flush. Other workers have suggested strontium carbonate as the likely geochemical control. Some combination of these factors may have led to the anomalous behavior of the observed data, where inconsistent trends in peak concentrations with increasing depth are otherwise difficult to interpret.

Contour interpretations of strontium concentration distributions are shown for sample depths 36, 113, 188, 264, and 339 cm in Figures 22 to 26, respectively. Similar to the iodide contour plots, these contour plots show the earlier breakthrough in outside slow zone followed by earlier flushing in the same outside zone. However, the relative contrast in concentrations between the two zones is much less for strontium than for iodide. In addition, an apparent increase in inner-zone concentrations due to breakthrough, simultaneous with a decrease in outer-zone concentrations due to flushing, is less frequently observed. These differences are attributed to the complications added by the nonconservative nature of the strontium tracer. Lastly, the three-dimensional effects of the discrete point application of tracer is again observed at the earliest plotted time at sample depth 36 cm. Unlike the iodide simulation, these effects are notable in both the slow and fast zones, for the fast zone has not begun to flush and yet the contours are convoluted.

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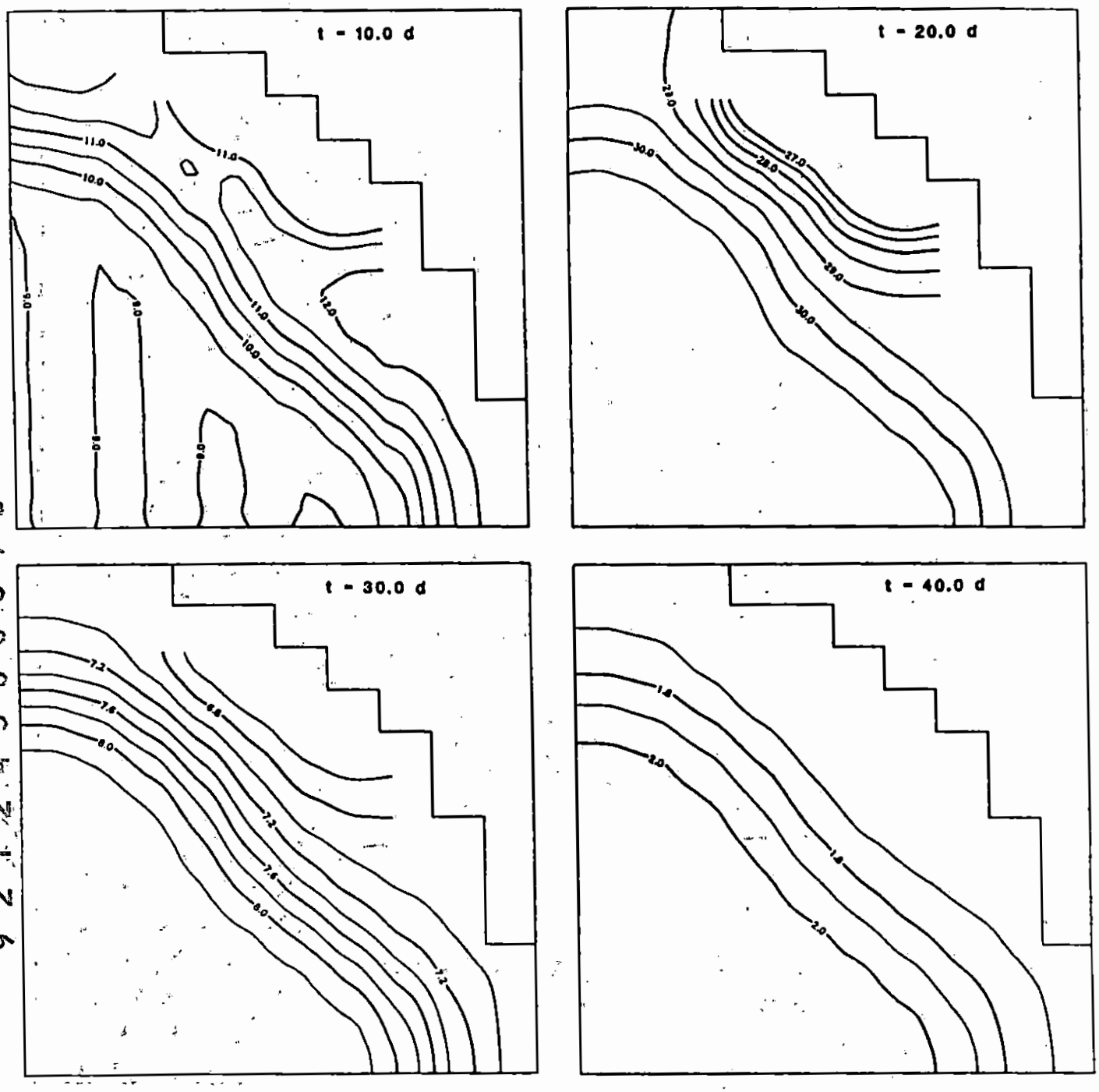

Figure 22. Contour plots of strontium concentration distribution in the horizontal plane at 36-cm depth.

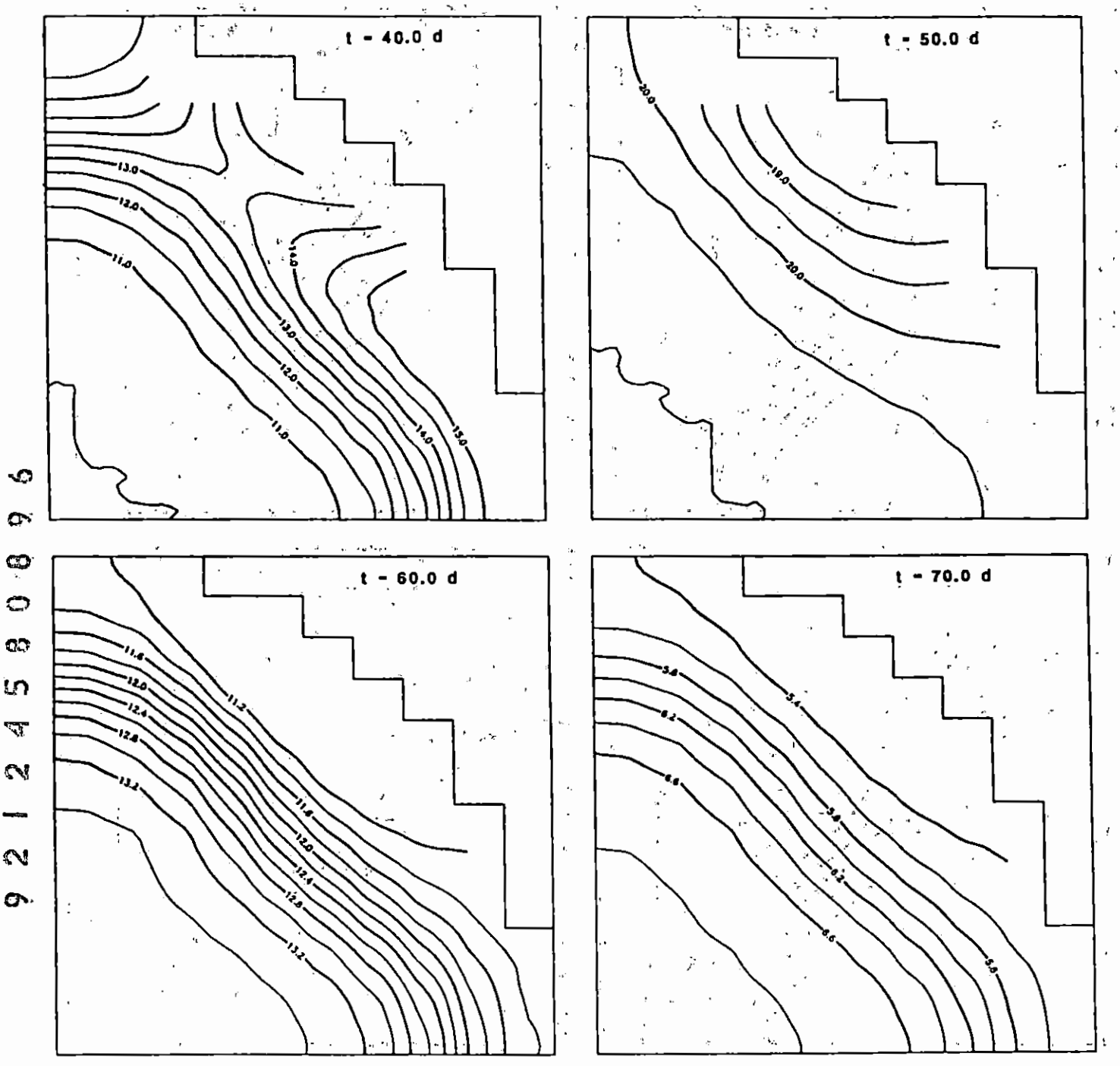

Figure 23. Contour plots of strontium concentration distribution in the horizontal plane at 113-cm depth.

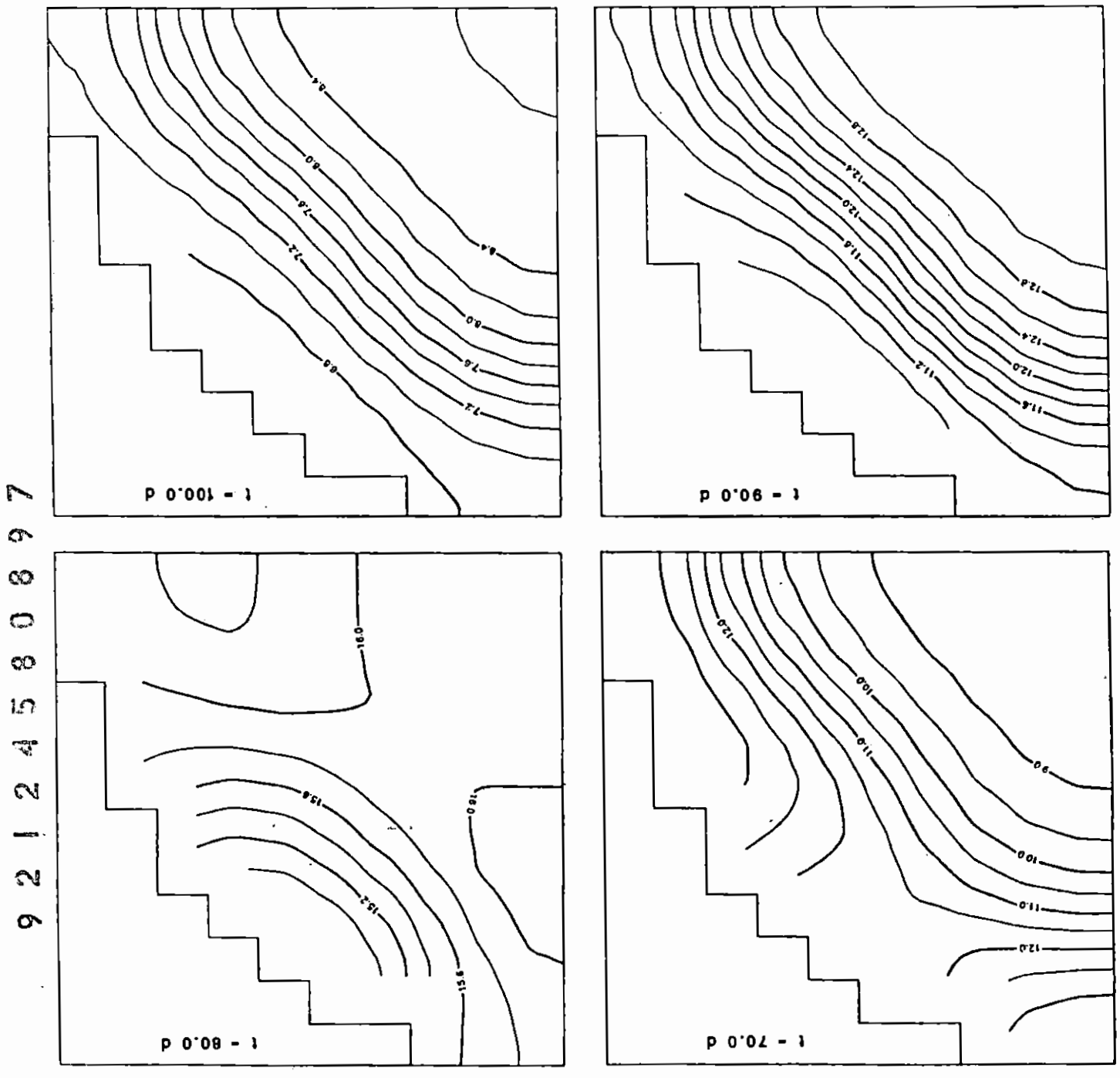

Figure 24. Contour plots of strontium concentration distribution in the horizontal plane at 188-cm depth.

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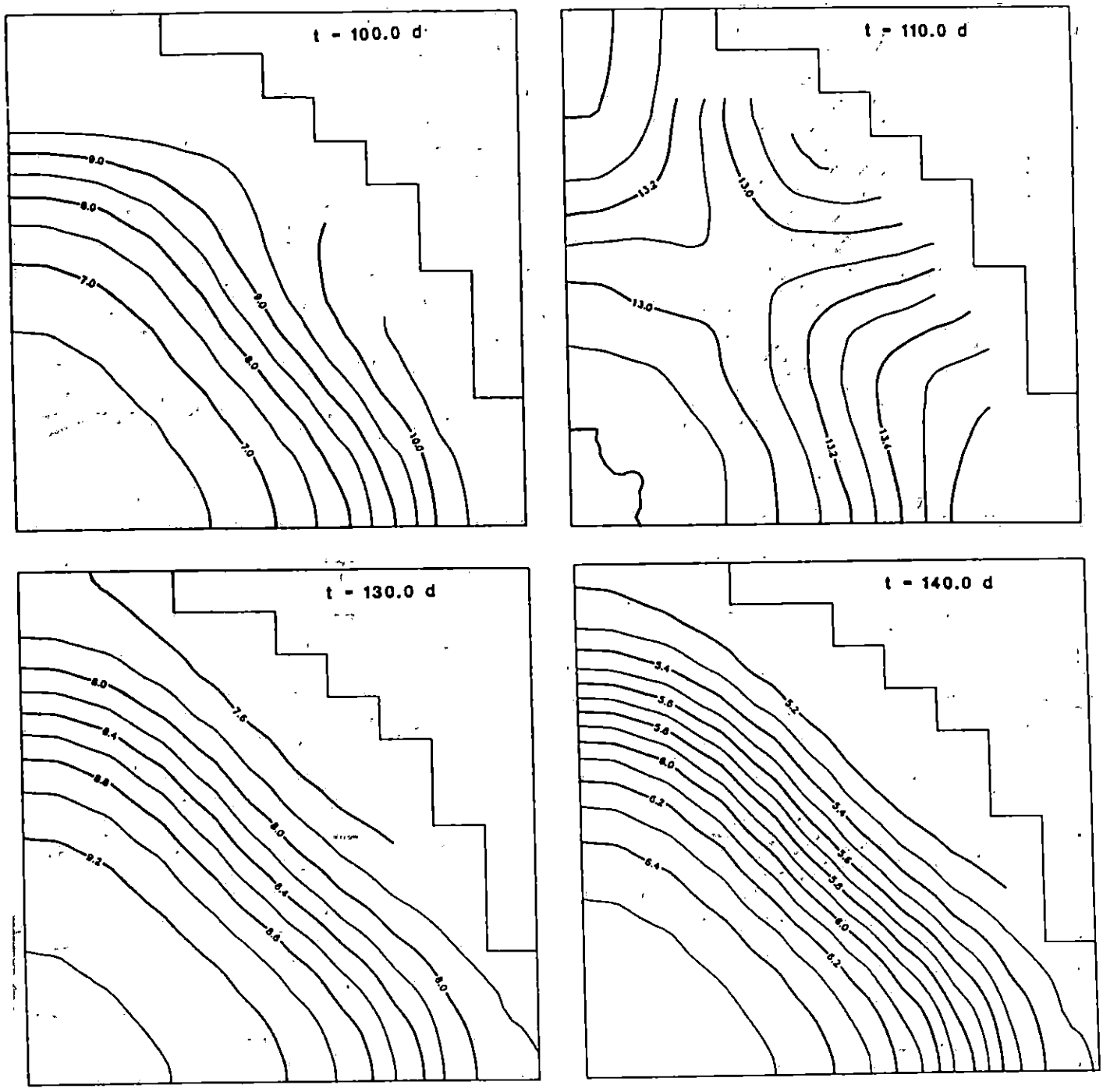

Figure 25. Contour plots of strontium concentration distribution in the horizontal plane at 264-cm depth.

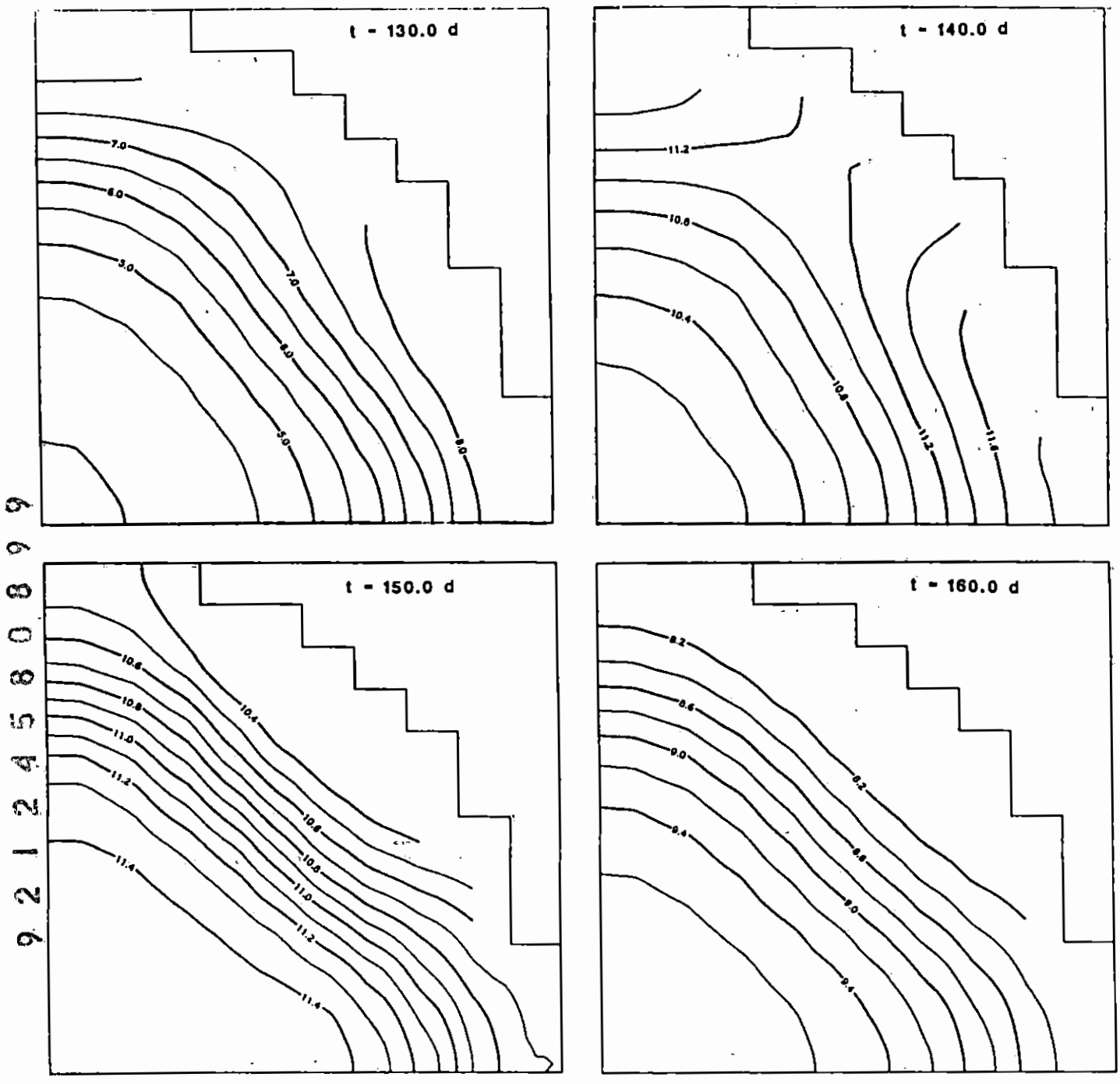

Figure 26. Contour plots of strontium concentration distribution in the horizontal plane at 339-cm depth.

SUMMARY AND RECOMMENDATIONS

The analysis performed has used two selected models for flow and transport simulations in one- and three-dimensional modes. The simulations have demonstrated the capabilities of the models used to describe the transport of conservative and nonconservative tracers in caisson B given the data available. One-dimensional simulations of flow and transport have been utilized for preliminary analysis, whereas three-dimensional transport simulation has been performed to establish the three-dimensional effects of nonuniform tracer applications and material heterogeneities. These analyses of flow and transport suggest the following:

1. Calibration of the flow parameters estimated by van Genuchten et al. (1986) on the basis of gravity drainage in caisson A indicates the parameters must be adjusted for hysteresis effects for application to caisson B.
2. Breakthrough curves for one-dimensional strontium simulations using the Freundlich isotherm, fit the shape and peak arrival times of the observed data better than the linear approximation.
3. The breakthrough data for sampling depth of 264 cm typically shows anomalous peak arrival times and the effluent data exhibit an anomalous double-peak shape possibly due to three-dimensional effects.
4. The observed data for strontium show inconsistent trends in peak concentrations with depth suggestive of poorly defined experimental conditions such as periods of unsteady flow and geochemical reactions with the tuff or the flush.

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5. The inclusion of two different water flow zones in the three-dimensional simulation better describes the observed breakthrough for the effluent.
6. The two zones as modeled simulate excessive dispersive-like mixing effects for iodide at sampling depths of 339 and 415 cm.
7. Contour plots of simulated iodide and strontium concentration distributions consistently show a concentration gradient interface between the two zones that expands at later time and with greater depth. The gradient across the interface is lessened for strontium by adsorption.
8. Breakthrough curves for strontium indicate the parameter values chosen based on one-dimensional model calibration may not be valid for the three-dimensional simulation.
9. There are differences in the response of iodide and strontium breakthrough upon expansion to three dimensions, possibly attributable to complexities in the interaction of nonlinear adsorption and properly described strontium experimental conditions or imposed boundary conditions.
10. Contour plots of iodide, and particularly strontium concentration distributions at 36-cm depth at the earliest time plotted, show the convoluted effects of the nonuniform tracer application.

The observations noted above give rise to the following recommendations:

1. If the experimental conditions for strontium could be better defined, the one-dimensional calibration could be extended to concurrent three-dimensional calibration of the differing iodide and strontium data, possibly leading to improved determination of effective three-dimensional parameters.

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2. The three-dimensional effects are potentially important and additional data collected in a more three-dimensional monitoring network might provide the data needed for better duplication of the experimental results.

3. Better understanding of the geochemical environment and its effects, particularly on strontium movement, is desired. The possibility of concurrent dissolution of the volcanic tuff with strontium carbonate precipitation should be examined. Potential spatial variability in the amount of total moisture content trapped as structural water may also be of interest. This could be determined by comparing neutron probe water contents with water contents determined by drying.

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Acknowledgments

This work was supported in part by research funds provided to GeoTrans, Inc., by the U. S. Nuclear Regulatory Commision through Los Alamos National Laboratory under agreement 9-X2D-0347D-1. Computer support was provided by GCS Associates. The authors acknowledge Charles Kincaid and Barry Lester for helpful suggestions in the problem formulation and simulation approaches.

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DISCUSSION

C. J. Duffy — I have one question about the transverse dispersivity. What theory did you have in mind that would allow you to use the transverse equal to the longitudinal?

P. S. Huyakorn — I just did that deliberately. I used a value of 2.5 because of the fact that I want to make sure that my numerical solution is reasonably accurate because my grid is very coarse. If I reduce the dispersivity, I must use a finer grid; otherwise, there will be too much numerical dispersion.

C. J. Duffy — It would appear that the three-dimensional effects are lost through all the transverse spreading.

P. S. Huyakorn — No, they are not lost. In fact, I think that if I reduced the value of lateral dispersivity (say by a factor of 10), we might see some double-peaked effect on the predicted effluent breakthrough curve. I need to emphasize, though, that we may need to use a more refined grid to ensure a reliable numerical solution for smaller dispersivity values.

C. J. Duffy — What kind of computer times are we talking about?

P. S. Huyakorn — We ran the three-dimensional transport problem on our Prime 550-II, which is not very powerful. It took about 28 to 30 hours to complete 160 time steps. We estimate that the same simulation would take only two minutes on a Los Alamos CRAY supercomputer.

I. P. Murarka — I noticed in the results you presented that when you use the experimental conditions values that were supposed to have been used and you do your calculations, then when you used the estimated values that the data analysts have derived, I see the shifts in the peaks and locations. That is kind of an unsettling situation to me because, generally speaking, true predictions for process-based models should be able to use and reliably predict things if the processes and the presentations are properly made. The other observation I have is that the average of the two velocities that you used for the fast and the slow zones is higher than the observed average velocities, and I wonder if there is

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some communication problem or if your results would look different if you use the observed average velocities?

P. S. Huyakorn

No, we did not take a straight average of the pore velocities in the two zones. Before averaging, we weighted the pore velocities in each zone by its water content value.

I. P. Murarka

I am not sure if you have the two average velocities you used, each being higher than the average observed velocity. One is 12.6 and the other is 17, which is both higher than 11.6. If you have taken that into account, then I don't have a particular problem with that.

J. C. Parker

It may be notational differences; Peter is talking about the Darcy velocities rather than pore water velocites.

D. J. Goode

I want to report that Tim McCartin, who is in the Office of Research at NRC, made some desperate attempts to try and run this problem in the last couple of weeks and he too ran into some severe convergence problems. He did finally use a transient run to get to steady state but had a lot of trouble with both FEMWATER and UNSAT 2.

My understanding of what you did concerning the transport problem was you started out with the uniform Darcy velocity throughout the region and then all you have changed is the linear velocities in the two different zones. I guess what I was expecting to see was to step back futher from that and to see some variation in hydraulic conductivity between the two zones with the resulting calculated nonuniform flow field. Maybe a better approach would be to have very small dispersivities and to look at a convection problem which might more accurately respresent how the water is moving as opposed to using dispersivities to account for this variability in velocities.

P. S. Huyakorn

The major difficulty here is that we have a very severe time constraint and so we used a logical approach and simplified the problem. We don't know for now, but I have a feeling that the 3-D effect of the flow is not as important as that of the transport. There could be some 3-D effects due to point source injections that could occur over the first 30

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to 40 cm from the top of the caisson, and I think that could be brought out by the simulation. Also, we are trying to illustrate that because of the permeability variations you get mixing that occurs between different layers that have different advection rates. In using our numerical model to do transport simulations, we had to introduce some small dispersivity value (on the order of a few centimers) to control numerical oscillations. This is because we had to run the code on a small minicomputer. If we could run the code on a supercomputer, it would be feasible to use a refined grid having on the order of 100,000 nodes. With such grid refinement, we could reduce the dispersivity to a small fraction of a centimeter. Nonetheless, our present simulation results indicate that the effluent breakthrough curves are strongly influenced by interzonal mixing. I should point out that we made a rather simplistic representation of hydraulic conductivity variation in our simulation. The actual situation is much more complicated. Undoubtedly, there are lateral as well as vertical variations of hydraulic conductivity of the soil material in the caisson.

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PANEL SUMMARY REPORT

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INTRODUCTION

The objective of this report is to summarize the various modeling approaches that were used to simulate solute transport in a variably saturated caisson. In particular, the technical strengths and weaknesses of each approach are discussed, and conclusions and recommendations for future studies are made. Five models are considered: (1) one-dimensional analytical and semianalytical solutions of the classical deterministic convection-dispersion equation (van Genuchten, Parker, and Kool, this report); (2) one-dimensional simulation using a continuous-time Markov process (Knighton and Wagenet, this report); (3) one-dimensional simulation using the time domain method and the frequency domain method (Duffy and Al-Hassan, this report); (4) one-dimensional numerical approach that combines a solution of the classical deterministic convection-dispersion equation with a chemical equilibrium speciation model (Cederberg, this report); and (5) three-dimensional numerical solution of the classical deterministic convection-dispersion equation (Huyakorn, Jones, Parker, Wadsworth, and White, this report). As part of the discussion, the input data and modeling results are summarized. The models were used in a data analysis mode, as opposed to a predictive mode. Thus, the following discussion will concentrate on the data analysis aspects of model use. Also, all the approaches were similar in that they were based on a convection-dispersion model of solute transport. Each discussion addresses the modeling approaches in the order listed above.

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SUMMARY OF APPROACHES

Van Genuchten et al. combined a numerical solution of the one-dimensional unsaturated flow equation with a nonlinear least-squares optimization scheme based on the Levenberg-Marquardt method. In addition, a multiparameter curve-fitting method developed by Parker and van Genuchten (1984) was used to

determine values for pore water velocity, dispersion coefficient, retardation factor, and pulse duration time from observed solute concentration distributions for the various depths in the caisson. Observed solute concentration distributions were fitted individually for a single depth and simultaneously for the several depths.

Knighton and Wagenet used a Markov process model employing discrete space representation to describe the movement of chemical molecules in the solution phase. For the analysis of the caisson data, a steady state form of the continuous-time Markov process was used. Furthermore, movement of the solute molecules was assumed to be downward and only between two adjacent soil layers.

The approach that Duffy and Al-Hassan take is stochastic in nature in that velocity and concentration are, in essence, treated as random quantities. Their approach to the problem lies between the deterministic physics-based method of Huyakorn et al. and Parker et al. and the probability-based procedure adopted by Knighton and Wagenet. The basic method starts with a convection-dispersion equation, which is then studied from the point of view of an input-output relationship. They show how a frequency-domain analysis can be applied to study convection and dispersion, how the frequency-domain method differs from a spatial moment procedure, and how a model with varying velocities can be incorporated.

The moment technique used by Duffy and Al-Hassan is useful because it is simple, because it offers a general approach to studying transport problems, and because it can easily be used with inputs that are not necessarily delta functions. The frequency domain approach to the moment problem further simplifies the use of the moment method and allows one to extend this whole procedure to problems with several velocities.

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Cederberg's approach involves the coupling of a one- or two-dimensional finite element transport code (ISOQUAD) with a chemical-equilibrium code (MICROOL). Whereas the other approaches described in this report use an empirical retardation factor to describe the partitioning of solute between fluid and solid, the TRANQL code calculates the speciation of the contaminant based on the chemical composition of the system and thermodynamic equilibrium constants. Once the distribution of the solute between the solution and the substrate has been calculated, the transport of dissolved constituents is simulated by solution of the classical advection-dispersion equation for porous media. The spatial derivatives of the equation are approximated with the Galerkin finite element method using linear or quadratic, isoparametric basis functions (Cederberg 1985).

The approach advanced by Huyakorn et al. is that of a three-dimensional deterministic model. FLAMINCO, a fully three-dimensional finite element code, is represented in this computational exercise. Results of one-dimensional simulations obtained with an earlier, two-dimensional version of this code (i.e., SATURN) are also shown; however, they are used to simply characterize the more complex three-dimensional problem. These one-dimensional simulations permit Huyakorn et al. to minimize the parameter sensitivity and calibration process conducted with the fully three-dimensional code.

Both the FLAMINCO and SATURN codes model moisture movement as well as solute migration. Moisture movement is assumed to be a Darcian flow process and solute transport is assumed to be the result of convective and Fickian dispersive processes. However, the moisture movement capabilities were used in only one dimension.

Distinguishing features of the Huyakorn et al. approach are its strict deterministic formulation and its three-dimensionality. With respect to the

dimensionality, it is apparent that when forced to define the moisture movement and solute transport problems in three dimensions, one is more likely to develop a fully consistent conceptual model of the system.

Huyakorn et al. are the only participants in the model comparison study to attempt a simulation of the moisture movement in caisson B. Because of the lack of data related to the possible spatial variability of soils placed in the caisson, Huyakorn et al. assumed a one-dimensional flow system exists. Later, during the transport simulation, they find it convenient to assume a two-zone (i.e., fast and slow zones) structure where each zone is independent and the physical location of these zones is assumed to be known and one-dimensional.

Three-dimensional transport simulations are shown for iodide and strontium. These results are the major contribution of the Huyakorn et al. paper. A two-zone one-dimensional model of the flow system is assumed and it leads to a bimodal distribution in the effluent curve. The similarity of this conceptual model to the one assumed by van Genuchten et al. is obvious. However, the Huyakorn et al. conceptual model differs in the use of somewhat more realistic parameters.

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DATA USED

The major emphasis was on tracer data, with concentrations of iodide (I), bromide (Br), lithium (Li), and strontium (Sr) being provided as functions of time and space. In addition, soil water data were also provided. Volumetric water content at all soil sampling depths (36 to 415 cm) remained essentially constant throughout the first unsteady state pulse experiment and the following steady state pulse experiment at values that ranged from 27% to 29%. The crushed tuff had a volumetric water content of 33% at saturation; hence, the experiments were performed at 82% to 88% saturation.

In addition, some soil moisture tension data were also provided. At the 36-cm and 339-cm depths, soil water tension values generally ranged from 5 to 20 cm of water during the steady state flow experiment. Outflow rates for caisson B ranged from 110 to 250 cm^3 min^{-1} during the steady state flow experiment.

Van Genuchten et al. used observed data on water content and tension in caisson A to calculate the hydraulic functions (water content versus tension and hydraulic conductivity versus water content) of the tuff in this caisson. Water content data at six depths and pressure heads at one depth were used. In addition, observed solute concentration distributions were used.

Knighton and Wagenet used 5-cm-thick soil layers by dividing the caisson into 130 layers. Constant volumetric flow rates for each layer were used along with the pore water volume for each layer to estimate the transition probabilities for the transport of nonreacting chemicals. Both of these were estimated from given measurements. No sources and sinks were allowed for the conservative solutes. Because a retardation factor was used to define sorption, bulk density, saturated water content, and a distribution coefficient were estimated for the reacting solutes.

The data requirements for the TRANQL code are quite different from those of other models of the workshop. In previously published applications of this code (Cederberg 1985), the pore water velocity was assumed to be steady and independent of solution composition. Transport parameters such as fluid velocity, dispersivity, and porosity were assumed to be constant in time but may be spatially variable. Calculation of the chemical speciation of the solute requires specification of the total concentrations of all major species that can complex with or compete with the solute in complexation reactions, the equilibrium constants for all important homogeneous and heterogenous

reactions, the specific surface areas of sorbing substrates, and the solution-to-solid ratio of the porous matrix. In addition, if electrostatic interactions between the solids and solution species are to be modeled, the capacitances of the electrical double layers must be estimated. The chemical equilibrium model assumed in TRANQL requires that the thermodynamically stable (or important metastable) solids be identified and included in the data base.

To justify the use of a fully three-dimensional modeling capability, one needs evidence and corresponding data that indicate the three-dimensionality of (1) the environment or (2) the boundary conditions imposed on the environment. Data available from the experiment, specifically the moisture content data, suggest at most a two-dimensional axisymmetric analysis is justified. The bulk of the data suggests a one-dimensional analysis. In light of this situation, it should come as no surprise when the conceptual model adopted for the three-dimensional analysis has a one-dimensional appearance. While data critical to a realistic three-dimensional analysis will not be found among the existing data, it remains to identify those data that are available, how they were obtained, and how they were used.

A single soil characterization was provided by van Genuchten et al. It is essential to an analysis of moisture movement in the vadose zone and includes a moisture retention curve and relative permeability curve. This particular soil characterization was based on soils in caisson A and proved to be inappropriate for direct application to caisson B.

Model parameters necessary for the three-dimensional simulation of solute transport were either taken from the data base, taken from the van Genuchten et al. parameter estimation work, or simply assumed. Values for Darcy velocity, effective porosity, average saturation, period of injection, and source concentrations were taken directly from the data. Analysis of the

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bimodal effluent curve by van Genuchten et al. suggested a similar approach be taken with the three-dimensional model. Consequently, the seepage velocities adopted for the two zones are based heavily upon their results. Huyakorn et al. adopt velocity values that have the additional validity of an area-averaged saturation that matches the observed average saturation value. However, the range of saturation values associated with the experiment (e.g., 0.88 to 0.82) was not matched by Huyakorn et al. (e.g., 1.0 to 0.72). Geochemical models and parameters used by Huyakorn et al. were identical to those of van Genuchten et al. Longitudinal and transverse dispersivity values adopted for the three-dimensional analysis were largely defined by the mesh resolution of the numerical model. The homogeneous and isotropic value of 2.5 cm is only slightly larger than that used by van Genuchten et al. for their "slow zone." A one-dimensional simulation showed that potential numerical difficulties existed if the dispersivity was reduced to 0.5 cm. Perhaps the most significant data distinction between the one-dimensional and three-dimensional models is the necessity in the latter case to assume a transverse or lateral dispersivity value. Huyakorn et al. assumed the transverse and longitudinal values of dispersivity are equal. The literature suggests the transverse value should be a fraction of the longitudinal value. Use of an isotropic value is an assumption for this modeling exercise.

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ADVANTAGES/DISADVANTAGES OF EACH APPROACH

The results of the inverse problem solution obtained by van Genuchten et al. were compared with hydraulic conductivity data computed by Abeele (1979 and 1984) using the instantaneous profile method. Both methods gave comparable results. However, it appears that the inverse method used by van Genuchten et al. requires fewer data, fewer hand calculations and less smoothing of the original data than the traditional instantaneous profile

method. It is, therefore, quite possible that the inverse method will in the future largely replace the instantaneous profile method for determining the hydraulic functions of soils from soil-water redistribution data.

The methods employed by van Genuchten et al. are very useful in obtaining soil physical parameters (hydraulic functions, dispersivities, retardation factors) from column and field transport studies. These parameters can be used in other models to make predictions of solute transport under different conditions. The methods are readily available and quite easy to use. Unfortunately, they are limited to well-controlled experiments in uniform soil profiles. For less well-controlled conditions and less-uniform soil profiles, assumptions should be made that allow the use of these methods.

The advantage of the approach used by Knighton and Wagenet is that the probabilistic approach provides an unconstrained method to estimate the movement of solutes through a porous media under the assumption that it is a random phenomenon. Structurally, the approach is simple and could provide the most general form of modeling the movement of solutes. The approach only depends on one's ability to observe/measure the distribution of chemicals, water, and several physicochemical properties of the soils that could affect solute migration. The calculation algorithm is simple and requires relatively few assumptions. Because it is a probability-based model, the uncertainties in transport can also be computed.

The disadvantage of this approach is that it requires data that answers the prediction question. That is, observed concentration distributions (spatial and temporal) must be available for the estimation purposes. Similarly, water content data are needed for each layer. It is not clear how one would a priori or observationally decide on the number of soil layers and their respective sizes. In field-scale environments, it is improper to assume

that spatial and temporal probabilities of transition for molecules will be independent and identically distributed. This approach is a data analysis method where the physical and chemical processes cannot be easily defined. Questions such as why a chemical will or will not move cannot be easily answered. Given there are large measurement errors and spatial-temporal variabilities in the moisture distribution are large, this approach would inherently have a large variance associated with any estimation. One can view multilayer and multidirectional transition probabilities as dispersion in the various directions. Therefore, it would be very demanding with respect to data needs when the interest is in field-scale transport/fate problems.

The strength of Duffy and Al-Hassan's approach to the problem resides in the use of this procedure in the identification and estimation of the velocities and other parameters. Thus, using a simple model for the physics along with the frequency domain approach, they can study whether different "cells" for the velocity model explain the observations. In addition, they can use the frequency procedure to estimate the dispersivities.

The results of attempts to model the caisson data using TRANQL were not available in time to be included in this report. Therefore, a final evaluation of the comparative advantages and disadvantages of this approach could not be made. However, some general comments concerning the applications of TRANQL and other similar coupled reaction/transport codes to the caisson experiment can still be made and are summarized below.

The use of a retardation factor in a classical advection-dispersion equation requires the following assumptions: (1) sorption is the dominant chemical interaction between the solute and the rock, (2) a single dominant aqueous species of each solute is present, (3) local chemical equilibrium between the solution and rock exists, and (4) sorption isotherms have been

obtained in solutions of the chemical compositions that exist along the solute flow path. If a K_d is used to describe the partitioning of solute between the rock and fluid, it also must be assumed that the degree of sorption is independent of solute concentration. The K_d value must be obtained with samples of the mineralogies that exist along the flow path.

The main advantage of the TRANQL code is its potential to describe solute transport under conditions in which the above assumptions are not valid. Previously, TRANQL has been used to model transport of a sorbing tracer in the presence of a conservative complexing ligand (Cederberg 1985). In that study it was shown that the sorption of cadmium (expressed as a K_d) varied over several orders of magnitude because of complexation with EDTA. In its current form, TRANQL can be used to describe the transport of solute more accurately than codes using retardation factors when aqueous speciation and nonlinear sorption are important. The extensive chemical data base required by the code, however, is a major disadvantage. For example, few of the data required for simulation of the transport of strontium are available. At present there are insufficient thermochemical data to adequately model sorption of strontium on tuff in the solutions used in the caisson. In its current form, TRANQL cannot be used to model systems in which precipitation, coprecipitation, or kinetic effects are important. As discussed in the next section, preliminary modeling results of the chemical data from the caissons (Siegel 1986) using the more comprehensive geochemical speciation code MINEQL suggest that these phenomena must be considered in simulations of this system. The fundamental chemical data required to accurately model these effects are also unavailable. In addition, modeling of these phenomena with either TRANQL or MINEQL requires detailed characterization of the mineralogy, surface area, and site-binding capacity of the tuff within the caissons. The difficulty in obtaining these

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data for this type of experiment is another disadvantage of this modeling approach.

Huyakorn et al. used most of the experimental data in its unadulterated form. They attempted to honor average values of the data if they found it difficult to honor the entire subset of data. For example, the period of injection is held at 6 days and not altered in order to produce a better match. Also, while the areal distribution of moisture content is not duplicated, the average saturation of 0.834 and effective porosity of 0.331 are duplicated in an area-average sense by the two-zone conceptual model.

In formulating a three-dimensional simulation, one is less likely to generate inconsistencies. For example, van Genuchten et al. implicitly assumed by using a two-zone model either (1) a two-zone infiltration distribution (i.e., proportionately greater flux associated with the fast zone and lesser flux associated with the slow zone) or (2) the communication of fluid from the slow to the fast zone. In the fully three-dimensional approach of Huyakorn et al., neither of these artificial assumptions is made. A pointwise uniform distribution of influent is employed to introduce water and solute. Strictly one-dimensional and independent moisture movement is enforced through the specification of uniform one-dimensional convection (i.e., velocity fields) in the three-dimensional model of solute transport.

The multidimensional character of transport phenomena, i.e., transverse velocity and dispersion, and its potentially significant influence on effluent from waste sites can only be studied and evaluated through the development and use of conceptual models that include multidimensional process descriptions. This may not require a fully three-dimensional deterministic model and may also be accomplished with a two-dimensional axisymmetric model or a stochastically based approach. Inclusion of multidimensional processes is a significant advantage of the Huyakorn et al. approach.

SUMMARY OF MODELING RESULTS

Concerning the multiparameter curve-fitting method used by van Genuchten et al., except for the 264-cm depth and the effluent, a good fit was obtained between observed and fitted bromide and iodide distribution curves. Peak location and peak height were especially well predicted. When several concentration distributions were fitted simultaneously, average dispersivities of 1 cm and 0.5 cm were obtained for iodide and bromide, respectively. Dispersivity values of 1 cm or less are typical for small laboratory columns, and the fact that such small dispersivity values were found for the large caisson indicates uniform packing and a relatively structureless porous medium.

The iodide effluent data could not be described using the parameters obtained by fitting the effluent concentration distributions at the shallower depths. Instead, two distinct and noninteracting flow regions with different pore water velocities needed to be invoked to describe the bimodal iodide concentrations in the effluent from caisson B. Although different flow regimes did undoubtedly exist in the caisson, as evidenced by the anomalous behavior at 264 cm, the selection of two flow regimes by van Genuchten et al. to fit the observed effluent iodide distributions is arbitrary, and there is no proof of their existence. In fact, the presence of saturated conditions in the lower end of the caisson, the presence of a thick gravel layer, and the concentration of flow through one central drain pipe may all have influenced the shape of the effluent curve. As such, too much confidence may have been put in the effluent concentration distribution. The strontium data were not well predicted using pore water velocities and dispersion coefficients estimated from the pooled iodide, bromide, and lithium data. The first

breakthroughs were well predicted, but the peak concentrations were not. Apparently, strontium chemistry, e.g., precipitation of strontium carbonate, was not properly taken into account. Without a better understanding of the experimental conditions (e.g., soil pH) and better inclusion of strontium chemistry in the model, further analysis of the strontium data is not warranted using the analytic approach of van Genuchten et al.

The continuous-time Markov process model (Knighton and Wagenet) provided generally good agreement between predicted and measured concentrations for the upper three sampling depths (36, 113, and 188 cm). Less acceptable agreement was obtained at deeper depths (264, 339, and 415 cm). The distribution coefficients used for lithium and strontium were 0.08 and 0.9 g/cm of soil, respectively. It appears that the predicted curves yield higher total mass in the soil system than that observed by approximately 30%. This error tends to increase with depth.

One important aspect of Duffy and Al-Hassan's findings is that the dispersivity did not vary greatly. They could explain the variations observed in the concentrations with their simple physical model and with a varying velocity mode. The additional checks on the constant dispersivity model they carried out by comparing their results with the dispersed zone width further helped to validate some of their findings.

This work could be extended and tested in several ways. It is not clear just how many zones would ultimately be chosen to be appropriate for predictive purposes. While one could try to use the effluent concentration as a predictive criteria, as pointed out, use of effluent concentrations may be problematical. An alternative test would be one that uses the data at the first three or four levels to estimate the number of zones and then to use zonal model parameters to predict concentrations at the 339- or 415-cm depths

for iodide and bromide. Alternatively, one might use just one species (e.g., iodide) for parameter estimation and then use the other species for predictive verification.

In order to decide how many zones are needed, it would be useful to carry out a goodness-of-fit test. Thus, one could start with a single-zone model and see how successive zone additions would reduce the fitted sum of squares. Once again this goodness-of-fit test should work well in the frequency domain approach because of the uncorrelated nature of the frequency components.

Overall, the model by Duffy and Al-Hassan offers an interesting approach to system identification. The model combines both aspects of a more complete physics-based description like the convection-dispersion equation and those of a more general nonphysics-based ("blackbox") procedure like transfer function analysis.

This system analysis, frequency-based method offers promise as a useful model that could also be extended to field experiments. An added extension would also incorporate velocity fluctuations and correlations along the flow path, though the latter could complicate the calculations required. Nevertheless, the framework for doing a more complete analysis is included within the structure of their model. Overall, the study illustrates a useful methodology for identification of system parameters and for possible use in field experimentation.

As discussed above, the behavior of strontium in the caisson could not be described using a retardation factor in either the stochastic or deterministic models. The strontium concentration profiles do not show the expected decrease in peak height with distance from the tracer source. The curve at 36 cm has two peaks, the peaks at 119 and 271 cm are slightly asymmetrical and small, and the peaks at 194 and 347 cm are sharp with high concentrations.

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The strontium introduced during unsteady state pulse 1 (USS 1) had not eluted completely by the time the experiment had ended. The arrival of the strontium peak from the USS pulse 1 at the 188- and 246-cm sampling points coincided with the appearance of the iodide peaks from the steady state pulse 1 and unsteady state pulse 2, respectively.

On the basis of preliminary speciation calculations, Cederberg suggested that the precipitation of strontianite, $SrCO_3$ might be occurring in the caisson. Additional calculations using the MINEQL computer code (Siegel 1986) suggest that several other phenomena must also be considered in any attempt to model transport of strontium in this system. These include (1) coprecipitation of strontium in calcite; (2) the consumption of acetate and production of bicarbonate by bacteria; and (3) dissolution of the tuff, concomitant release of silica, and consumption of protons. The preliminary calculations suggest that if the chemical system was open to the atmospheric carbon dioxide, then saturation with respect to $SrCO_3$ was not achieved. The observed concentrations of strontium, however, are consistent with coprecipitation of strontium with calcite when reasonable distribution coefficients are assumed (Stumm and Morgan 1981). Additional mineralogical and compositional data for the tuff within the caisson must be obtained in order to test this hypothesis.

Other chemical reactions also must be considered in the analysis of the strontium data. If the system was closed with respect to atmospheric CO_2, then saturation of strontianite occurred at the 188-cm depth. The sorption of strontium onto crushed tuff has been shown to be very sensitive to the presence of minor amounts of clay and clinoptilolite (see review by Tien et al. 1985). Thus anomalous behavior of the strontium in the caisson could also be due to variations of the strontium K_d within the crushed-rock matrix.

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Huyakorn et al. showed that soil characteristic curves developed from a drainage experiment conducted on caisson A were not directly applicable to caisson B experiments. The characteristic curves were altered to reflect imbibition curves and shown to produce results in much better agreement with the caisson B experiment. Three of four transport simulations were based entirely on an assumed soil moisture distribution and velocity profile. Because Huyakorn et al. were the only ones to attempt a simulation of soil moisture movement in caisson B and because the soil characteristic curves developed from caisson A were found to be inconsistent with the caisson B experimental evidence, one could conclude that the prediction of soil moisture movement is not readily achieved. This is particularly true if one relates apparent difficulties in interpreting solute migration to the spatial variability inherent to the soil system. More attention must be paid to the simulation of moisture movement in the caisson.

One-dimensional transport simulations are shown for iodide, bromide, and strontium. The purpose of these simulations was to verify the finite element algorithm common to both SATURN and FLAMINCO, develop the necessary input file entries for both codes, and test various simulation parameters (e.g., dispersivity and time step) before executing the fully three-dimensional code.

The simulation of iodide migration using the three-dimensional model with a two-zone conceptual model of moisture movement produced results very similar to the two-zone model of van Genuchten et al. This conceptual model is predicated largely on the accuracy of the effluent curve. As noted elsewhere in this review, the effluent data may be corrupted by the design of the caisson drain and may not reflect the true distribution of solute arriving at the base of the unsaturated zone. From a qualitative point of view, the arrival distributions for iodide at the shallow sampler depths agree with

observations. However, they fail to match either arrival time or peak concentration characteristics at the deepest two points (i.e., 335 and 415 cm). It appears transverse dispersion is too high in the model. This is also apparent in the effluent curve.

The effluent curve is also affected by the inappropriate surficial area associated with each portion of the bimodal effluent curve. If one is to base the conceptual model on the effluent curve, then a greater portion of the caisson surface must be associated with the fast path. A correction to this aspect of the two-zone model would create a more distinct bimodal effluent curve.

Statements to the effect that "the three-dimensional analysis fits the observed (iodide) data better than the one-dimensional results" are not appropriate. While such a characterization may be correct when comparing the one-zone and two-zone conceptual models, it certainly is inappropriate as a characterization of one- versus three-dimensional models. Such statements are clearly subjective and qualitative at best. Certainly, no well-defined quantitative measure of fit has been used to reach such a conclusion.

The strontium transport simulation using the three-dimensional model with two-zone moisture movement failed to retain the contrast between zones necessary to match the distinctly different arrival distribution observed at 188 cm. Some of the observations, particularly the one at 188 cm, exhibit much less dispersion than the simulation. Huyakorn et al. suggest the poor match to strontium data is attributable to either (1) the use of parameters in a three-dimensional setting that were fit in a one-dimensional setting or (2) the complex nonconservative nature of the strontium tracer. Both probably contribute to the poor match; however, the geochemical complexity of strontium in this particular caisson experiment is clearly not included in the

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conceptual models for either linear or Freundlich sorption isotherms used in the transport simulations.

The value of using a multidimensional deterministic model to simulate the caisson experiment lies in the more fully consistent conceptual model. Initial conditions, boundary conditions, and internal structure must all be specified for the simulation of an axisymmetric two-dimensional or fully three-dimensional analysis of the caisson. By including mechanistic process models and all necessary dimensions, one is commonly more willing to use fewer "fitted" data. Hence, the simulations tend to duplicate the experimental conditions and reveal those mechanisms, processes, and reactions that we do not yet understand. For example, in this caisson experiment, the multidimensional approach employed the reported period of injection and water application rate. This duplication of the experiment revealed some nonphysical aspects of one-dimensional modeling applied to the same experiment.

However, it is clear that the data base from this caisson study did not support the use of a fully three-dimensional model. Moreover, the voluminous data necessary to simulate with a three-dimensional deterministic model may be more profitably used in a statistical or stochastic characterization of the physical system. When the two-zone model posed by Huyakorn et al. is viewed as one possible realization of reality, one comes away with the impression that two-dimensional contour plots of "the areal distribution" of slute are an inappropriate method of presenting results. The deterministic approach conveys an unrealistic level of certainty in the prediction when these contours are the primary medium used to communicate the results.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations are divided into those concerning the modeling efforts and those related to the caisson experiments. Caution must be exercised in evaluating this effort as a "comparative modeling" effort. All modelers used the experimental data to calculate/estimate values for the parameters and then used these calculated values to reproduce/predict the concentration profiles for various depths. At best, therefore, this effort can be classified as the use of models for data analysis with various approaches. No effort was made to use independently derived parameter values for prediction of the tracer behavior. Therefore, it is not possible to indicate which model parameters are transferable to other situations.

The calculated/predicted values were generally shown in graphs superimposed with observed/measured values. A qualitative interpretation on the reasonableness of predicted versus observed values generally indicated that matches were reasonable for most depths. It is recommended that a more rigorous objective approach be used to compare observed versus predicted values. A sum-of-squares approach or an average absolute residual-value estimation approach could be adopted for this purpose. Alternate conceptual models of solute transport exist and should be included in any future comparative study. A substantially more complete data set should also be collected before a comprehensive comparative study of model approaches can be conducted.

Alternative approaches to modeling solute transport representing the range of available approaches should be used in the design of future caisson experiments. These same approaches should be used in blind tests of predictive capability by simulating proposed experiments in detail before conducting the experiments in the caisson.

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The first objective of the study was to develop a comparison of approaches taken to describe transport in the vadose zone. However, all of the approaches taken in the study are based on the convection-dispersion equation. Alternate approaches to describing transport were not included. Because of this, the actual comparison of approaches became a comparison of parameter estimation methods.

Data available from the experiments are not sufficient to discriminate among alternate modeling approaches even if they had been included. The validity of the convection-dispersion model can be neither established nor refuted as a result of this study. Spatial variabilities of soil and solute properties in the caisson environment were not determined. It is possible that a 6-m-deep caisson is too shallow to provide data useful in discriminating among alternate transport theories. Significantly longer transport pathways in the vadose zone may be required.

The ultimate desire is to predict (extrapolate) based on limited data the long-term (i.e., hundreds to thousands of years) response of moisture movement and solute transport on the field scale. Investigations on the scale of caissons must be performed with a purpose related to the ultimate need. Modeling must recognize the minimal data, long-term and field-scale aspects of the regulatory need.

The definition of validation includes the concept of (1) a confirmation of a good representation of the actual processes occurring in the real system by the conceptual model and computer codes and (2) the comparison of calculations with field observations and experimental measurements. Validation of the modeling capability cannot be achieved with experimental measurements alone. Furthermore, the possibility that field-scale models applicable to the long time periods of interest will not be validated is now

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being recognized. At the heart of this issue is the nature of long-term predictions; they are extrapolations. Confidence in our ability to extrapolate is low.

During the workshop, the suggestion was made that simple models might well provide a sufficient prediction on which to base management decisions. Before discussing such a concept, one must acknowledge that simple models must be based on correct and established physical principles and mathematical models. Simple models based on incorrect physical and mathematical constructs are wrong, not simple. Simple models will result from an integration of detailed and mechanistic understanding of the environment. The decisions to be made by managers will affect many generations and they must be based on correct physics. This workshop has not established or refuted the convection-dispersion model of solute transport. Its use in assessing the long-term impacts of waste disposal on the field scale is still in question.

Concerning specific modeling approaches, the following comments are made. While the probabilistic approach of Knighton and Wagenet is one method to analyze data, we are still very far away from using this approach for predictions. The main questions follow:

1. Are probabilities a function of the porous media?
2. Are probabilities a function of the chemical?
3. Are probabilities dependent on hydrology?
4. Can probabilities be obtained a priori and absolutely?
5. What probability distribution functions are appropriate?

Experiments in large caissons are a valid intermediate step between laboratory column studies and field studies. However, caisson experiments need to be done carefully with well-controlled upper and lower boundary conditions. In particular, measurements of inflow and outflow need to be made

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so that mass balance calculations are possible for the water, as well as for the chemicals applied.

Although the hydraulic properties of the soil were reasonably well described with van Genuchten's equation, further evaluation is necessary. This could be done by initiating a transient infiltration experiment in caisson A and by comparing observed and computed (using the previously determined hydraulic functions) water content profiles in caisson A. Such a comparison might also show the importance of hysteresis, if any, in the hydraulic functions. The comparison by Huyakorn et al. in which the hydraulic functions of caisson A were used for caisson B showed significant discrepancies, but this may largely be due to different soil properties in caisson B. It is nearly impossible to construct two large caissons with identical soil properties. Even though inclusion of hysteresis in the hydraulic functions by Huyakorn et al. significantly improved the predictions of water flow in caisson B, this is no proof that the hydraulic functions of caisson A were correct for either caisson A or caisson B.

For unsaturated transport experiments in caissons, the whole caisson should remain unsaturated, including its lower end. It is suggested that several solute measurements per depth be made in order to evaluate the spatial distribution of water flow velocities. If chemical analysis of samples becomes a problem, it may be better to sample fewer depths and to take more samples per depth. Surface evaporation losses from the caissons should be prevented. The surface distribution system should be improved.

There was a consensus among modelers and panelists that the caisson experiment had not been designed properly for the study of the transport of nonconservative (reactive) tracers. Several deficiencies in the chemical and mineralogical data obtained from the experiment prevented application of the

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chemical subroutines of TRANQL to this study. The required data include a continuous record of the alkalinity of the solutions at the sampler locations and mineralogical analyses of representative samples of the crushed tuff in the caisson. The use of crushed Bandelier Tuff with highly reactive mineral surfaces presents additional problems. The freshly exposed grain surfaces will release silica, calcium, and magnesium and will consume protons. A large number of heterogeneous and homogeneous reactions are possible in such a reactive system and the use of a retardation factor to describe solute-rock interactions may be inappropriate. In future caisson experiments, mineralogical and chemical analyses of representative samples from different depths within the caisson should be taken before and after the experiment. If possible, the tuff in the caisson should be pre-equilibrated with the background electrolyte for a period of time sufficient to "age" the solids and obtain a chemically stable system.

The data from this experiment have shown that, even in carefully packed, uniform caissons, variations in flow field can occur that strongly affect transport of chemicals. Field studies should be initiated to determine the variation in flow over a field.

Comments concerning the conduct of caisson experiments and model development and application include (1) the purpose of caisson experiments; (2) how experiments on the scale of a caisson may be misused; and (3) the relationship between experiments, models, and the ultimate need.

1. Purpose of Caisson Experiments

The validity of conceptual, physical, chemical, and mathematical models of the subsurface must be established. Caisson-scale experiments can play a role in this; however, ultimately field-scale experiments must be conducted.

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The predictability of future events must be established. This may involve transient as well as steady-state experimental studies designed to provide confidence in predictive capability. Models that yield the mean, the variance, and the level of confidence in solute migration predictions would seem to be in order.

Development is needed of instruments, measurement methods, and methods of data analysis which are uniquely suited to the experimental conditions (i.e., field, caisson, or laboratory) and the modeling capability.

2. Potential Misuse of Caissons

When based on laboratory-scale columns, our understanding of moisture movement and solute transport was flawed. Regulation based on that understanding was and is flawed. An expectation on our part that caisson-scale experiments and models will provide the ultimate tool for regulation is ill conceived. Regulation of waste disposal on the field scale must be done with conceptual, physical, and chemical models that are developed from and validated to our knowledge of field-scale phenomena.

3. Experiments, Models, and the Ultimate Need

The ultimate need is for a simulation capability that extrapolates to provide long-term predictions concerning field-scale processes while requiring a minimum of field data. Perhaps the extrapolation issue and the minimum data issue can be set aside in light of the scope of the caisson experiment, but the field-scale issue must be dealt with. Theory must be developed based on a conceptual model of the field system. Caisson-scale experiments to be conducted must be designed and completed

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in the context of the field-scale conceptual model; i.e., one must pose and answer questions at a caisson scale that are relevant to the field-scale conceptual model.

Before one can determine whether further caisson-scale experiments are needed, the field-scale conceptual model needs to be developed. Within the context of such a conceptual model, one may find issues that can be resolved by conducting idealized and controlled experiments on the caisson scale. A well-coordinated effort that fully considers the relationships between field and caisson scales, and experimental and modeling methods, is needed before further experiments are conducted.

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TRANSCRIPT OF GENERAL DISCUSSION

INTRODUCTION

The second day of the workshop was devoted to a general discussion of issues relevant to modeling and conducting field experiments for solute transport through porous media. The discussion was led by the panel with participation from the audience.

There was no agenda for this discussion. Questions were asked about the presentations of the previous day as well as the applicability of current approaches to geochemical modeling. We present this transcript so readers can gain more insight into the thinking of the participants on these issues. Such interactions as presented here are often lost to those who did not attend the workshop. It is our hope that by including this material a more complete presentation of the workshop is provided.

E. P. S.

H. R. F.

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C. T. Kincaid

One of the things that was talked about yesterday was moisture movement; however, most of the presentations assumed that aspect of the experiment. Jack Parker did curve fitting to get the moisture characteristics, and Peter Huyakorn eventually applied this on caisson B. One thing that was in contrast when Jack spoke, and later Peter, was that Jack concluded that soil modeling for the moisture characteristic was essentially good while Peter concluded that it had to be corrected. You have been able to curve-fit this information and estimate these properties. You showed this by using the data to predict the coefficients and then by modeling the curves from which the coefficients were derived. However, all of your work had to do with caisson A. The next thing was the presentation by Peter, who concluded he could not use the experimentally derived curves that you had supplied but would rather rely on a hysteretic argument that an imbibition curve is more appropriate. Indeed one might also see this as a difficulty in taking data from one caisson and applying it to another. The modeled soils may fail simply due to variabilities that may occur in the packing of the soils themselves. Which of these explanations (i.e., imbibition or variability) do you think really explains it, Jack, or is it just in doubt?

J. C. Parker

Well, it has to be said that the truth is in doubt since we don't have the detailed data on caisson B for verification. It seems quite feasible that the discrepancies between the two is due at least in part, if not largely, to hysteresis. The magnitude of the difference in the moisture retention curve could easily be attributable to hysteresis in the retention functions. The little bit of manipulation with the $K(\theta)$ function might be hysteresis or it could as easily be variability between the caissons. The difference in the conductivity function only amounted to a large factor of about 2, which is not a large variation for conductivity.

C. T. Kincaid

This was just one more point I observed in hearing both presentations concerning the soil and its variability.

J. C. Parker

It could surely be answered if in addition to some drainage experiments, some data during

the infiltration experiment was also obtained. That data could have been collected without much additional effort.

I. P. Murarka

Given that there were lots of data available compared to no data, this was a large data set compared to what one may want to have, which is still undefined. Given that, we have a lot of data and people used that data to estimate many of the parameters that drive the models and their calculations regardless of the approach taken. Now I would like to step back one step and say in the predictive sense we would have some major properties of the media based on how a modeler or a predictor wants to go about may it be a hydraulic property, may it be a geochemical property, or may it be both and something about the characteristics of the material that would be placed in the environment and how it is going to enter the system before it gets transported, dispersed, replaced, or left behind in its movement in the water. I didn't quite see and maybe it wasn't asked of you, but has anybody done something where you take the known properties that one has measured and not worry about the tracer experiment, use those properties to predict the solute concentrations and see how well the caisson experiments did? The "commonly used" parameter values mainly pulled out of the hat or out of the blue sky or the clouded sky, I think that is where you get into the comparison of how well can we predict is versus how well can we describe or analyze data sets with a variety of approaches. I didn't see any large discrepancies or differences in the simulated results when it comes to concentration versus time or space profiles. They were pretty much, loosely stated, the same: there were no real rigorous differences seen. I don't know how one would estimate the probability under those conditions, but maybe there is a way to do that. Alternatively, since this data has been backed out, whether they have been supported by hypothesis or process knowledge doesn't matter if a similar experiment was repeated with a different moisture content and a different concentration of the chemicals involved predict those results using these parameters and see how well you do. I think we are still further away from the predictability question, but that is just the kind of comments or questions that I have

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in terms of where we go or what the value of this exercise is or how do we make sense of this exercise. I still think it is a data analysis exercise at this point in time. It is still a parameter estimation exercise using one or another approach. I wonder if anybody can say something about the plans and maybe Dan Goode is the right person to look at it or maybe the persons who did the modeling or even Everett could shed some light on that. I think at this point I'm not sure I'm in a position to say that one approach is better than another and that in fact any of them can be used as predictable approaches.

J. C. Parker

A number of the analyses essentially did use the observed data to predict the convective component. There is no rationale for picking out a dispersion coefficient, or whatever other name you want to put on it, in terms of conditional probabilities for moving molecules around or however you want to describe the mixing.

J. W. Mercer

Even the convective component, you did not take the exact input data that was provided?

J. C. Parker

We did treat the convective component as an unknown. However, others used the advertised pulse durations and input concentrations and the measured average water content and the measured drainage flux to predict the convective movement. Of course, the result was that some of the samplers were over predicted and some were under predicted while the double-peak effluent was hit about in the middle.

C. J. Duffy

Given this hydraulic data base, can we predict either the breakthrough in points in the column and the effluent?

J. C. Parker

The answer is no, at least not with very good precision.

P. J. Wierenga

It looks to me that what you could do is repeat this experiment, and then knowing the hydraulic properties of the soil and assuming the dispersivities that were measured are between 0.5 and 2 cm, you could predict the flux and solute distributions as a function of time.

C. J. Duffy

I think you can do that within the column,

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but the critical thing would be getting the proper velocity distribution through the column to predict that effluent. All our theories didn't seem to work too well out there. We had to derive a new theory just to describe the effluent. It is not very good for predictability if our theory within the column doesn't help predict the system performance.

P. J. Wierenga

But the effluent data are tricky because first you have a layer of fairly saturated material above the bottom of the caisson. Then you collect effluent at one single point, and so what are you measuring? What is happening in the corners away from the collection point? The water and solute has probably stagnated. And so I don't think you should pay too much attention to the effluent as it is presented. If I had a recommendation to make, I would desaturate a column. I would install a vacuum system in the lower end and unsaturate the whole column. This way you don't have to look at a saturated-unsaturated system. In this part of the country, the groundwater table is mostly rather deep and you don't really work with saturated flow conditions except maybe at interfaces. So I would rather have this system unsaturated. If you did have a number of vacuum pipes, you could extract the solution from each of them, measure the solution concentration, and get a better representation of what comes out of the profile.

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C. J. Duffy

I certainly agree that improvements in experimental design may simplify the analysis of future experiments. However, I feel that the results observed here are useful and constitute reasonable parameter estimates. I would have hoped that we all could have done a better job with the effluent. The question here is can't our models accommodate these observed complications?

P. J. Wierenga

Sure, but you can only accommodate it if you put in enough parameters. Now you have arbitrarily set it to where we have only two velocities. Why only two? Why not make it ten? And on what basis are you going to choose the velocities?

W. A. Jury

Just to reinforce what Ishwar said, I think what might be a reasonable question to ask in

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respect to the data that you have now is whether the data itself is capable of validating any model. Sometimes the data set is not accurate enough, contains its own uncertainties, and deviates from the assumptions of a model that doesn't have more parameters than you have ways of testing it. For that you need candidate models and you need objective model validation criteria. I didn't see any procedures for determining whether the model fits the data or not. There were a lot of statements saying that this isn't any good and that is good. That approach isn't sufficiently objective to proceed to the next step of trying to distinguish between candidate hypotheses. If you find, for example, that this data set cannot discriminate between one-dimensional models that make completely different assumptions, then you may have to design additional sampling ports or something of this nature before you can proceed. But nothing I saw yesterday told me the convection-dispersion equation was valid or invalid. There were just too many data that deviated from the exact hypotheses of any one-dimensional model. But that could have been quantified with sum-of-squares estimation rejected by a test, so you could carry through at least some way of determining how well a model is agreeing with data after it has been calibrated. That point I think should be kept in mind.

D. J. Goode

I guess my general perspective, starting with the base case of the one-dimensional advection-dispersion equation, is that it seems that the model works reasonably well. It seems it is predicting the concentrations at the sampling points in the caisson. I think the exercise of combining two flow paths to generate the effluent concentration seems to lend support to the idea that the effluent concentration is still a reasonable parameter to be looking at. We came up with a relatively straightforward explanation and it seems to match relatively well. I think the weakness or where the base-case one-dimensional model falls down is in predicting the effluent concentrations. In this case, I think that would be an important conclusion that would come out of this workshop. There must be field situations where you're going to have more than two flow paths and a much larger scale, and there has

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to be some procedure for incorporating the complexities and for predicting the performance, that is, the infiltration or the tracer movement on a large scale. I'm not sure that solving the one-dimensional advection dispersion equation in a deterministic way with high dispersion coefficients is the way of going about doing that. In my mind, that solution does not fit the effluent concentration very well, and I don't think it would on a larger scale either. And so I see that the one-dimensional approach did very well in terms of the data analysis looking at point concentrations, but we have to do more than that to go from point values to the large-scale behavior. I think the combination of the two flow paths was an initial start at that problem, but I am not sure that is the way to go. On a larger scale, I think that that approach might not work as the number of flow paths gets to be extremely large. But that large-scale problem is the one that leads me towards the stochastic analysis or something like that. It seems that if we had run a stochastic multidimensional model, we would have gotten some kind of effluent curve. It wouldn't match the one we observed, but it would have the same sort of nature in that it would not have one peak with a Gaussian dispersion around it. That would give us the information that we shouldn't expect to see one peak with Gaussian dispersion come out the end. I think that is something very important to bring into the regulatory program. Maybe we wouldn't predict exactly the right curve but maybe we could give the nature of the curve, that you are not going to be looking for a single peak but for a much longer duration in the outflow pulse than you would get from the one-dimensional model.

I. P. Murarka

Let me follow up on that statement. Let's separate the nonreactive chemicals where the one-dimensional analysis in the effluent even seemed reasonable. Now I want to emphasize the word "analysis" of the data, not prediction of the results of prior given tracer information for that particular site. The question will continue to come--can we predict for a site without doing any tracer experiments at that place-- and let's make sure we separate that. Because even in this

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particular case where more data than normally would be available was obtained, still there are discrepancies in describing by all sorts of averaging and simplifying assumptions. In fact, the key part of the entire analysis is strictly an arithmetic calculation. A single arithmetic calculation is driving all the models. There is no reason for picking two velocities except saying that I know that by doing this way my answer will match the data. There is no real reason for an aquifer to be separated by the kind of step function used because that is what the model will let you do. But the point it brings up particularly for strontium is that we're doing physics to describe chemistry. Why aren't we doing chemistry to define chemistry? That's why I applauded Gail for what she has done. In the strontium case even though weakly accommodated by numerical mixing that Peter created, it is more likely happening the way Gail defined and it can be tested. The fact that the experiment was not done to test out the geochemical processes is just an unfortunate event. That's no reason to say you can't do it because we didn't get you the data. The same will hold true if you look at hydrology. You are hearing the same thing from them too, that there was not enough data to define the flow field variation in this particular caisson experiment. So it is no different for either side of the coin. In fact, the precipitation phenomenon is real and if time permits, I have the chromium geochemistry slides, and I can show very clearly that the fundamental geochemistry of chromium does work and can predict for soil conditions and you can be right on target. Precipitation, most of the time, is grouped under adsorption and desorption and then as hysteresis. When you form a low solubility compound because of precipitation and it doesn't come back in as fast any more, you say there is a desorption hysteresis. No, there is a solubility change and the chemical is not going to move out. This is very consistent with the precipitation-dissolution reaction to have a very long flat tail which is near solubility concentration limit. There is no question in my mind about that. We just can't do it numerically yet or Gail didn't try to do it yet. But it is happening and with iodine and bromide it didn't.

R. J. Wagenet

I am not sure that I recognize the gist of

your comment. It has been well recognized by soil physicists and soil chemists for a number of years that linked models that describe transport as well as solution chemistry and sorption are necessary to describe transient solute fluxes when there is sumultaneous precipitation, dissolution, and sorption going on. I think the unique aspect of this study is that the chemistry models that contain consideration of strontium may not have been worked out. If that is your comment, I agree. If you are talking more generically about solute transport and the need to describe chemistry in general, I think that has already been done.

I. P. Murarka

I disagree with you. It may have been done theoretically, but every model I have seen on solute migration uses a K_d. If you can define all chemistry by one single coefficient, then I would have to accept that all the chemistry work is completed.

R. J. Wagenet

Everybody uses different representations of cation exchange. It would be difficult to use a single sorption coefficient across all studies.

I. P. Murarka

Yesterday I did not see any of that in any of the modeling exercises for this caisson.

R. J. Wagenet

That is because they do not exist for strontium yet.

P. J. Wierenga

A lot of this has been done in the soil science area in the 50's and 60's but hasn't been followed outside of the soil science area. But Jeff is right; a lot of this work has been done and these models have fairly good applicability. There are may be some errors in there or some things you would do differently as an engineer, but nevertheless the principle is correct. What Ishwar Murarka is concerned about is that the geochemistry for strontium and many of the elements we are looking at have not been worked out.

R. J. Wagenet

I agree with that statement. My point is the idea of considering chemistry during transport is not new. The linked models that consider them during the transport process also exist.

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G. A. Cederberg

When I started to learn about chemistry transport, I had to go to the soil science literature. I didn't go to the hydrology literature, and I think the missing link is where you are doing field-scale analysis of transport and a lot of people are hydrologists looking at flow fields and not going to the soil science literature nor worrying about the chemistry. I think from a regulatory point of view you need to know the geochemistry because some of the single ions are what are toxic, not the complexes. So you need that speciation, and chlorides are not going to kill you but heavy metals will, and how they are complexed in the soil is what will determine toxicity. So I think the engineering companies should get involved in saying they can't give all the answers because there needs to be work in the area of chemistry and make that a valid part of the program.

I. P. Murarka

The principles are not what I am talking about. I am talking about the practice. Proper use of the information is what I am talking about, or not using it.

R. J. Wagenet

I think not using it is the key. The information on what to do and how to do it exists. Maybe not for the specific case of the strontium and its geochemistry, but the models and the formulation of models that include a description of sorption during transport are present in the literature. It is a matter of appropriately interacting the strontium solubility, precipitation, and sorption with the other components of an inorganic solution phase.

I. P. Murarka

They have all been reviewed and the major problem is insufficient thermodynamic/kinetic data base for their use. So I again agree in principle that there is chemistry and hydrology that must be used, but its availability is very, very limited.

M. D. Siegel

I'm not sure that is the point for this particular experiment. I think there could have been more characterization in the caisson experiment that would have given some useful geochemical information. I think in the case of strontium, the limitation is not so much due to thermodynamic data because strontium is pretty well understood. I think

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that not enough characterization was done of the mineralogy or of the water chemistry. I think if they would continue to collect water chemistry data at all sampling points throughout the course of the experiment, we might be able to explain a bit more about the strange shape of the strontium curves. It may be that it was precipitation, but you can't rule out changes in the effective K_d during transport due to changes in the calcium concentrations. That would be the major species competing with strontium for the sorption sites and perhaps the lithium might be doing something too. We noticed yesterday at two levels nicely shaped peaks happened to arrive at the same time as the iodide, bromide, and lithium peaks from later pulses. The experiment wasn't designed to take into account the particular behavior of strontium. The strontium peak was moving much more slowly than the other peaks. This was a system in which the chemistry was changing and a K_d would not be able to handle that sort of problem.

P. J. Wierenga

I want you to realize that experiments such as these take an enormous amount of time and effort, and the people here have done quite a good job in doing these experiments. As a modeler, one may say that one could have done this or that, which is a problem with field experiments. I feel that the modelers and the experimentalists should work very close together. I may not have much regard for pH as a soil physicist, but I am convinced that if you don't measure pH then you will never be able to predict transport of some of the more complex elements. So I think I would argue for close cooperation between the chemists, geochemists, soil scientists, hydrologists, and the modelers. A lot of work has been done during this experiment, although not all measurements were taken that we now, two or three years after the experiment, would like to have. I don't think the experiment was set up to do strontium transport in the first place. Initially, they only wanted to look at noninteracting chemicals. We should also remember that they have a lot more data than they have shown us in this report. This experiment was done two or three years ago, but in the meantime they have done a lot of small-column studies, and additional

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large-column studies, so this is only a fraction of the work that has been done.

M. D. Siegel

Part of the problem of linking the geochemistry to the flow has often been that there is not enough thermochemical data nor a lot of effort to bridge that gap. But I think there could be some more simple chemical measurements that could be made in the next round of experiments and I think that we certainly did learn a lot from the first set.

I. P. Murarka

Strictly speaking, structurally everything is available. But when you begin to try to use them, they are not. Try to run an equilibrium reaction chemistry with a flow model. Show me how you are going to implant the geochemistry with a Saturn or a Flaminco. General knowledge is available, but in the computational framework it is still not that far along where you can do the coupled computations.

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M. D. Siegel

You might be able to use a K_d if you had some sense of its spatial variation. You could use the correct K_d in a code like Flaminco before resorting to a more detailed coupled chemistry and hydrology.

I. P. Murarka

I think where you are heading is correct if you can find the varying K_d depending on some chemical property of the caisson material. You can temporarily substitute without doing the detailed geochemistry. But the problem is, particularly in the chromium work, we have shown for two units of pH change, the K_d changes by six orders of magnitude for the same soil material. So now you get into an environmental situation where no matter how well you measure the pH you can't measure and come close to it. So as soon as you get into that and begin to see deviation between your calculated number and observed number, what I am about to say is that doesn't tell you that your model is wrong or that your experimental data is wrong or that you can't explain it because something is missing. It just very well may be that the level of microscale operations is such that you almost have to take every grain out, measure everything about it, and put it back exactly the same way and then see what happens to the tracer.

Now, when you get to the macroscale, the predictive error may be such that we may be reaching close to that error.

A. L. Gutjahr

I would like to address the comment that Jeff made of making a distinction between different purposes that one might use an experiment like this for. One of them is what might be called a physical or scientific description. In that kind of a case, what you would really want to have is a very complete suite of data and characterize everything to try and describe whether something like a convective-dispersion equation really works. Also to try and describe some of the chemical mechanisms and for that you would almost have to take the thing completely apart. Another use for this kind of experiment is for management purposes where you are saying that you don't understand all the mechanisms that underlie this. The third category that is related to the other two is the data analytic and design aspects of this kind of experiment, and for those two purposes they are different. It might be interesting to take a look at the data that was collected to do a kind of a stochastic modeling approach to things based upon hydrologic data in general, and then try to see how much additional information do you need to tie things down and sort of get to a good agreement. Not to try and match everything completely. We always want more data, but when we take the whole thing apart, it is also destroyed. By going out and sampling, we may actually be changing things more and maybe that's not what one really wants, especially for the management purpose. For the management purpose, you want to go out and do some kind of a general description of what is happening and see how much data you need to tie this down and get some specific description.

J. W. Mercer

I would like to add something in terms of regulatory use of these results. One of the comments Dan made earlier was that they want any kind of predictions to be on the conservative side. So, I would think that at a lot of these facilities, even though from a scientific point of view looking at the chemicals that are more reactive is more challenging, from a regulatory point of view maybe that is not what you are interested in. Maybe you are interested in the faster movers

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and actually your predictive capabilities are a little easier because you are not all that concerned with the ones that are going to get tied up. Is that not true?

D. J. Goode

From my point of view, I think we all agree that geochemistry is a very important part of the problem that we are dealing with, but maybe the fact that the one modeling group that attempted to use geochemistry is not yet able to present final results is indicative of the problem. It is a much more complex situation that we are dealing with and requires a lot more information that may or may not be available. Geochemistry is important and it is important for us to be able to handle reactive as well as nonreactive constituents because, as I mentioned, we also have responsibility to try and minimize the cost of disposal of waste if performance analyses are based on sound physical, chemical, hydrologic principles. The people that are applying for licenses, be they DOE or commercial operators, will attempt to take credit for adsorption and other chemical processes which will tend to limit the migration rate of nuclides.

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J. W. Mercer

I would add that if I were coming to you for an application, I would try to show that the chemicals that weren't going to move weren't going to move by using a geochemical model and not a geochemical effluent transport model. I think I could make convincing arguments that they would get tied up without actually having to combine the two just from a practical way of convincing you.

D. J. Goode

The other thing that comes to mind though is my last slide about how uncertainty and sensitivity and conservatism are all related to each other. The transport of some of these radionuclides are extremely sensitive to the geochemistry. Ishwar Murarka is saying that even a one-unit change in pH can radically change the transport problem. I think that geochemistry is an area where we are even more likely to be conservative because it is so sensitive to some parameters which are, at this stage, very uncertain.

W. A. Jury

I think if you talk about the use you might put this model to, I think it is important to distinguish between the type of environment this experiment was conducted in and the

real-world environment that such chemicals might accidentally be released in. It is utterly unjustified to assume that any sort of conclusion you draw from this experiment is applicable to undisturbed soil unless you make a subsequent attempt to verify that in the natural environment. Therefore, I get back to what Allan said concerning the reason for which we are doing this. This might be a very useful screening tool to determine the chromatographic arrival of chemicals. It might be useful to study specific processes. But you are not studying the field any more than you are by studying it in a small soil column in a laboratory. If you start out by thinking that you have the right equation, you might mislead yourself into thinking that that equation will apply somewhere else.

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R. J. Wagenet

My comments are much the same. It seems to me that if we identify the purpose as being one of management guidance, then I don't know if we necessarily have to launch a more in-depth presentation of the geochemistry of the system. I'm not yet sure whether in a field situation my ability to predict the presence of a chemical at a certain depth with time is a function of the sensitivity of the model to geochemical processes which are varying spatially or temporally or rather a function of the model's sensitivity to transport-related processes like convection and dispersion. So if we consider only models intended for management, it may not be necessary to employ a fundamental representation of basic processes to provide an estimate that is useful. Under such conditions of use, such as for NRC purposes, it would be a waste of time to produce a more sophisticated chemistry when in fact the variability of the system hydraulically may control our ability to produce a management-oriented prediction. So I think some consideration should be given to the kind of use of the model as well as extending our understanding of basic process.

A. El-Kadi

Is it possible that some sort of discontinuity occurred like a breakdown or freezing?

J. C. Parker

The whole experiment is run under unsaturated conditions. If it was ponded at the surface, I could see where you could get some channeling along the edge if it froze or

something, but the fluxes are being added so as to maintain unsaturated conditions.

C. J. Duffy

The great uncertainty with regard to the conservative species is the advective motion. We did a reasonable job in getting the breakthroughs at sampling points within the column. Our analyses showed that very small variations in the velocity produced very complex mixing processes in the outflow. That is what I really want to emphasize because the local information didn't allow us to predict the effluent and I would have hoped that it would.

P. J. Wierenga

That comes back to what Bill said. We have been talking about chemistry, and we all realize that chemistry is very important, but advection is very important also. What you saw at 264 cm in my opinion is not unusual. I have a similar lysimeter setup, and my breakthrough peak at 5 m is higher than the one at 4 m, which it shouldn't be. It should be lower. Such behavior is apparently inherent in the system even though we worked very hard to get it as uniform as possible. If this is happening in these lysimeters, just imagine what will happen in a real soil. I would say that if your models can't predict what happens in lysimeters, what are you going to do in real soils?

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I. P. Murarka

There is more information in the data to calculate the varying velocity. Nobody tried to do it. You got concentration profiles which are time dependent and basically telling you that the early arrivals are higher-velocity arrivals, the peaks are lower-velocity arrivals; calculate each of those velocities. Everybody chose not to use that even in this data set.

C. J. Duffy

Where did the velocity come from?

I. P. Murarka

The velocity got chosen by taking one single average or multiple averages.

C. J. Duffy

Actually, there were several different approaches. In my case I used 1, 2, 3, 10, and 20 different flow tubes. We calculated apparent velocity distribution and breakthrough and it showed there was some fluctuation, but the range wasn't all that large. If that is the case, that doesn't foretell great things for predictability.

What we tried to do was calculate the velocity distribution from the effluent.

I. P. Murarka

From the effluent you can't do it because that is a single point measurement.

J. C. Parker

You won't be able to predict from the point measurements. You can fit velocities to the different points. You have seven or eight differentsuction ports and out of those one gave a high velocity and seven gave a low velocity. If you assume you have a representative sample and try to predict the effluent from that and make the rash assumption that these are representing stream tubes from those velocities, there is no way you are going to come close to predicting the actual effluent. You are going to have one little peak from the high-velocity zone and a big peak from the low-velocity zone because all of your samplers happen to be in the low-velocity zone.

W. A. Jury

One fundamental problem I see with proceeding too far without getting a better data base is that your effluent averages over the entire exit surface. Depending on your point of view, you could think of that as providing information about solute travel times from which you could estimate a solute velocity distribution in the soil. To provide the same information within the caisson, you are going to have to get a lot of replicates of solution samplers at a given depth. For example, in a field experiment we just completed, we had sixteen solution samplers at each depth. From this information, we were able to calculate an apparent velocity distribution at each depth and found that it was identical from 30 cm to 300 cm. That is the kind of information you need at each sampling depth to compare an effluent to a solution concentration. You have to average over the same cross-sectional area. Otherwise, you are not looking at the same realization. You could explore one hypothesis by adding tracers of different types over part of the surface, but unless the flow regime is as simple as that hypothesis yesterday, that it is going down the middle and the edges differently, you won't pick it up that way either. So the only other answer is to replicate your cross-sectional area monitoring at one or two points in your caisson and then use that

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statistic to derive a velocity distribution and see if it describes the effluent velocity distribution using various model hypotheses.

D. J. Goode

I wanted to address something that Bill Jury said earlier. I was sorry to hear that he doesn't think that this is any more applicable than a lab test because at $150,000 each it would have been a lot cheaper to run lab tests.

W. A. Jury

I said you should not assume that it is unless you carry through and test it.

D. J. Goode

I think that the original purpose the NRC saw in this project was to get closer to the field scale. I think we have done that, but the idea was to go to a large scale and attempt to run basically a lab test and see what effect was simply due to trying to go into a bigger experiment as opposed to going to a more complex or natural situation. Frankly, that has been achieved and there has been a lot of good information from that point of view. Just taking a lab column and making it 10 to 100 times as big, we do see some different effects which the models used to analyze lab columns do not adequately explain on that scale. So it is not the problem of going to a more natural and complex situation in this experiment, some sort of physical-scale effect of just going to a very big lab column, which I consider this to be.

W. A. Jury

The only sense in which I made that comment was that I thought I heard a suggestion that this was going to be used to derive a regulatory model. They used to use lab columns for regulatory purposes and I don't want them to use caisson columns either. I want the models that are used to simulate the real environment for purposes of litigation or whatever to be derived from field-scale experiments. That was my only point.

C. J. Duffy

I think it does make a major contribution or step towards full-scale field experiments because of these advective effects. Obviously, when we increase the scale of the experiment, these advective effects appear no matter how well you control the situation. This experiment is intermediate to the laboratory and the field, and I think that is the importance of it. We still have some

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work to do on our predictive capabilities. There are complications even here where we have tried to control the experiment.

I. P. Murarka

That comment is very correct when you have a nonreacting chemical involved, but I don't believe when it comes to strontium you can tell any more or any less about convective effect on that shape.

T. Jones

I would like to ask the panelists if they think this problem brings up another line of research in conjunction with more field-scale tests and more tracer tests. If you look at the data set you have about eight levels and two samplers at every level, and only one point that shows a different result. The rest are fairly consistent. However, if you believe the effluent data, it shows that one data point really described more than half of the solute transport, maybe 60% to 70%. If we go back to our classical way of characterizing soils, we generate a desorption curve, and a conductivity curve. Based on that idea, there is no reason to expect there to be those two mean velocities going on out there. Even with intense sampling you almost missed it. My question is do we need to step back to fundamental soil properties and try to develop theories that just take fundamental properties like pore size distribution, desorption curves, and conductivities. Based on that idea can we predict lots of different realizations that could happen when we put it all back into a caisson or it is laid down by wind or by rivers? Then given these basic soil properties, we could conjecture a range of density distributions or packing scenarios or something that would give us a range of realizations that might happen out there. I don't know that there is a lot of research going on trying to predict that from more fundamental soil properties. I am not sure we can measure all the possibilities out there. Maybe we need to work on a more fundamental level in terms of what could happen if you take Bandelier tuff and pack it 1000 times. How many different kinds of structures can be created? Twenty years ago there was a lot of research in predicting conductivity and maybe the mistake was the feeling that we were predicting a unique property. There are some unique properties. Maybe we need to try and predict ranges of

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things that can happen at random when we do different treatments.

M. D. Siegel

I think what you are saying is valid and illustrates the most powerful use of the models as opposed to the experiments. I just don't see how we can ever accurately predict the migration of contaminants in any natural setting. Hopefully, we can use the model and available data to calculate an envelope of potential discharges. If that envelope of potential discharges is lower than the limits set by the regulations, then we've achieved something very useful. At best, I think we can hope to bound the discharge. Your observation that this type of approach hasn't been looked at for low-level waste is important because it may imply something about how you set up your future experiments.

T. Jones

The question is what is it about the Bandelier Tuff and how it is packed that made you predict that one possible outcome would have been to have two mean velocities or next time you pack it you will have so many different velocities that it just becomes a larger dispersion problem? What is it about that soil that makes that a possible outcome and there's nothing in the water flow or dispersion modes to account for that? That is a parameter estimation model from basic soil properties to predict what range of conductivities you can get based on a range of densities you can pack it to and how those densities form a pattern within the column. What is a realistic range of velocities it could have out there?

M. D. Siegel

We also want to know just how important that variation would be on the integrated discharge. You need both types of information to get some insight into the real range in the field. But before you spend a lot of time investing in those types of experiments, you might want to see whether it really matters to the integrated discharge.

I. P. Murarka

There is a simpler way. We got only one point measurement at any given depth. The caisson can be measured at several points on the same surface. You don't have to create 1000 columns if we just increase the number of measurement points on the same surface. Except for the 264-cm depth for the nonreactive chemical, everything seemed to be

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turning out pretty good, until you get to the effluent where you are looking at the integrated average. If you get different parameter estimates for the different point measurements doing the same experiment, then you have a basis for seeing how variable that field is and then you can use that variability to look at the effluent, which is an integrated subject, before you to creating 10-20-50 caissons.

P. S. Huyakorn

I wish to caution you about the difficulty in doing a detailed three-dimensional numerical simulation on variably saturated flow. Given you have a very elegant stochastic way of generating a single realization of the spatial variability in order to do a detailed numerical simulation of such a thing. The problem is not surmountable right now. It is the practicality of doing things when you deal with a variably saturated flow you can't predict a priori whether you get a solution at all, particularly when you are dealing with complex three-dimensional flow fields. Leaving aside all these complexities, you are trying to add on and I think one has got to be aware of that problem. Don't take the modeling for granted because when you deal with a variably saturated flow, it is very difficult to get a good numerical solution particularly if you want to apply it to field scale. Given the fact you can come up with an elegant stochastic way of creating a single realization, how you get a solution is a very important issue.

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I. P. Murarka

Are you saying that the flow field on a three-dimensional basis may not be estimated?

P. S. Huyakorn

A numerical approximation may not be great in a situation like this, which involves say 6 to 10 orders of magnitude change in values of hydraulic conductivity in the flow region.

C. J. Duffy

It does bring up a real important point regarding the difficulty of using the hydraulics alone for analyzing transport process. It may mean that the travel paths we are searching for cannot be derived without an extremely accurate evaluation of the hydraulics of the system.

W. A. Jury

If you look at all the solution sampling ports as replicates trying to estimate heterogeneous solute velocity in the caisson,

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the data from each sampling port is an observation of a velocity averaged from the surface to the depth of the observation. I think there were seven sampling ports inside the soil. What sort of velocity distribution is deduced from all seven samplers by obtaining the first moment of the concentration distribution? Does that velocity field project onto the effluent when it is given the weight of 1/7 per sample? Or is it as Tim says, only one of them was different from the other six and you need 60% of the field to behave that way in order to explain the effluent? Addressing questions like this might give you some clue as to whether your statistics are anywhere near sufficient enough to pick up the heterogeneity of the system while you are sampling it.

C. J. Duffy

Your latter point was correct; there was only one fast data point.

W. A. Jury

Based on your replicates in the soil, you're completely unjustified in giving that anything other than a partial weight unless it is sampling a different part of the volume than the other samplers.

R. J. Wagenet

I agree that what Bill is saying is logical, but I return to what Peter Wierenga said at the beginning of the discussion. We should be careful about making too much out of the effluent data. The depth you make the gravel in the bottom of the lysimeter influences the pattern in the outflow. You would get a different pattern if you make the gravel twice as thick. We never try to match effluent data as a criterion for how well the model is doing. There are too many uncertainties at that boundary. I think our descriptions inside the columns are a truer indication of whether the models do or do not work.

H. R. Fuentes

At the present time, we are planning a new experiment, thus have a very unique opportunity and chance of perhaps launching an experiment which may satisfy the wishes of different modelers. It has been mentioned here by different people that we need more data. I have to think of the constraints in terms of money and resources. But I think that knowing how good the previous experiments were and what models can do is

important. I would like to ask for suggestions on how we could perform better experiments. The experiment is intended to look at spatial variability problems in the caisson. I would like to hear from those who have interest in optimizing the understanding of the conservative and nonconservative tracers in this type of experiment.

R. J. Wagenet

I think we need to focus on what role the caissons themselves play in the development of better predictive models. We should consider whether we need field experiments that are part of the caisson design, or that are supplemented or complemented by the caissons, or maybe not do any more experiments with the caissons at all.

G. A. Cederberg

Some comments were made this morning about the purpose of the experiments and whether it is for management, regulatory or test models. We need a better idea about the purpose. I don't think you can do one experiment and get the answer for multipurposes--if you could tell us some of the purposes you have in mind.

H. R. Fuentes

My objective is to provide the information that the sponsor wants within defined time and budget constraints, which I assume to be regulatory in nature.

C. T. Kincaid

The intent of the regulatory body and regulations is to provide a safe environment and to make decisions to do that, we have to look at the long-term character of these disposal options. The points that Jeff has made as to whether we want a management or a research tool, and the temporal and spatial scales, are relevent. He is correct in that we need to make management decisions based on the time frames and data collected in the field. It is very important to recognize the tools are not really here today to make long-term predictions with confidence or any measure of certainty or uncertainty. That is a key capability absent in our technology. So in answering the role caissons play, I believe it might be best to see if you agree that we need to look at this in the longer term and look at the field first. We need to envision the kind of conceptual model needed in the field that can be supported by data we can afford to collect. Just where that may lead us in terms of predictive capability has

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not been resolved. Consequently, caissons may not play a role.

T. Jones

It seems that the purpose of the experiment is three things. One is we wanted to test our conceptualization of how the transport occurred. Two, we wanted to test whether three or four approaches to implementing that conception model had a relative advantage or disadvantage over each other. Three, how well can we actually measure what is going on in the field? I think the modelers changed the conceptual model based on data on what they would have predicted. We packed a nice uniform column that had a steady state flow regime and essentially uniform velocity and uniform properties, and it looks like those weren't the results. So I think it shows us we could not predict with a conceptual model how transport would occur within the caisson. On the second problem of given the conceptual model, can the models describe that? I think the answer is yes, that based on experimental information, we changed the conceptual model and all the modelers came up with the same conceptual model and all the approaches handled it equally well. So that given that conceptual model, all those approaches can implement that conceptual model. The third thing is can we measure what is going on? We're talking about 1 sample point out of 16 that really gave us the key to explain this effluent concentration. I think Peter had the right answer. If you can't conceptualize what happens in a caisson, how can you conceptualize what happens in a 20-acre burial ground with a 200-m water table? So I think that is what we've found, and it emphasizes that it is not given with any blank-check sampling scheme that you'll be able to measure exactly what is going on. Developing a model has turned out to be the trivial thing. Given that you know what processes and you know the velocities, then you can build Markov models, filter models, convective-dispersive models. There are lots of ways to describe given processes. The problem is what is going on out there and we failed. Everyone predicted what would go on in a caisson and that is not what happened. We don't have any trouble explaining what happened after the fact and that's important. That shows we can model if we know what is going on. But the problem is in the conceptualization.

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M. D. Siegel

I think that to achieve the most reasonable objectives, we have to take into account the whole process leading from the initial experiments to the assessment of compliance of a particular site with regulations. I think we have to keep in mind what type of data we will be able to take at the actual site. A lot of data will not be available simply because we have destroyed the site. So I think we need to limit our experiments and our models in a sense by recognition of those limitations. I think the most useful thing we can get out of the caissons and the laboratory tests is some confidence that the n+1 caisson would give us a discharge that is less than the bound calculated from our earlier tests. We then might have some confidence that we can bound the discharge from a real site if not calculate it exactly.

D. J. Goode

There are a lot of issues here that could be brought into play. I think that it is somewhat difficult to deal with this because the amount of investigation that has gone into the existing sites is minimum. It is hard for us to bring a lot of experience to bear on the actual situation at a real site. I think there are some limited objectives that we can try to get out of the comparative model study and we have achieved some of those this morning. In terms of future work with the caissons, it has been suggested we look at more basic properties, smaller scale, as a tool for predicting large-scale performance. The direction we are going is running more experiments with the scale of interest. That scale of interest is the size of your facility and the time scale, often very, very long. So what we need are ways of dealing with that problem. I personally have given up on lab experiments as far as taking core samples, etc. Most of our work will be on a larger scale. From that perspective I think one of the real values here is using models for data analysis and running a large-scale field test. One of the more difficult problems we haven't been able to address is what you have to incorporate into the large-scale model to predict long-term performance. I think there were some very interesting concepts about predicting effluent concentration outputs. The caisson experiment gives us point measurements within the caisson with which to predict the

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larger-scale behavior of the effluent, although there is some uncertainty about whether the effluent is a valid measurement of system performance.

J. W. Mercer

I get the sense that at least the few people who have responded feel that additional caisson studies would be worthwhile. Although it wasn't said, I know that these kinds of field tests are quite expensive and I am sure the NRC has budgetary constraints and they have already sunk a certain investment into these caisson studies, and so there are some arguments from that point of view that would make them worth continuing on. Getting back to Hector's question as to what can we suggest to him as a means to improve the measurements that he makes as to current and future caisson studies, the modeling and the experimentation go hand in hand, and I would like to ask if you have done any modeling to help guide your experimental setup? What are you basing your current experiment setup on?

H. R. Fuentes

We have been basing the design on all the experimental data we have collected up to this time. These data bases need to be analyzed as this was the purpose of the workshop. We also realize that we need to sample more points at a greater frequency. This is needed to evaluate potential variability, so we can do better modeling to improve field experiments and modeling techniques.

C. J. Duffy

Is there interest in performing some of the geochemical analyses before the experiment?

H. R. Fuentes

Yes, there is. I agree with that approach. We are developing that capability for future caisson and field experiments.

J. W. Mercer

Are the experiments going to be performed with conservative tracers, nonconservative tracers, or both?

H. R. Fuentes

Iodide, bromide, lithium, cesium, and strontium will again be used.

G. A. Cederberg

I think the comment Chris made earlier is appropriate, in the planning before you did an experiment since you were running calcium chloride through the system, you should have been able to get a good estimate of the

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velocity, and then based on that, you could have done some simple calculations to ensure your tracers don't overlap. If you had done some brief chemistry on the strontium, you could have ensured that the iodide wouldn't have lapped the strontium. I think that it is not even ultrasophisticated other than just sitting down and hypothesizing what might happen and perhaps finding some design problems very quickly.

H. R. Fuentes

I strongly agree with that statement. That is what we should be doing.

J. C. Parker

I would like to emphasize again the importance of taking more observations in any sampling plane. The concern obviously is to not build up the cost of the experiments excessively. I want to suggest a few economical moves. One, cut down the number of tracers. Why do bromide and iodide when they both behave identically? It is double the effort for nothing. And I wouldn't do the lithium. It exhibits minor retardation and yields little unique information. I would do the strontium because it is an interesting chemical problem, but I would only do one nonreactive tracer. Now you've cut down your analyses by one-half and you can put in twice as many samplers for no more effort. I would still like to see more samplers but would not mind seeing fewer number of depths sampled. Perhaps you could retain the six different depths that are sampled with only three samplers per depth and then at two or three depths with ten samplers per depth. These are some possible tradeoffs in trying to reduce the samples and still get more useful information to model. I would also like to see the distribution system altered so that you didn't have the point source problem.

D. J. Goode

I would like to see the number of tracers further reduced and not use strontium unless more work is done up front. If we are interested in spatial variability, then that complexity on the basis of the work that we have seen so far cannot be adequately handled. Then it would be premature to use strontium.

R. J. Wagenet

I have two comments. I would continue to use the strontium. It is the one species that produced behavior that we didn't understand.

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If we are going to build models useful in the field, we should understand what geochemical process it is that we are not describing properly with a simple K_d. I also think we should consider whether the whole experiment should be run under steady-state or transient-state water flow conditions. In my opinion, the steady-state water conditions are really a very limited test of the ability of different modeling approaches to describe what you will see in the field. It could well be that the convective-dispersive equation is entirely adequate or entirely inadequate under transient field conditions. You can approximate such a case by using transient conditions in the caisson. Such a study would involve taking more measurements at each depth in the caisson in order to calculate water fluxes. There is an additional tradeoff in terms of the intensity of measuring matric potential or water contents, but those are relatively easy measurements to make in that they don't involve laboratory analysis. I would like to see a transient water flow condition.

B. G. Jones

One of the things that supported the differences in velocities is that the water content was measured in a three-dimensional sense with differing radial measurement. The water contents were consistently higher towards the center of the caisson. The placement of the solute samplers should be such that they sample in a radial pattern to observe radial differences as opposed to the current sampling scheme which concentrated samplers at the center of the caissons. The current sampling scheme missed the faster flow zones except for the 264-cm depth.

C. J. Duffy

Conducting this kind of an anatomy of the caisson, I think samples ought to be taken at the end of the experiment to look at the distribution of chemistry as well as the hydraulic properties.

A. El-Kadi

Can multiple tracers be used at different locations to examine mixing?

C. J. Duffy

Usually it is wise to use multiple tracers to verify and this test indicated that bromide and iodide behave in a similar manner. Tracers injected at different locations might very well be useful.

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D. J. Goode

I want to respond to Jeff Wagenet's comment. We run across very few situations where steady state is not sufficient. We saw this fact when we were out looking at the LANL trenches we were shown out in the field that below a certain depth, once the initial moisture deficit was overcome, moisture content really doesn't change. I think the area where the transient problem may be very important is in an area that we are not really addressing and that is a dual porosity system, but from a porous medium approach. I guess I'm inclined to believe that the steady state is going to be sufficient.

P. J. Wierenga

One could easily do steady and transient experiments because after the soil has been drained for a while, you can start injecting again and then you have basically a transient tracer experiment. After the new front has reached the bottom, you can inject a second tracer which is moving at a steady flow rate. If the dispersivities that were evaluated from the steady state experiments are at all applicable, then one should be able to use them to predict the transient front. Peter Huyakorn may say that it will not work because hysteresis is not taken into account in the hydraulic properties and that may be true. As far as improvements, the simulated flux was lower than the measured flux. One reason could be that in a large installation like this, you can have considerable evaporation from the surface. The surface of these caissons is really not very well sealed and vapor moves through cracks. In this dry climate, there is an enormous vapor gradient from the wet surface of the lysimeter into the atmosphere.

C. T. Kincaid

One of the intents of the work in developing correct models is to try and distinguish between alternate hypotheses. Transient tests done in a caisson and used in a numerical experiment as done here may distinguish between alternate hypotheses much better than a simple steady-state experiment. Transient experiments contribute to our assessment of long-term predictability. Perhaps alternative models are equally good in explaining a steady state experiment, but for the very long term, you must have the hypothesis that actually works. Transient experiments may play a valuable role.

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R. J. Wagenet

You have two steady states possible within your system. One is the hydraulic steady state and the other is a chemical balance that may or may not come to steady state. If the experiments were designed to simply be a steady state water flow regime, then it is possible that nonsteady state chemical conditions will be important in dictating the ability of the water flow models to depict distributions of the chemical. I believe that experiments that consider such effects through multiple pulses or alternating concentrations at the surface will demonstrate the importance of something like Gail Cederberg's chemistry routines. Just because it is a steady state with regard to the water doesn't mean that it is a steady state with respect to the chemical.

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J. C. Parker

But nobody has even a semiquantitive model to describe the variation in hydraulic properties with the chemistry.

R. J. Wagenet

I'm not talking about the variation in the hydraulic properties. I am talking about systems in which chemical fluxes are not at steady state. By having buried materials that are contributing chemicals over time at different concentrations and in different amounts, you are going to have a chemical non-steady state that is going to influence the ability of any model to describe the transient fluxes of chemical to deeper depths. So while you may be able to describe the water flow with the steady state water flow model, you do need to consider the chemical entering then exiting the solution phase and interacting with the exchange phase. The experimental conditions should consider such effects.

T. Jones

The experiment was designed to take all of the uncertainty out of the hydrology and say, given a steady state water flow, can you predict solute transport. The concensus was that the dominant problem was the hydrologic problem not be solute transport problem. Maybe this experiment points out that when we try to build perfect hydrology, the variability that comes out of that tends to dominate the transport as if dispersion is not related to the hydrology to begin with.

I. P. Murarka

In general, I will agree with your statement that hydrology is certainly a controlling factor because chemical cannot be transported without the water. So you have to know the transport media, the water, and its behavior in the system. But I am not sure if the problem is understanding how the hydrodynamics work or is it how a particular system's hydrology is. The distinction I am making is that it is a characterization of a particular formation and how the variability, integrity, nonintegrity with respect to how its hydrologic behavior is. Is the problem there or is the problem not understanding "Is water going to go downgradient?" I want to distinguish that and make sure that the problem is not brought together as a single issue because we can predict if we knew everything we want to know. But is that the problem? We have transferred from that of prediction to saying "If you can't tell me how everything is, then I can't tell you what it will do." Therefore, have we really got the knowledge we need in terms of prediction?

T. Jones

I think your point is well taken, but we are not at a point where we are going out to verify Darcy's Law. We do think that we know that water runs downgradient, and the problem is what gradients are going to be out there. I think it has to do with variations in soil properties and there are lots of theoretical questions that need to be resolved that aren't necessarily going to come out of just doing tracer experiments. There has to be a way of saying "If I did it 100 times, would I always get the same result?" Or redo the tests on the caisson to see whether we are always going to get the same results. We have to show that on the same pack we get some kind of reproducible effect.

I. P. Murarka

I think as soon as you talk about transport over a long period of time or plume development or chemical distribution in an environment over a long period of time, I think the major uncertainty is that in the source term--its duration, time concentration, and its dissolution characteristics and its release characteristics, and I don't believe these experiments are set up for that. So I am not saying you should expect it out of caisson experiments, but if that can be incorporated somewhere along the line, I can show you all sorts of computations using two or three

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different kinds of approaches to predicting. If the release duration is small the concentration is never going to reach the point of performance that is of concern, but if the duration is increased by threefold, you may have problems. So I want to make sure that somewhere along the line for management decision making and regulatory decision making that work gets started on what is going to come out and why would it come out. I am not sure that is totally a hydrology problem. We can worry about the spatial variability and the temporal variability and there is no reason to believe that the hydraulic properties will remain the same for 500 years for the same field. When you get into the prediction mode, the issues are enormous. Essentially prediction is used because we cannot observe or otherwise calculate, and therefore do we have confidence in the process that is used for these predictions and some of the process parameters--are they quantified within some defined limits of acceptance.

P. J. Wierenga

We have discussed for quite a while the lysimeters. There seems to be a concensus that lysimeter experiments are useful and that they help us understand the phenomena during transport in real soils. In the future should we not also be doing some field experiments on undisturbed soil?

T. Jones

I have an argument about doing specific field experiments unless you can extrapolate that information. You take a 2-m caisson and hesitate to extrapolate to an acre field and from that to a 10-acre field. Where does it stop? You can't allow yourself to go to the limit and do every test and eliminate all ability to predict and extrapolate. There has to be some balance, and the reason you do the experiment is to verify that given some information you could have predicted what happened. It seems like the concensus is away from modeling and toward empirical experimentation. We can't afford to do all the experiments we would need to do that. Where an experiment builds up confidence in models, it is useful, but in and of itself, it is of limited benefit.

J. Gruber

If we have to model the hydrology over that many years, maybe we have to put more emphasis on the chemistry because that may be

easier to model in the long term. We know that hydrology is variable in time. I don't know of any references that tell me about the variability of the chemistry. For example, we are talking about strontium, but if we were talking about lead, I would be able to say not to worry about it because you can activate it in the middle of the reactor, and in the core it is chemically isolated and there are many radioisotopes. The bulk of low-level waste has such a small specific activity that the chance it is isolated chemically is very good, so I think the reason why 90% of this workshop is concentrating on hydrology is just a historical reason. Geochemists are 10 years behind the hydrologists.

M. D. Siegel

I would like to make some specific recommendations that could reduce some of the uncertainties in the geochemical knowledge. The first would be to look at the potential chemical evolution of the water in the caisson due to rock-water reactions. We are dealing with a potentially reactive system of crushed tuff with reactive surfaces. The chemical evolution of the water is being superimposed over the tracer injection. If you look at the data as Gail Cederberg plotted it, you see a 100% change in the calcium concentration throughout time and the entire caisson throughout any given time. The second suggestion is to do some studies of the mineralogy at several depths in the caisson both before and after the tracer test. A third point would be to look at the potential contrasts in the properties of the material, directly in contact with the samplers that is the tuff flour, and the bulk of the matrix in the caisson. Things to look for would be changes in the surface area as well as mineralogy. These properties affect the sorption occurring directly at the samplers themselves. Another suggestion is to take measurements of the alkalinity or the total carbon while you're taking the calcium. You should continue taking samples of all the chemical components till the end of the test. It looked like many of the analyses were stopped at different points before the strontium peak had passed by. The final suggestion is change the timing of the successive pulses to allow that strontium peak to elute before the next batch of nonreactive tracers is injected.

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J. C. Parker

Given the preceeding comments, would it be more economical and would you get more information for the effort if you did these geochemical studies on columns in the laboratory where you could control the conditions more closely and take more intensive measurements without all the hydrologic problems overlying them?

M. D. Siegel

I think from the caisson test, you get a feel for the interaction between the chemical processes and the flow processes.

J. C. Parker

If you want to know more about the geochemistry, is that really helping you any? Why not remove the problems associated with the flow field? I think that laboratory columns give you a lot of information more rapidly than you get in the field. If you want the simplest system to evaluate the geochemistry, then I assume batch test would be the route although batch tests have their own types of problems. For example, you do a batch test with a particular matrix solution which may vary temporally in the flow system. However, I would presume that for basic thermodynamic quantities, you would almost have to go back to batch studies.

G. A. Cederberg

When I was involved at Stanford, there were some column experiments done to get some thermodynamic data. However, I think in the column experiment, if you did strontium under similar conditions as the field, you might not have seen the precipitation effect because your column might be too short. You might see different effects.

M. D. Siegel

Why do you feel we have to choose between field and column tests?

J. C. Parker

Perhaps you can get more information on the chemistry from column experiments more economically. The whole idea of going to the caissons is to look at larger-scale effects--but it's not really a scale effect that is the problem in the chemistry.

M. D. Siegel

Perhaps caissons just give you greater variety of chemical conditions than you would normally get in the laboratory.

R. J. Wagenet

I think the point Jack is making is that the caisson may well give you a variety of

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conditions for the geochemistry, but it gives it to you in the presence of uncertainty about what the flow regime is. Therefore, you can't separate out the fundamental geochemistry from the flow. However, in a smaller soil column, you reduce the uncertainty you have with respect to the flow system and yet still have flow conditions similar to a caisson. Such experiments would provide answers on the geochemistry that are more reliable than can be produced in the caissons.

M. D. Siegel — But we're not interested in just geochemistry. We do want to put it all back together again.

R. J. Wagenet — Granted, and such integration would be present in a soil column. You would still have flow in the column though just like in a caisson but on a smaller scale, with better flow control, and at less cost to do the study.

J. C. Parker — I don't see the scale problem on the chemistry. The scale problem is in the hydrology.

M. D. Siegel — Could you then extrapolate the chemical data from the laboratory to large-scale field sites?

J. C. Parker — If you knew the hydrology.

G. A. Cederberg — I think it's hit or miss whether you can take lab data and use it as field data.

J. C. Parker — There certainly are some unknowns concerning the effects of heterogeneity on geochemical problems.

D. J. Goode — We need to do a lot more work on strontium in a caisson. I think this happens all the time in experimentation. You start out to address one issue and run into four or five others. How can you backtrack and remove some of the variables and get to the main issue? I think we should remove strontium and transient flow and try to describe transport of a nonreactive tracer under steady state flow conditions in a caisson.

T. Jones — Why do you think we have not been able to describe transport in a steady state flow?

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D. J. Goode — Because of spatial variability.

T. Jones — The caisson does not show you cannot describe transport under steady state flow.

D. J. Goode — I think we should minimize the number of variables. We shouldn't do strontium now because we don't have a handle on it in a batch test or in a lab column.

M. D. Siegel — I disagree with that. The data is there, but the data needed to characterize this particular experiment was not taken. I think a lot of people are saying you could do strontium in a lab column and address a lot of issues that haven't been addressed so far.

I. P. Murarka — I think there are two points here. The fundamental geochemistry doesn't change, and where in your particular case that does or doesn't work is the issue. I think more of the fundamental thermodynamic kinetic reactions for strontium are known for all the pH conditions that we need to know. So there are no real uncertainties about that. That is a different scale problem. But the issue immediately comes when applied to a particular soil mineralogical condition. What are the participants in that system that will respond and use certain reactions of the strontium. I come back to defining the desired system. If you want spatial variability, I don't think you should put in a homogeneous caisson. You should create conditions that are nonhomogeneous. If you are going to create the best possible homogeneous caisson and then look at the data and say it can't be homogeneous because we can't use only one velocity and we used only one data, we had 30 data points but we used only one--I am exaggerating obviously to make a point. I think that conclusion of a spatial variability is kind of blowing with the wind rather than stopping and thinking about it. Even if you had a flow field where you could get the flow velocity, I can guarantee that given 11-17 cm/d range you had that wasn't even used, let alone if you had from 9-25 at particular xyz locations, I don't think it would have made that much difference. Let's assume all those things and see what you could do with that information. I think we ought to give some thought to what would be gained by having that additional information. I think there is a more rational approach.

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P. J. Wierenga

I'm sure if Bill Jury were here he would point us in the direction of field experiments. I think caisson experiements are the present and field experiments are the future. How are we going to do the field experiments; what will we measure and how will we set them up? What kind of parameters will we look at?

J. C. Parker

I feel that the utility of additional caisson experiments may be minimal. For further investigations on the geochemical problems, it seems to me it would be better to back off to the laboratory scale where flow can be controlled more precisely. The problem on the hydrologic end is clearly the variability of the hydraulic properties of the medium. The caisson is a very contrived system which has variations undoubtedly due to some inadvertent fault of the way the materials are packed. Perhaps they get compacted more in the middle than the outside. I'm sure if we put in enough samplers and take enough measurements, we could describe the variations and describe the flow. But then that tells you what the spatial variability in a compacted caisson is and I don't know if that extrapolates to anything in the field. What we want to know in the field burial problem that pertains to the spatial variability is how can we approximate the variability and describe it as it occurs in a field situation. I would argue in lieu of looking in detail at the variability of hydraulics in caissons that one go to a larger-scale experiment to look at the variability.

C. J. Duffy

It seems to me that the tuff material has been proposed as packing for an engineered barrier. Thus these experiments tell us a lot about performance of engineered systems.

M. D. Siegel

I don't think we'll ever be able to predict movement at the waste disposal sites. I think that we are involved in a 10- to 20-year learning experience on gaining confidence in our ability to do predictions. If we can predict something in a caisson, we have a little more confidence in our ability to predict something in a larger-scale experiment. I think if we try to go right now to the field sites, we're going to run

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into the same problem. It is an inductive process where we're going to do a number of predictions and the X+1 prediction is going to be the real important one. However, we will never be able to test that one because the "experiment" will be over after our lifetimes.

J. Gruber

The discussion this morning showed us that we don't have enough measuring points in the caisson in order to distinguish between models. So far as I understood, all the models were the same and could all boil down to a dispersive-convective flow model, and if we had more measuring points in the caisson, we could take other models and test whether they will be able to predict or describe what is going on in the caissons. Then the step towards the field is possible. But in this workshop not all possible models were tested.

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I. P. Murarka

From a regulatory standpoint, granted there are certain decisions to be made with or without information and to the level an analysis is possible. One of the things that ends up is that we're going to monitor it because we recognize we have not made a perfect prediction and a perfect decision which guarantees we're sure what will happen will have acceptable consequences. The monitoring is the safeguard for the uncertainty. When everything else fails, the only way we can learn about what happens is by measuring and observing it. Then we can postulate any analysis, theory, hypothesis, or explanation and say we think this is consistent with this kind of behavior, and this is the classical scientific development where you observe, you hypothesize, you infer, and you test. A lot of the theories get developed, and a lot of the theories are really hypotheses. I think that perfect prediction should not be expected until our fifth generation has tried to do it. I don't think it will happen in our lifetime. If you can come up with a caisson experiment and say in fact the hydraulic variability is the major factor in terms of prediction errors or description errors on the concentration below the caissons or a certain distance of travel then relative to some other process, then I think this process serves very well. But the translating of the numerical values from these experiments to any field scale or any other caisson including the one in Washington, I think that is expecting a lot.

J. W. Mercer

I would like to add something concerning the statement that this workshop did not test all different modeling approaches and that is certainly true, but one of the results of the experimentation and the workshop is that all these results will be made available to the public and hopefully it will provide a data set to other modelers with other approaches that can test their different modeling approaches.

R. J. Wagenet

I was really intrigued by the comment that we should focus our attentions on the caissons for the next short run. I don't agree with that. I think it is important at this point in our experience with predictive models to make observations in the field and see if we are even in the right ballpark in predicting what we observe. For example, many of the issues Bill Jury is investigating have arisen directly from his field studies, particularly the movement of pesticides according to transport phenomenon that are unidentified by laboratory, lysimeter, or soil-column-type studies. I don't know what we'll find if we look on a field scale beneath the burial pits. Until we do I don't know whether the caissons are leading us forwards or sideways in terms of understanding how to predict chemical movement for regulatory purposes. So I think a field experiment, though we don't have time to discuss it, should be part of the next step in designing a way to better regulate based on modeling.

J. W. Mercer

It isn't as though the field experiments aren't taking place. Bill Jury is doing them but with other chemicals. Isn't there a lot of transfer value?

R. J. Wagenet

I'm sure there is, but similarly, why would you want to do another caisson study if you've already studied the movement of noninteracting solutes in porous medium? In fact, we will learn something new by doing another field study in a different soil with different hydrology and different boundary conditions. I don't think one set of observations is going to carry us through a number of different scenarios in nature. That is why I believe that a field experiment at this point is important. It is also important to milk the present caisson study

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for all you can get out of it. For a small cost, that is a logical thing to do. On the larger scale, I feel that multiple field observations in different locations would provide data that most modelers really need.

I. P. Murarka

I think the difference in values between laboratory, large controlled field-scale experiments, and uncontrolled field-scale experiments are different and they have different purposes. Let's not try to say one will serve the purposes and let's not try to say one will serve the purpose of the other. What we are doing under very controlled laboratory conditions is that we can quantify and describe exactly what the processes are and how they work. In a little bit less-controlled field-scale experiment, we are able to describe how they are able to work in complexity, and all fundamental processes that we defined and understood are still applicable when the system is more complex. Then when we go to the uncontrolled complete field scale, when we know very little about what else is going on, have we got enough of the fundamental understanding of different processes that work together from a vareity of fields and actually occur in a natural environment? Are we equipped to do it within 100-200-5%, whatever the level? So it is just a progressive building of why, what happens can be said with some confidence. I think that has a great deal of value, and I am not sure if a single experiment of each type is sufficient to describe the multidimensional points of operations that we have in front of us.

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ACKNOWLEDGMENTS

The editors would like to thank those involved in workshop preparation as well as the participants. Special thanks goes to W. L. Polzer, who was the principal investigator on this project, and J. W. Nyhan, who initiated the idea for the modeling study reported herein. Thanks also to Sylvia Gonzales and Rebekah Opperman for typing the report.

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H. R. F.

9 2 1 2 4 5 8 0 9 7 5

NRC FORM 335 (2-84) NRCM 1102, 3201, 3202

U.S. NUCLEAR REGULATORY COMMISSION

BIBLIOGRAPHIC DATA SHEET

SEE INSTRUCTIONS ON THE REVERSE.

1. REPORT NUMBER (Assigned by TIDC, add Vol. No., if any)
NUREG/CR-4615
LA-10730-MS
Vol. 2

2. TITLE AND SUBTITLE
Modeling Study of Solute Transport in the Unsaturated Zone
Workshop Proceedings

3. LEAVE BLANK

4. DATE REPORT COMPLETED
MONTH: February YEAR: 1987

5. AUTHOR(S)
E. P. Springer, H. R. Fuentes

6. DATE REPORT ISSUED
MONTH: April YEAR: 1987

7. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)
Los Alamos National Laboratory
Los Alamos, NM 87545

8. PROJECT/TASK/WORK UNIT NUMBER

9. FIN OR GRANT NUMBER
A7150

10. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)
Division of Waste Management
Office of Nuclear Materials Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555

11a. TYPE OF REPORT
Technical

b. PERIOD COVERED (Inclusive dates)

12. SUPPLEMENTARY NOTES

13. ABSTRACT (200 words or less)

These proceedings include the technical papers, a panel summary report, and discussions held at the workshop on Modelong of Solute Transport in the Unsaturated Zone held June 19-20, 1986, at Los Alamos, New Mexico. The central focus of the workshop was the analysis of data collected by Los Alamos under agreement with the U. S. Nuclear Regulatory Commission on intermediate-scale caisson experiments. Five different modeling approaches were used. The purpose was to evaluate models for near-surface waste disposal of low-level radioactive wastes. The workshop was part of a larger study being conducted by Los Alamos on transport in the unsaturated zone under agreement with the U. S. Nuclear Regulatory Commission.

14. DOCUMENT ANALYSIS - a. KEYWORDS/DESCRIPTORS
Modeling
Solute Transport
Porous Media
Unsaturated Flow

b. IDENTIFIERS/OPEN-ENDED TERMS

15. AVAILABILITY STATEMENT
Unlimited

16. SECURITY CLASSIFICATION
(This page) Unclassified
(This report) Unclassified

17. NUMBER OF PAGES

18. PRICE

9212240597 6

*U. S. GOVERNMENT PRINTING OFFICE: 1987-181-682:60069

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