Department of Energy
Oak Ridge Operations
Weldon Spring Site
Remedial Action Project Office
Route 2, Highway 94 South
St. Charles, Missouri 63303

September 14, 1989

Mr. Dan Wall
Remedial Project Manager
U.S. Environmental Protection
Agency
Region VII
726 Minnesota Avenue
Kansas City, Kansas 66101

Dear Mr. Wall:

THE EFFECTS OF A PERTURBED SOURCE ON CONTAMINANT TRANSPORT NEAR THE WELDON SPRING QUARRY

Enclosed for your retention and information is a copy of the technical memo "The Effects of a Perturbed Source on Contaminant Transport Near the Weldon Spring Quarry" prepared in support of the environmental compliance process for bulk-waste management at the quarry.

If you have any questions please feel free to call.

Sincerely,

Steve McCracken
Acting Project Manager
Weldon Spring Site
Remedial Action Project

Enclosure:
As stated

cc w/ enclosure:
B. Hlavacek PMC (2 copies)

Department of Energy
Oak Ridge Operations
Weldon Spring Site
Remedial Action Project Office
Route 2, Highway 94 South
St. Charles, Missouri 63303

3589-89-I-DOE-321

September 14, 1989

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Mr. David E. Bedan
State of Missouri Department of
Natural Resources
Post Office Box 176
Jefferson City, Missouri 65102

Dear Mr. Bedan

THE EFFECTS OF A PERTURBED SOURCE ON CONTAMINANT TRANSPORT NEAR THE WELDON SPRING QUARRY

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B. Hlavacek PMC

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

ANL/EES-TM-370

THE EFFECTS OF A PERTURBED SOURCE ON CONTAMINANT TRANSPORT NEAR THE WELDON SPRING QUARRY

by

D. Tomasko

Energy and Environmental Systems Division

March 1989

work sponsored by

U.S. DEPARTMENT OF ENERGY
Oak Ridge Operations Office

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FOREWORD

The Weldon Spring site is located near Weldon Spring, Missouri, about 30 mi west of St. Louis. At various times since the 1940s, portions of the site have been used as ordnance works by the U.S. Army and for uranium processing and waste storage facilities by the U.S. Atomic Energy Commission. As a result of these uses, two areas at the site -- the chemical plant and raffinate pits area and the quarry -- are contaminated with chemical and radioactive waste. On July 30, 1987, the U.S. Environmental Protection Agency (EPA) listed the quarry on its National Priorities List.

As current owner of the site, the U.S. Department of Energy is conducting the Weldon Spring Site Remedial Action Project as Major Project Number 182 under the Surplus Facilities Management Program (SFMP). The major goals of the SFMP are to eliminate potential hazards to the public and the environment that are associated with contamination at SFMP sites and to make surplus property available for other uses to the extent possible. Remedial actions under the SFMP are conducted in accordance with the National Environmental Policy Act and subject to EPA oversight under the Comprehensive Environmental Response, Compensation, and Liability Act, as amended by the Superfund Amendments and Reauthorization Act.

This report presents the results of solute transport modeling, which facilitates an analysis of the effects of disturbing the contaminant source (i.e., through remedial action) on nearby wells and surface water. The analysis is intended as an aid in selecting a remedial action alternative.

THE EFFECTS OF A PERTURBED SOURCE ON CONTAMINANT TRANSPORT NEAR THE WELDON SPRING QUARRY

by

D. Tomasko

ABSTRACT

The effects of a perturbed contamination source at the Weldon Spring quarry in St. Charles County, Missouri, on downstream solute concentrations were investigated using one-dimensional analytic solutions to an advection-dispersion equation developed for both constant-strength and multiple-stepped source functions. A sensitivity study using parameter base-case values and ranges consistent with the geologic conceptualization of the quarry area indicates that the parameters having the greatest effect on predicted concentrations are the distance from the quarry to the point of interest, the average linear groundwater velocity, the contaminant retardation coefficient, and the amplitude and duration of the source perturbation caused by response action activities. Use of base-case parameter values and realistic values for the amplitude and duration of the source perturbation produced a small effect on solute concentrations near the western extremity of the nearby municipal well field, as well as small uncertainties in the predicted results for the assumed model. The effect of simplifying assumptions made in deriving the analytic solution is unknown: use of a multidimensional flow and transport model and additional field work are needed to validate the model.

1 BACKGROUND

1.1 OBJECTIVE

The U.S. Department of Energy (DOE) plans to perform a response action at the Weldon Spring quarry. Specific activities that are a part of this action can be divided into five areas: (1) removal and treatment of contaminated water from the quarry pond and other sources, (2) removal of bulk wastes, (3) potential removal of any residual materials remaining after bulk-waste removal, (4) potential restoration of groundwater, and (5) potential restoration of nearby properties. This report presents analyses having three major objectives: (1) to estimate the effects of a perturbed contaminant source at the quarry on downstream solute concentrations, (2) to compare downstream concentrations for a no-action alternative with those calculated for the remedial action program, and (3) to perform a sensitivity study to assess the reliability of the predicted results.

1.2 SITE DESCRIPTION

The Weldon Spring quarry is part of a DOE surplus facility located in St. Charles County, Missouri, about 4 mi south of the Weldon Spring Chemical Plant and 30 mi west of St. Louis (Fig. 1). The quarry is located near Route 94 about 700 ft from the Femme Osage Slough, 3,000 ft from a municipal well field, and 1 mi from the Missouri River (Fig. 2). Originally, the quarry was used to supply limestone and sand for construction. The 9-acre site was later used for the disposal of soils and other materials contaminated by trinitrotoluene (TNT) during the 1940s and 1950s and the disposal of low-level radioactive wastes during the late 1950s and 1960s. The quarry is filled with about 95,000 yd^3 of radioactively or chemically contaminated wastes, including drums, concrete and steel rubble, machinery, process residues, uncontained wastes, and contaminated soils.

1.2.1 Geologic Setting

The Weldon Spring quarry is located in low limestone hills near the west bank of the Missouri River. The mid-Ordovician bedrock of the quarry area is predominantly limestone and dolomite. Nearby are elevated deposits of Bushberg sandstone and silty clay. In the vicinity of the quarry, the carbonate rocks dip to the northeast at a gradient of 60-80 ft/mi (Berkeley Geosciences Associates 1984).

The bedrock is overlain in the upland areas by 10-40 ft of silty clay derived primarily from glacial loess and till. In the Missouri River bottomland areas, the bedrock is overlain by up to 100 ft of alluvial material. Figure 3 shows an idealized geologic section of the quarry. The sides of the quarry expose the Ordovician Kimmswick formation (Fig. 3), while the bedrock floor of the quarry, presently covered with clay and waste rubble, lies in the upper portion of the Decorah formation (Fig. 4). The Decorah formation is 20-40 ft thick, and its upper portion is predominantly fossiliferous limestone with shale partings (Berkeley Geosciences Associates 1984). The Kimmswick formation, mined during quarry operations, is predominantly a crystalline limestone about 70 ft thick. It is characterized by solution-enlarged features associated with the intersection of vertical joints and bedding planes.

East and south of the quarry (Fig. 3), bottomland alluvium, sand, and gravels replace the Plattin, Decorah, and Kimmswick limestones and shales. Locally, the alluvium is composed of a surficial layer of 10 ft of silt underlain by about 20 ft of sand. The thickness of the silt layer increases toward the river. Beneath the sand is about 70 ft of sand and gravel. This water-bearing alluvium is a major contributor to the domestic water supplies of nearby towns.

1.2.2 Groundwater

Groundwater flow in the vicinity of the quarry occurs in alluvium, fractured limestone and dolomite, and the sandstone of the St. Peter formation (Berkeley Geosciences Associates 1984). Water-table conditions (unconfined aquifers) are typically found in areas of significant alluvial deposits; semiconfined conditions (confined to leaky aquifers) occur where layers of varying permeability are present. Flow in the limestone

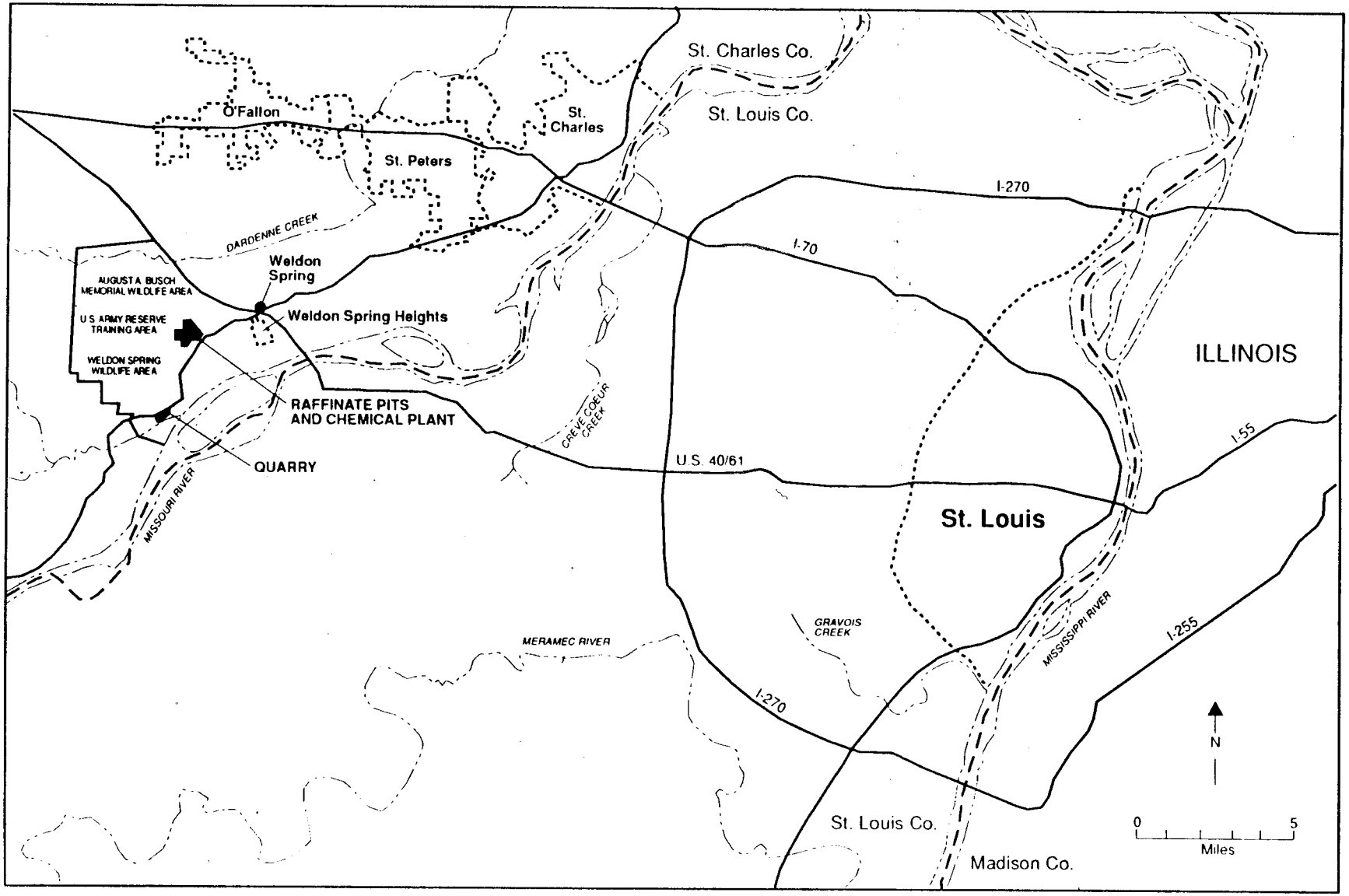

FIGURE 1 Location of the Weldon Spring Site, Weldon Spring, Missouri (Source: MacDonnell et al. 1989)

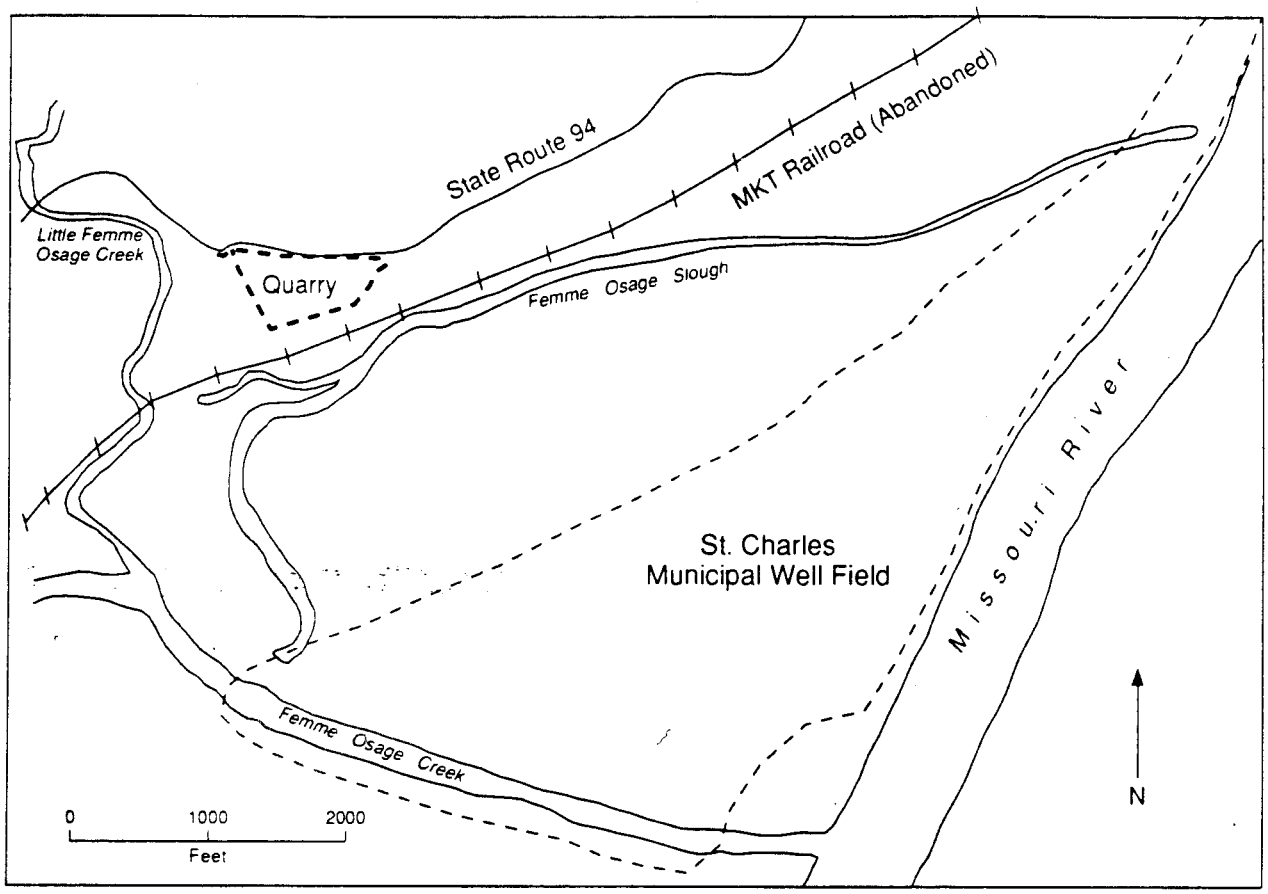

FIGURE 2 Location of the Weldon Spring Quarry Relative to the Missouri River and the Municipal Well Field

is primarily through secondary porosity provided by fractures and solution features. The St. Peter formation, about 300 ft below the floor of the quarry, contains a confined groundwater aquifer. The degree of connection between the St. Peter formation and overlying formations is not fully understood.

A shallow groundwater divide is believed to exist beneath a ridge that runs through the Weldon Spring Chemical Plant, about 4 mi north of the quarry. As a result of this divide, shallow groundwater flow near the quarry is expected to be in a southeasterly direction toward the Missouri River. Water levels measured on September 5, 1980, support this hypothesis.

In the immediate vicinity of the quarry, groundwater flows primarily from north to south (Morrison-Knudson Engineers, Inc. 1988), although water-level measurements taken in 1987 indicate a possible mounding of groundwater at the quarry, due to local recharge (Fig. 5). If groundwater flow in the fractured bedrock below the quarry is assumed to be primarily horizontal (low vertical leakage), then groundwater flow near the quarry can be modeled as if it were one-dimensional. This approach should produce conservative estimates for the downstream solute concentrations.

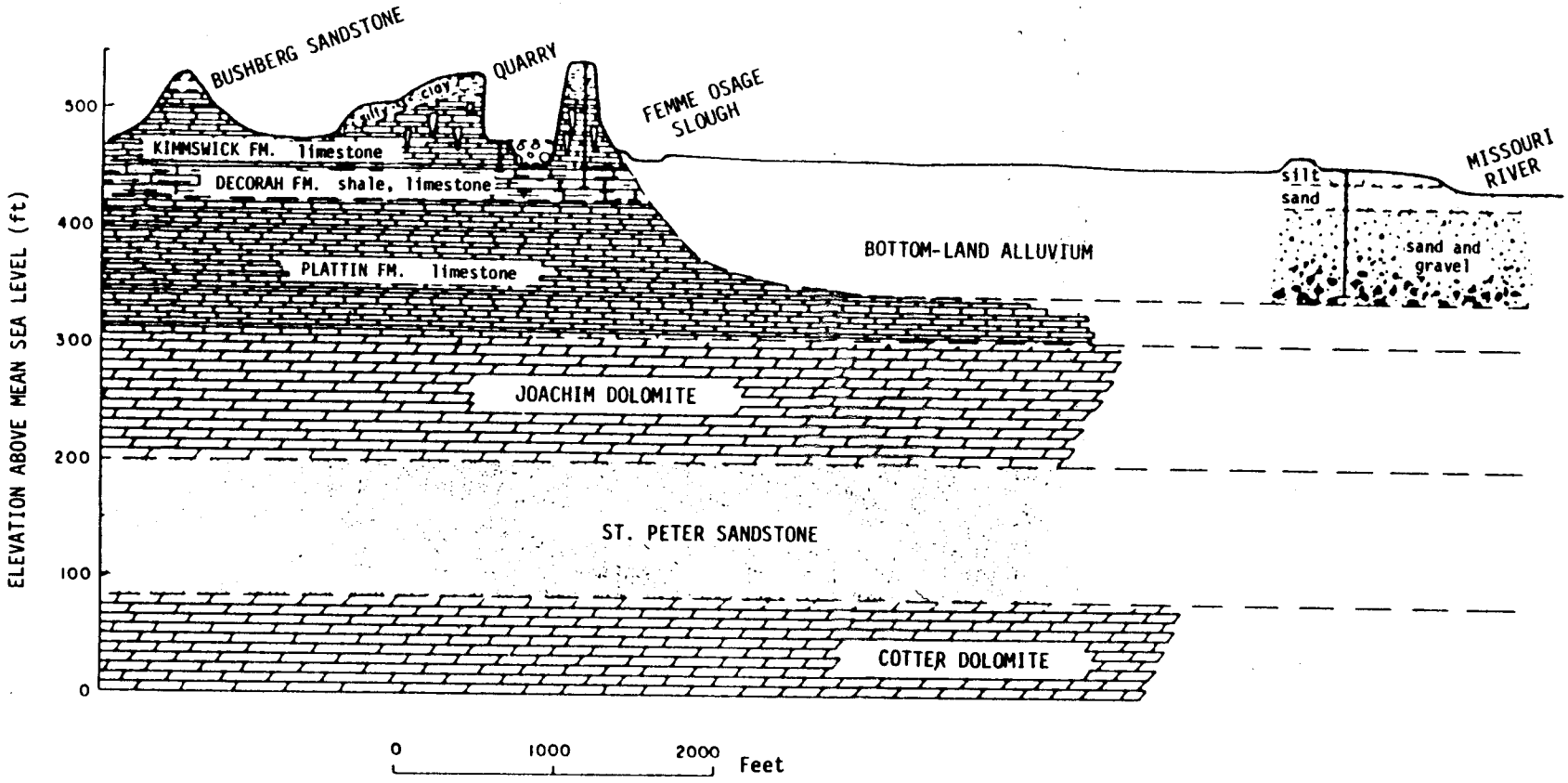

FIGURE 3 Idealized Vertical Section through the Weldon Spring Quarry (Source: Berkeley Geosciences Associates 1984)

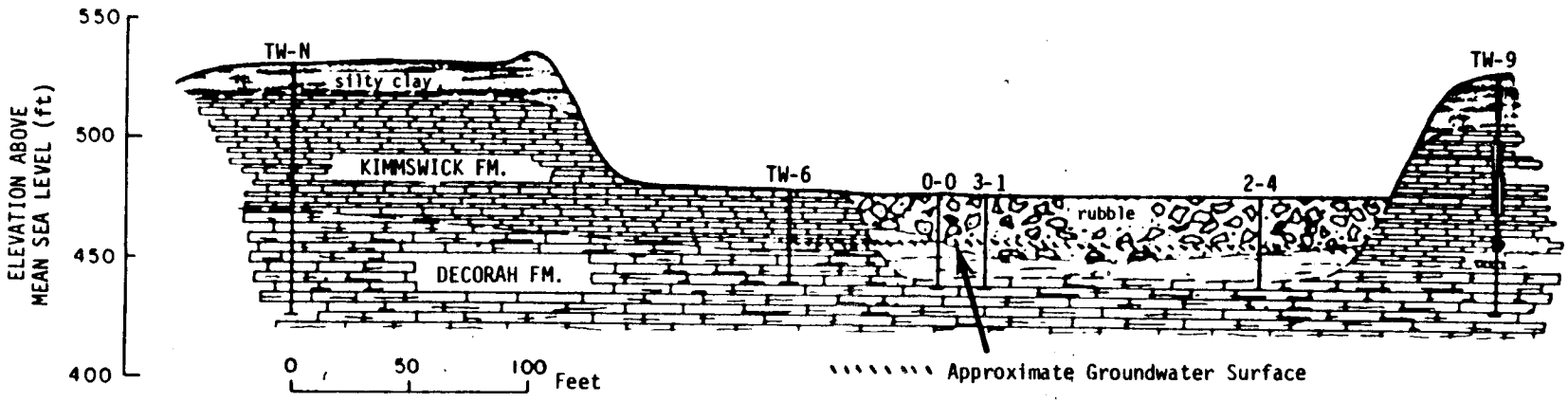

FIGURE 4 Detailed North-South Vertical Section through the Weldon Spring Quarry (Source: Berkeley Geosciences Associates 1984)

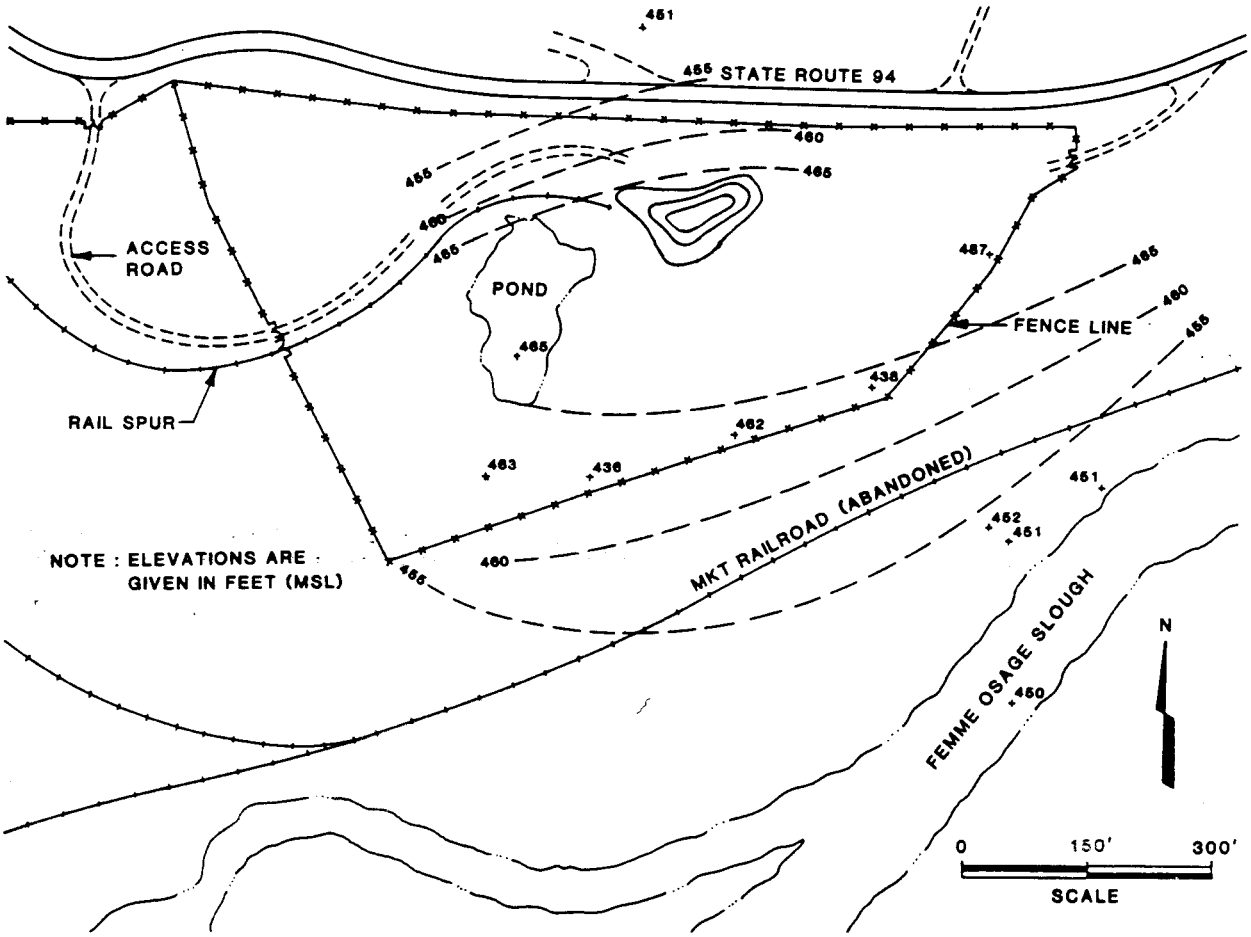

FIGURE 5 Water Levels Measured near the Weldon Spring Quarry in 1987 (Source: Adapted from MacDonnell et al. 1989)

Contaminated water from the quarry is thus expected to flow toward the Femme Osage Slough and the St. Charles municipal well field, which is completed in the alluvium and located near the Missouri River (Fig. 2). Near the quarry, flow is likely to take place through secondary porosity features in the fractured limestone formations. Near the well field, the flow may be a combination of flow through fractures and flow through a porous medium composed of bottomland alluvium.

2 CONTAMINANT TRANSPORT MODEL

2.1 ASSUMPTIONS

This section presents the development of an analytical model for predicting the effects of a perturbed source on contaminant transport. In order to develop a closed-form, analytical solution, simplifying assumptions were made for both the groundwater flow system and the processes affecting contaminant transport. These simplifications are discussed below.

The first approximation made in developing an analytical expression for contaminant transport from a perturbed source was that the groundwater flow system is one-dimensional in a direction approximately parallel to the observed hydraulic gradient. On a regional scale, groundwater flow passes through the quarry area in a northwest to southeast direction, as indicated by the water levels shown in Fig. 5. In the immediate vicinity of the quarry, the ponded water may act as a local hydrologic high. Water levels shown in Fig. 5 indicate that the predominant groundwater flow direction is also to the south and east. For a narrow contaminant plume, groundwater flow in a plane parallel to the surface can be considered one-dimensional. Although flow in the vertical direction (formation to formation) is possible, no data are currently available to assess the vertical leakage rate. For simplicity, it was assumed to be zero.

In addition to the assumption of one-dimensional flow, the rock matrix was assumed to be homogeneous and isotropic from the quarry to the Missouri River. Variations in material properties between river alluvium and fractured limestone were accounted for by assuming a range of constant flow velocities for the transport calculations. Choosing an appropriate range of velocities allows a conservative calculation to be performed.

For both the river alluvium and fractured dolomite and limestone, an equivalent single-porosity medium was used for the calculations. As demonstrated by Tomasko et al. (1987), a fractured porous medium can behave in one of three ways: (1) as an equivalent single-porosity medium with a total porosity equal to the sum of the fracture and matrix porosities, (2) as an equivalent single-porosity medium with a total porosity equal to that of the fracture alone (fracture flow), or (3) as a double-porosity system (Streltsova-Adams 1978) in which the fractures provide a high-permeability channel of low storativity and the surrounding rock matrix provides a low-permeability medium with high storativity. For the fractured quarry limestone, the equivalent porous medium appears to behave like a type 2 system (Berkeley Geosciences Associates 1984). Flow appears to be confined to the fractures, and the surrounding intact limestone provides little permeability for flow or storage. For the river alluvium, the system should behave like an ideal porous medium.

The velocities used in the transport calculations were chosen to be representative of an equivalent porous medium that simulates an average flow through two systems: (1) a fractured limestone and (2) a flood plain alluvium. Since the flow velocities through the alluvium can be much lower than fracture flow velocities, the velocities used in this study are significantly lower than the velocity expected in any

individual fracture. This approximation is consistent with recent concentration measurements made in the alluvium north and south of the Femme Osage Slough, which indicate low average velocities and long travel times between the quarry and the points of measurement (Morrison-Knudson Engineers, Inc. 1988). No groundwater flow calculations were performed for this study.

In all of the calculations, the Femme Osage Slough and the municipal well field were assumed to have a negligible effect on the flow pattern in the vicinity of the quarry. The effects of this assumption on the calculated results are unknown at this time and will be investigated further with a more detailed multidimensional numerical model and validated with additional field measurements as part of a groundwater restoration decision process.

In addition to the above assumptions about the groundwater flow system, the following assumptions were made for performing the transport calculations: solutes from the quarry immediately enter a zone of saturated groundwater (no vadose), the half-lives of any radionuclides in the groundwater are long compared to the time scale of the calculations, a point source of contamination has existed at the quarry for 40 yr, perturbations to the quarry source caused by response activities can be represented with a simple time-dependent multistep function, and sorption can be represented with a linear isotherm (reactions are fast and reversible). In general, these assumptions should produce conservative predictions for the downstream solute concentrations.

2.2 THEORETICAL BASIS

The following partial differential advection-dispersion equation from Freeze and Cherry (1979) describes the transport of a contaminant under steady-state flow conditions for the above simplifying assumptions:

$$\frac{\partial C}{\partial t} + \frac{V}{R}\frac{\partial C}{\partial X} = \frac{D}{R}\frac{\partial^2 C}{\partial X^2} \tag{1}$$

where:

R = Solute retardation factor given by:

$$R = 1 + \frac{\rho_b}{\phi} K_d \tag{2}$$

ρ_b = Bulk density,

C = Concentration of the contaminant,

V = Average linear groundwater velocity (Darcy velocity/effective porosity),

D = Dispersion coefficient,

t = Time,

K_d = Distribution coefficient,

ϕ = Effective porosity, and

X = Distance from the quarry in a direction parallel to groundwater flow.

The dispersion coefficient, D, was assumed to follow the functional form presented by Bear (1972):

$$D = \alpha V \tag{3}$$

where α = dispersivity. Diffusional effects were assumed to be negligible.

Dispersivity was generally assumed to depend on scale:

$$\alpha = 0.1L \tag{4}$$

where L is the separation distance between the origin of the source (X = 0) and the point of measurement (Lallemand-Barres and Peaudecerf 1978). At large separations, dispersivity appears to approach a maximum value of about 500 ft (Grisak and Pickens 1980). Therefore, a maximum value of α = 500 ft was assumed for the calculations in this study, giving

$$\begin{aligned} \alpha &= 0.1L \text{ for } 0.1L \leq 500 \text{ ft} \\ \alpha &= 500 \text{ ft for } 0.1L > 500 \text{ ft.} \end{aligned} \tag{5}$$

For a constant source C_0 at X = 0, Eq. 1 has the following solution in Laplace space:

$$\frac{\bar{C}}{C_0} = \frac{1}{S} e^{VX/2D} e^{-\sqrt{V^2X^2/4D^2+SX^2R/D}} \tag{6}$$

In Eq. 6, S is the Laplace variable and $\bar{C}$ is the solute concentration in Laplace space. Equation 6 has the form:

$$\frac{1}{S} e^{-\sqrt{A(B+S)}} \tag{7}$$

The inverse Laplace transform of Eq. 7 is given in the tables of Ditkin and Prudnikov (1967) as:

$$L^{-1}\left[\frac{e^{-\sqrt{A(B+S)}}}{S}\right] = \frac{1}{2}\left[e^{-\sqrt{AB}}\ \mathrm{ERFC}\left(\frac{1}{2}\sqrt{A/t} - \sqrt{Bt}\right) + e^{\sqrt{AB}}\ \mathrm{ERFC}\left(\frac{1}{2}\sqrt{A/t} + \sqrt{Bt}\right)\right] \tag{8}$$

where ERFC is the complementary error function given by Hildebrand (1976) as:

$$\mathrm{ERFC}(\gamma) = 1 - \mathrm{ERF}(\gamma) = 1 - 2/\sqrt{\pi}\int_0^{\gamma} e^{-\lambda^2}\,d\lambda \tag{9}$$

The inverse Laplace transform of Eq. 6 can be found by using the inverse relationship presented in Eq. 8. The result is:

$$\frac{C}{C_0} = \frac{e^{VX/2D}}{2}\left[e^{-\sqrt{AB}}\ \mathrm{ERFC}\left(\frac{1}{2}\sqrt{A/t} - \sqrt{Bt}\right) + e^{\sqrt{AB}}\ \mathrm{ERFC}\left(\frac{1}{2}\sqrt{A/t} + \sqrt{Bt}\right)\right] \tag{10}$$

where:

$$A = \frac{RX^2}{D} \tag{11}$$

and

$$B = \frac{V^2}{4DR} \tag{12}$$

Reintroducing the physical parameters gives:

$$\frac{C}{C_0} = \frac{1}{2}\left[\mathrm{ERFC}\left(\frac{XR - Vt}{2\sqrt{DRt}}\right) + e^{VX/D}\ \mathrm{ERFC}\left(\frac{XR + Vt}{2\sqrt{DRt}}\right)\right] \tag{13}$$

For no sorption (R = 1), Eq. 13 reduces to the well-known analytic solution first presented by Ogata and Banks (1961):

$$\frac{C}{C_0} = \frac{1}{2}\left[\mathrm{ERFC}\left(\frac{X - Vt}{2\sqrt{Dt}}\right) + e^{VX/D}\ \mathrm{ERFC}\left(\frac{X + Vt}{2\sqrt{Dt}}\right)\right] \tag{14}$$

Equations 13 and 14 were used to calculate the downstream solute concentration for the no-action alternative.

For a simple step function, the concentration at X = 0 is no longer constant with time. Instead, at time = 0 the concentration is C_0, and remains C_0 until time = Δt_1, at which point the concentration returns to zero (Fig. 6). This type of process represents cleanup of the quarry without any increase in the contaminant source distribution. At X = 0, the time-dependent source concentration is given by the following expression:

$$\frac{C}{C_0} = U(t - 0) - U(t - \Delta t_1) \tag{15}$$

where U is the unit function (Hildebrand 1976).

The Laplace-transformed source distribution is given by:

$$\frac{\bar{C}}{C_0} = \frac{1}{S}\left(1 - e^{-\Delta t_1 S}\right) \tag{16}$$

The solution to Eq. 1 in Laplace space for a simple step function source at X = 0 is given by:

$$\frac{\bar{C}}{C_0} = \frac{1}{S}\left(1 - e^{-\Delta t_1 S}\right) e^{VX/2D}\, e^{-\sqrt{V^2X^2/4D^2 + SX^2R/D}} \tag{17}$$

This expression can be inverted term-wise to yield the time-dependent solute concentration for one-dimensional transport with advection, dispersion, and retardation using Eq. 8 and the following shift identity for Laplace transforms (Hildebrand 1976):

$$e^{-\Delta t S} f(S) = L\,[f(t - \Delta t)H(t - \Delta t)] \tag{18}$$

where H is the Heaviside function (Hildebrand 1976) such that:

$$\begin{aligned} H(t - \Delta t) &= 0 \text{ for } t < \Delta t \\ H(t - \Delta t) &= 1 \text{ for } t \geq \Delta t \end{aligned} \tag{19}$$

The result is given by the following expression:

$$\begin{aligned} \frac{C}{C_0} = {} & \frac{1}{2}\left[\mathrm{ERFC}\left(\frac{XR - VT}{2\sqrt{DRt}}\right) + e^{VX/D}\,\mathrm{ERFC}\left(\frac{XR + Vt}{2\sqrt{DRt}}\right)\right] \\ & - \frac{1}{2} H(t - \Delta t_1)\left\{\mathrm{ERFC}\left[\frac{XR - V(t - \Delta t_1)}{2\sqrt{DR(t - \Delta t_1)}}\right]\right. \\ & \left. + e^{VX/D}\,\mathrm{ERFC}\left[\frac{XR + V(t - \Delta t_1)}{2\sqrt{DR(t - \Delta t_1)}}\right]\right\} \end{aligned} \tag{20}$$

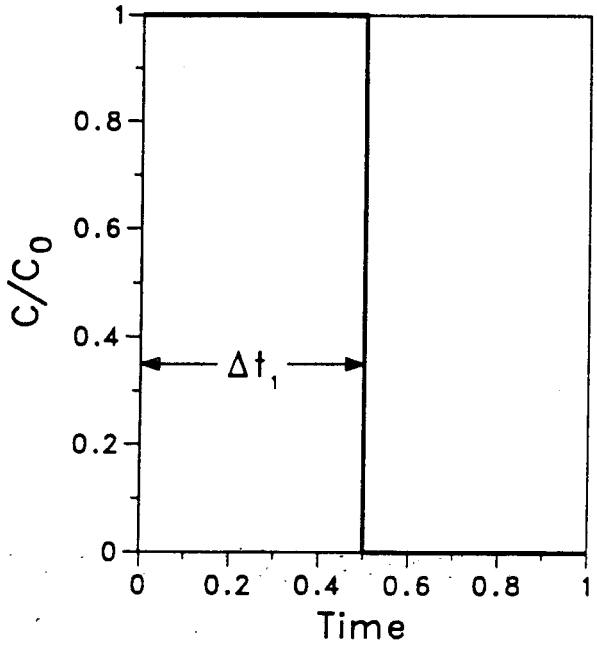

FIGURE 6 Simple Step Function Source for the Weldon Spring Quarry Model

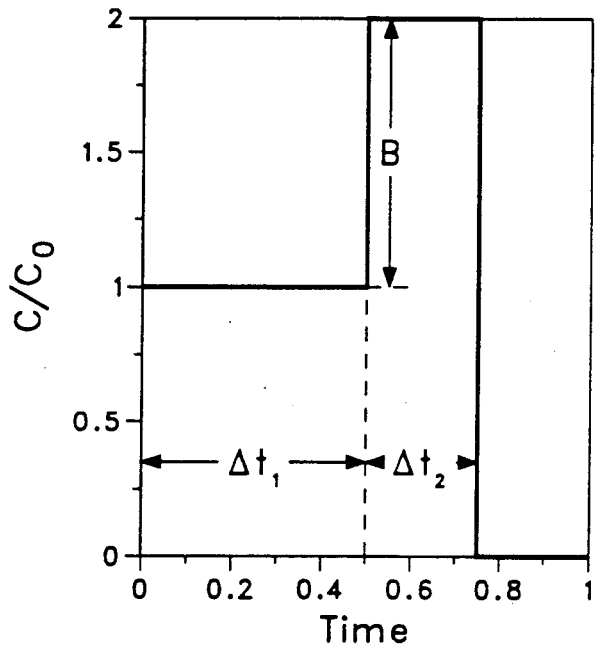

FIGURE 7 Multiple-Stepped Function Source for the Weldon Spring Quarry Model

For a multiple, stepped solute source (Fig. 7), the concentration at X = 0 can be represented with the following equation:

$$\frac{C}{C_0} = U(t - 0) + bU(t - \Delta t_1) - [(b + 1)\, U(t - \Delta t_1 - \Delta t_2)] \tag{21}$$

where bC_0 is the amplitude of the source perturbation above C_0, Δt_1 is the duration of constant source strength C_0, and Δt_2 is the duration of the perturbed source strength. This source was used to simulate cleanup at the quarry with a perturbation in the source concentration.

In Laplace space, Eq. 21 becomes:

$$\frac{\bar{C}}{C_0} = \frac{1}{S}\left[1 + be^{-\Delta t_1 S} - (b + 1)\, e^{-(\Delta t_1 + \Delta t_2)S}\right] \tag{22}$$

and the solution of Eq. 1 in Laplace space for a multiple, stepped-source function is:

$$\frac{\bar{C}}{C_0} = \frac{1}{S}\left[1 + be^{-\Delta t_1 S} - (b + 1)\, e^{-(\Delta t_1 + \Delta t_2)S}\right] \times \left(e^{VX/2D}\, e^{-\sqrt{V^2X^2/4D^2 + SX^2R/D}}\right) \tag{23}$$

The inverted analytic solution for one-dimensional solute transport with advection, dispersion, and retardation is then found term-wise, as before, using the Ditkin and Prudnikov (1967) relation and the Laplace transform shift identity. The result is:

$$
\begin{aligned}
\frac{C}{C_0} = \frac{1}{2} & \left[\mathrm{ERFC}\left(\frac{XR - Vt}{2\sqrt{DRt}}\right) + e^{VX/D}\,\mathrm{ERFC}\left(\frac{XR + Vt}{2\sqrt{DRt}}\right)\right] \\
& + \frac{b}{2} H(t - \Delta t_1) \left\{ \mathrm{ERFC}\left[\frac{XR - V(t - \Delta t_1)}{2\sqrt{DR(t - \Delta t_1)}}\right] \right. \\
& \left. + e^{VX/D}\,\mathrm{ERFC}\left[\frac{XR + V(t - \Delta t_1)}{2\sqrt{DR(t - \Delta t_1)}}\right]\right\} \\
& - \frac{(b + 1)}{2} H(t - \Delta t_1 - \Delta t_2) \left\{ \mathrm{ERFC}\left[\frac{XR - V(t - \Delta t_1 - \Delta t_2)}{2\sqrt{DR(t - \Delta t_1 - \Delta t_2)}}\right] \right. \\
& \left. + e^{VX/D}\,\mathrm{ERFC}\left[\frac{XR + V(t - \Delta t_1 - \Delta t_2)}{2\sqrt{DR(t - \Delta t_1 - \Delta t_2)}}\right]\right\}
\end{aligned}
\tag{24}
$$

A computer program was written to evaluate Eqs. 13, 14, and 24 for a range of parameters relevant to conditions expected near the Weldon Spring quarry. The complementary error function, ERFC, was modeled using an algorithm from Abramowitz and Stegun (1972). To implement the algorithm, the following relationship was developed:

$$\mathrm{ERFC}(-X) = 2 - \mathrm{ERFC}(X) \tag{25}$$

3 PARAMETER VALUES AND RANGES

In calculating the downstream solute concentration with Eqs. 13 and 24, values were assigned to the following independent variables: the distance from the quarry to the point of interest, X, measured in a direction parallel to the direction of groundwater flow (northwest to southeast); the average linear velocity of the groundwater, V; the value of the dispersion coefficient, D; the amplitude of the perturbation, b; the duration of the constant source strength, Δt_1; the duration of the source perturbation, Δt_2; and the degree of solute retardation, R. These values were then varied over ranges consistent with the geologic conceptualization of the quarry area to perform a sensitivity study to evaluate the reliability of the calculations. Details of the selection process for the parameter values and ranges are given below.

Three separation distances, 1,000, 2,500, and 5,000 ft, were used in the calculations performed for this study. These separation distances correspond to the approximate distances from the quarry to the Femme Osage Slough, the western extremity of the municipal well field, and the west bank of the Missouri River, respectively (Fig. 3). A base-case value of 2,500 ft was used to investigate the effects of other parameters, except for retardation and dispersivity, on the downstream solute concentrations. This value was chosen because it provides a conservative estimate of the distance to the municipal well field (2,700 ft). For retardation and dispersivity, a base-case value of 1,000 ft was used to facilitate the graphical presentation. For all calculations, the porous medium between the quarry and the point of calculation was assumed to be homogeneous and isotropic.

In order to simulate different equivalent-porosity media, the average groundwater velocity was varied between 100 and 1,000 ft/yr. A base-case value of 300 ft/yr was selected to investigate the effects of other parameters on the downstream concentrations. The base-case velocity is consistent with point-dilution measurements made in the fractured limestone near the quarry (Berkeley Geosciences Associates 1984) and is a reasonable compromise between the high fluid velocities expected in the fractured limestone and the low velocities expected in the flood plain alluvium.

Solute transport can be affected by dispersion as well as advection. As discussed earlier, dispersion was assumed to be the product of dispersivity and groundwater velocity (Eq. 3); diffusional effects here are assumed to be negligible. Dispersivity was assumed to depend on the scale, with a maximum value of 500 ft (Eq. 5). The dispersion coefficient used in this study ranged from a low of 1.5×10^4 ft^2/yr to a high of 1.5×10^5 ft^2/yr. For the sensitivity analysis, the dispersion coefficient was allowed to vary over three orders of magnitude (3×10^3 to 3×10^6 ft^2/yr) for a separation distance of 1,000 ft and a fluid velocity of 300 ft/yr.

In addition to the above hydrogeologic parameters, downstream solute concentrations can be affected by Δt_1, Δt_2, and b. For all of the calculations, the duration time (Δt_1) of the constant strength source (C_0) was assumed to be 40 yr. This value corresponds to having a constant-value contaminant source in the quarry since the late 1940s. This assumption is valid for chemical contaminants such as residues from the manufacture of TNT, but it is about 10-15 yr too long for radionuclide disposal in the

early 1960s (Berkeley Geosciences Associates 1984). Since the predicted downstream solute concentrations achieve nearly steady-state values in times considerably less than 40 yr, the use of a 40-yr duration should produce conservative results.

No attempt was made to calibrate the transport model to field measurements because of the following factors: the fracture geometry below the bulk wastes is unknown, the hydrogeologic processes at the boundary between the fractured limestone and alluvial aquifers are not understood, and a point measurement in a complex three-dimensional flow field has an inherently large degree of uncertainty for contaminant plume characterization.

In order to investigate the effect of the source perturbation on the solute concentration, both its amplitude and duration were varied. The amplitude was varied over a 100% range in value from C_0 to $2C_0$. It is unlikely that remedial action activities at the quarry will more than double the contaminant source strength (quarry waste waters are well mixed after 30 yr of contaminant residence, steel canisters have probably rusted through, and few, if any, additional clean fractures will be exposed to the contamination). A base-case value of 100% amplitude change was used in evaluating the effect of changes in other parameters. A base-case cleanup time of two years was assumed for Δt_2 (Fig. 7). The sensitivity of the calculations to this parameter was investigated by allowing the cleanup time to range from one to ten years, even though the cleanup activities are expected to be completed in about two years.

The last parameter of interest for the study is the retardation factor, R. This factor, as shown in Eq. 2, is a function of the solute distribution coefficient, K_d. Since distribution coefficients vary significantly for different classes of dissolved materials and geologic conditions, assigning a single value becomes difficult. Conservative results can be obtained by assuming a K_d value of zero (R = 1). This case corresponds to no sorption along the chosen flow path. The effects of a nonzero value for R were investigated by performing calculations with an R of 1, 5, 10, and 25. A base-case value of R = 1 was used for the study to obtain conservative results and because no in-situ field measurements are available for this parameter.

4 RESULTS AND DISCUSSION

Figure 8 shows the effect of separation distance on the downstream solute concentration as a function of time. In these plots, and all subsequent plots, the solid line represents the downstream concentrations for a constant-strength source at the quarry (X = 0) as calculated with Eq. 13 or 14 and the dashed line represents the concentrations calculated for the stepped source shown in Fig. 7 using Eq. 24. All calculations begin at t = 0, 40 yr ago (1948). Forty years later (1988), the source is assumed to either (1) be perturbed and then reduced to zero after some time (response action scenario) or (2) remain at the same constant value (no-action alternative). Ordinate values in the plots are normalized to the initial contaminant concentration value, C_0.

In Fig. 8, all parameters are the same (V = 300 ft/yr, $D = \alpha V$, b = 100%, Δt_1 = 40 yr, Δt_2 = 2 yr, and R = 1) except for X, the separation distance, which is 1,000, 2,500, and 5,000 ft in parts a, b, and c, respectively. In all cases, the constant-strength source approaches a steady-state value ($C/C_0 = 1$) in less than 40 yr. As the separation distance increases, the solute breakthrough curve (BTC) broadens. That is, a longer time is required to achieve the same value of C/C_0. A broader BTC is caused by the combined effects of a larger separation distance and an increased dispersion coefficient. If the dispersion coefficient were zero, or some small constant value, slug flow would exist and the BTC would be a Heaviside function with a breakthrough time about equal to X/V.

For the stepped source, the time-dependent concentration profile behaves the same as the constant-strength source for the first 40 yr of the calculation. At 40 yr, the perturbed source first increases the downstream concentrations above the constant-strength source values and then reduces the concentrations to zero due to the assumed cleanup activities. As is clear from Fig. 8, increasing the separation distance between the source and the point of interest decreases the effect of the perturbation on the downstream concentrations. A plot of the maximum difference between C/C_0 calculated with a stepped source and C/C_0 calculated with a constant-strength source is shown in Fig. 9 as a function of separation distance. Discontinuous breaks in the slope of the plot are the result of using four calculations to span the range of the independent variable (separation distance).

Figure 10 shows the effect of the average linear groundwater velocity on the downstream solute concentration for X = 2,500 ft, $D = \alpha V$, b = 100%, Δt_1 = 40 yr, Δt_2 = 2 yr, and R = 1. Increasing the velocity (from 100 to 1,000 ft/yr) leads to earlier solute breakthrough times and a stronger perturbed source influence. Figure 11 shows the effect of velocity on the maximum difference between C/C_0 calculated with a constant-source strength and C/C_0 calculated with a perturbed source at a separation distance of 2,500 ft. As expected, increasing the velocity increases the maximum change.

Figure 12 illustrates the effect of dispersion on the downstream contaminant concentrations. In the calculations for Fig. 12, the dispersion coefficient was allowed to vary over three orders of magnitude from a low of 3×10^3 ft^2/yr to a high of 3×10^6 ft^2/yr for X = 1,000 ft, V = 300 ft/yr, b = 100%, Δt_1 = 40 yr, Δt_2 = 2 yr, and

R = 1. As expected, increasing the dispersion coefficient broadens the BTC and produces a slightly less pronounced peak amplitude in C/C_0. Compared to other parameter effects (such as distance, velocity, and retardation), dispersion is a secondary process.

Figure 13 shows the effect of the amplitude of the source perturbation on downstream concentrations for X = 2,500 ft, V = 300 ft/yr, D = 7.5×10^4 ft^2/yr, Δt_1 = 40 yr, Δt_2 = 2 yr, and R = 1. Increasing the amplitude of the perturbation (from 50 to 100%) increases the effect on the dimensionless solute concentrations. The increase in the maximum change in C/C_0 relative to a constant-strength source at a separation distance of 2,500 ft is nearly linear, as shown in Fig. 14. For small perturbations in source strength, the effect on downstream concentrations can be expected to be small.

Figure 15 shows the effect caused by the duration of the source perturbation for X = 2,500 ft, V = 300 ft/yr, D = 7.5×10^4 ft^2/yr, b = 100%, Δt_1 = 40 yr, and R = 1. Increasing the duration of the perturbation from one to ten years significantly increases the downstream concentrations. For a realistic cleanup time of two years, C/C_0 increases by a maximum of about 16%. Figure 16 shows the increase in C/C_0 relative to a constant-strength source at a separation distance of 2,500 ft. Discontinuous breaks in the slope of the response curves are the result of using four calculations to span the range of the independent variable (duration of the perturbation). An increase in the duration of the perturbation increases the maximum change between the two models.

Finally, Fig. 17 illustrates the effect of retardation on the downstream solute concentration for X = 1,000 ft, V = 300 ft/yr, D = 3×10^4 ft^2/yr, b = 100%, Δt_1 = 40 yr, and Δt_2 = 2 yr. A separation distance of 1,000 ft was used for the retardation sensitivity calculations to emphasize the effect. At larger separations, realistically estimated changes of R do not produce observable changes in the solute concentrations. As the degree of retardation is increased, the effect of the perturbed source on the solute concentrations decreases and the time to achieve a steady-state solution or return to zero are both increased (see Fig. 18). These findings are in agreement with classical transport theory.

For the range of the parameters selected for the sensitivity analyses reported in this study, the following parameters have the greatest effect on the downstream solute concentrations: separation distance, retardation coefficient, and average linear velocity of the groundwater. Parameters of secondary significance are the amplitude of the perturbation and its duration. The least significant parameter is the system's dispersion coefficient. Since the separation distance from the quarry to the point of interest is precisely known, it will have no effect on the uncertainty of the predicted concentrations. While uncertainty in the retardation coefficient for the solute can have a very significant effect on uncertainties in the predicted downstream solute concentrations, the effects can be minimized by assuming the most conservative value for K_d, i.e., $K_d = 0$ (R = 1). When R = 1, downstream concentration values are maximized and breakthrough times are minimized.

For a given separation distance and a conservative value for K_d, the greatest uncertainties in the concentration calculations are produced by uncertainties in the average groundwater velocity and the amplitude and duration of the source perturbation. For cleanup times less than about two years, a source perturbation

amplitude of 50%, and a groundwater velocity of 300 ft/yr, the maximum change in C/C_0 between the stepped and constant sources is less than about 5% (Fig. 14) at the well field (X = 2,500 ft). This difference, as discussed above, is a conservative value for the model due to an assumed retardation coefficient of zero. Even small values of K_d can further reduce the maximum change.

While the above sensitivity study is valid for the assumed model, field values may be different. Differences can arise from any of the simplifying assumptions made to develop an analytic solution to the advection-dispersion transport equation. These include effects due to a multidimensional, heterogeneous, and anisotropic flow system; use of an equivalent porous medium model; effects caused by the Femme Osage Slough and pumping at the municipal well field; and the shape of the time-dependent source at the quarry. Investigation of these effects will require use of a more complex numerical model and additional field work for model validation.

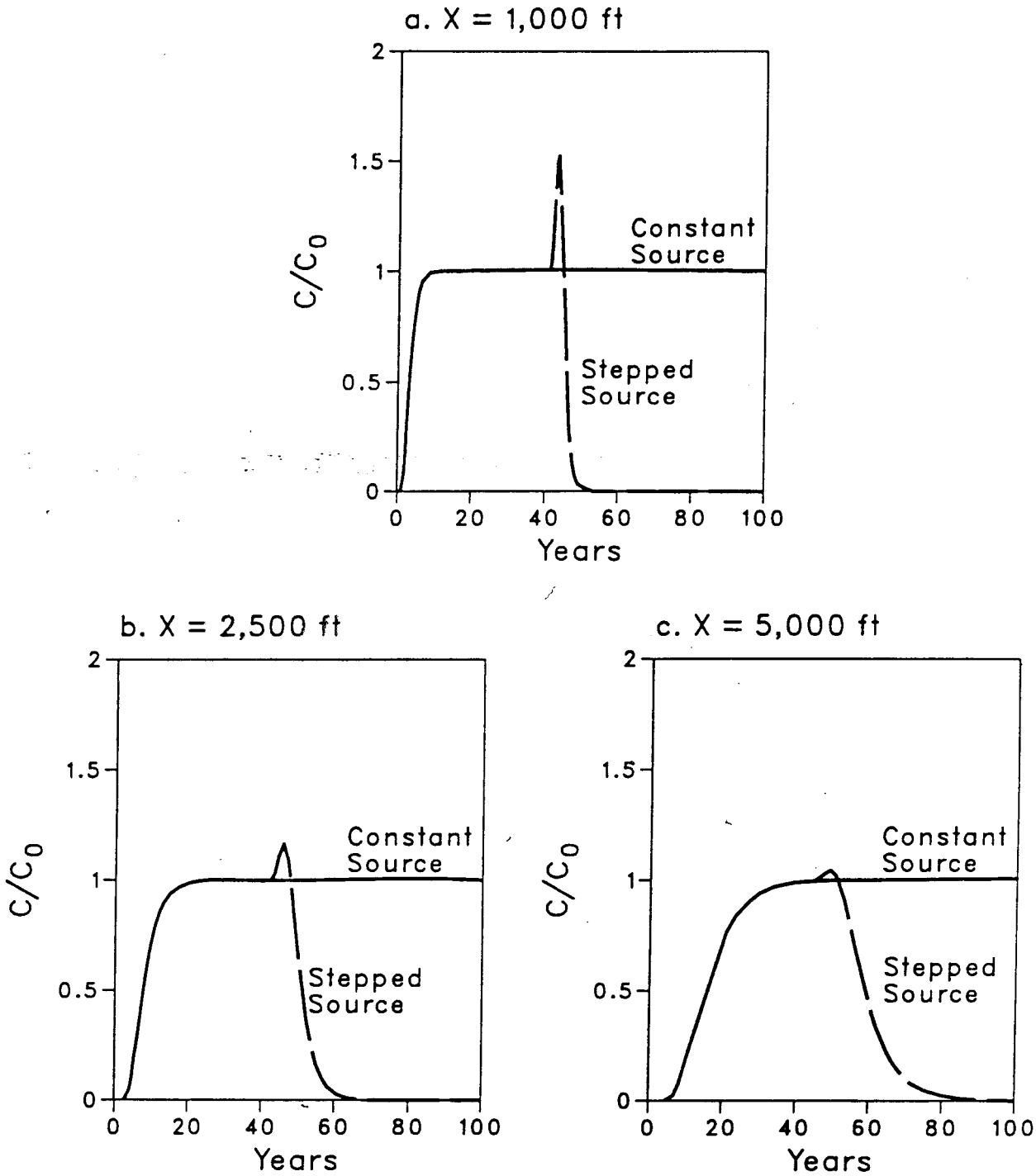

FIGURE 8 Solute Concentration as Function of Time for Various Separation Distances: (a) 1,000 ft, (b) 2,500 ft, and (c) 5,000 ft (V = 300 ft/yr, D = 3 x 10^4 ft^2/yr, b = 100%, Δt_1 = 40 yr, Δt_2 = 2 yr, and R = 1)

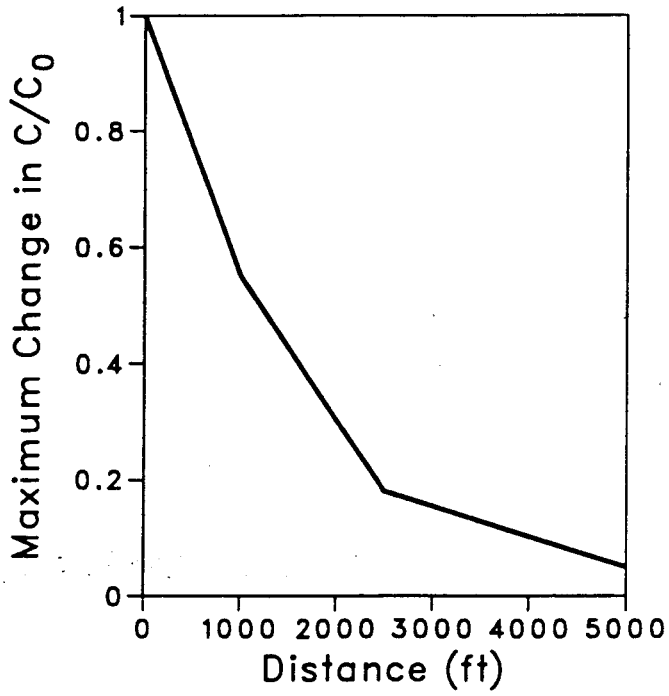

FIGURE 9 Maximum Change in C/C_0 as a Function of Distance from the Quarry

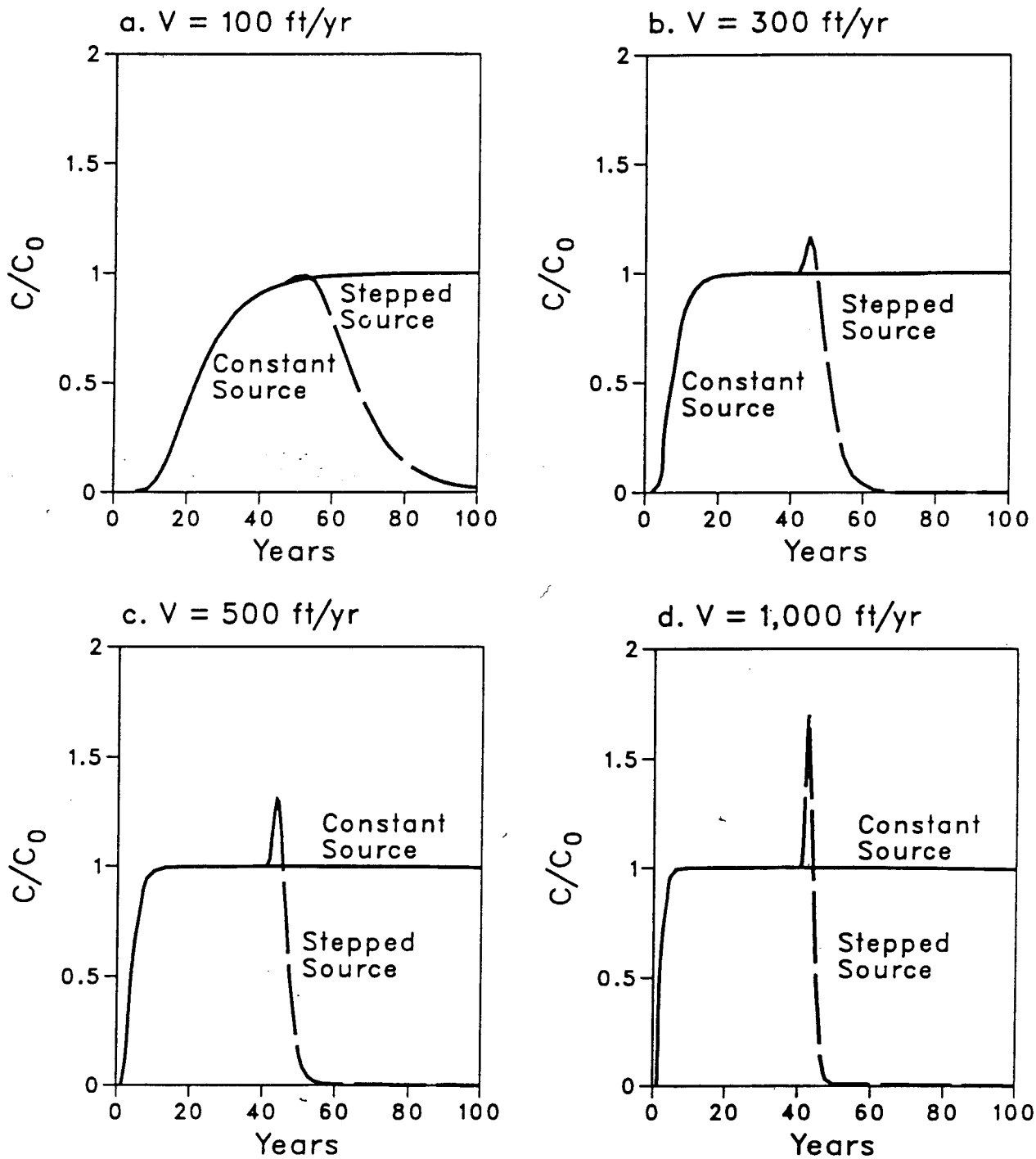

FIGURE 10 Solute Concentration as a Function of Time for Various Groundwater Velocities: (a) 100 ft/yr, (b) 300 ft/yr, (c) 500 ft/yr, and (d) 1,000 ft/yr ($X = 2{,}500$ ft, $D = 2.5 \times 10^4$ ft^2/yr, $b = 100\%$, $\Delta t_1 = 40$ yr, $\Delta t_2 = 2$ yr, and $R = 1$)

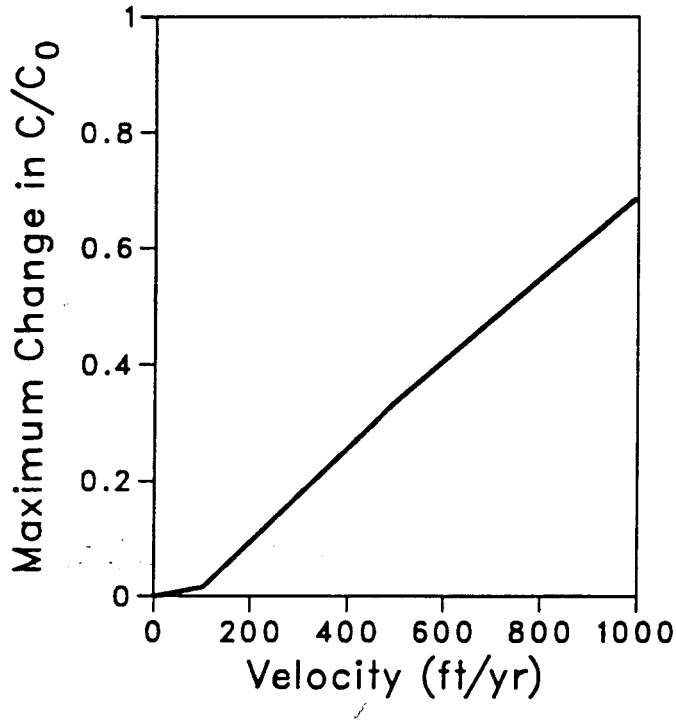

FIGURE 11 Maximum Change in C/C_0 as a Function of the Average Linear Groundwater Velocity at X = 2,500 ft

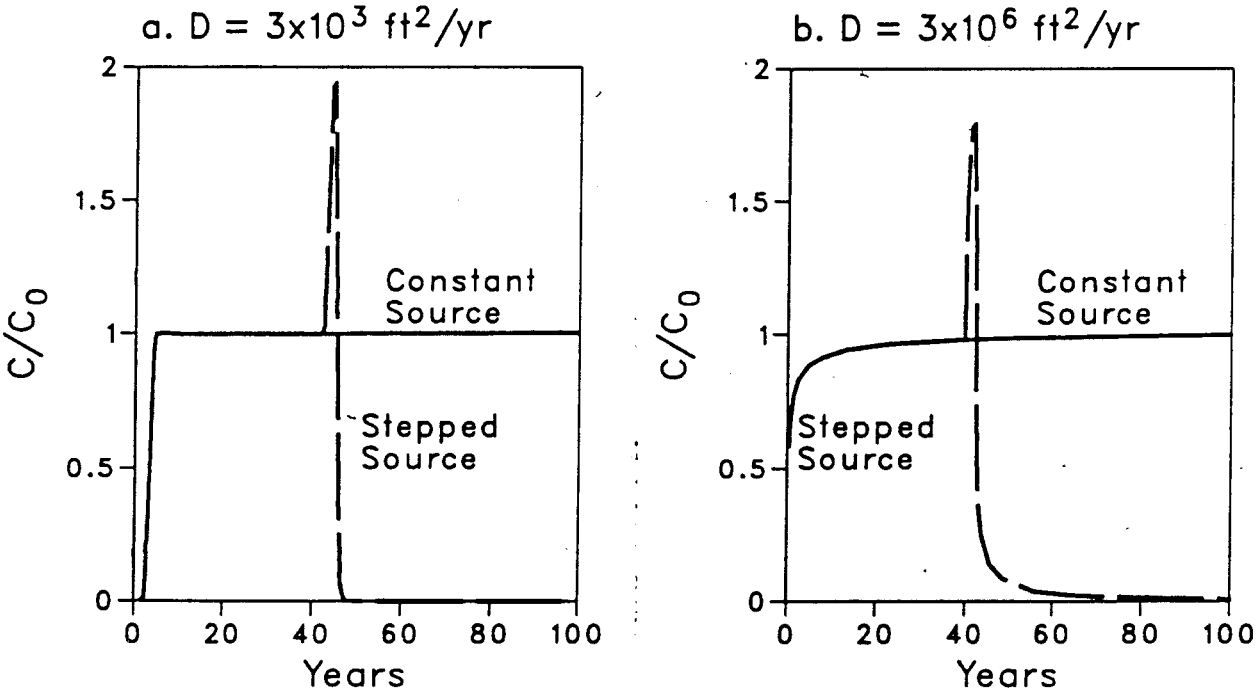

FIGURE 12 Solute Concentration as a Function of Time for Different Dispersion Coefficients: (a) 3 x 10^3 ft^2/yr and (b) 3 x 10^6 ft^2/yr (X = 1,000 ft, V = 300 ft/yr, b = 100%, Δt_1 = 40 yr, Δt_2 = 2 yr, and R = 1)

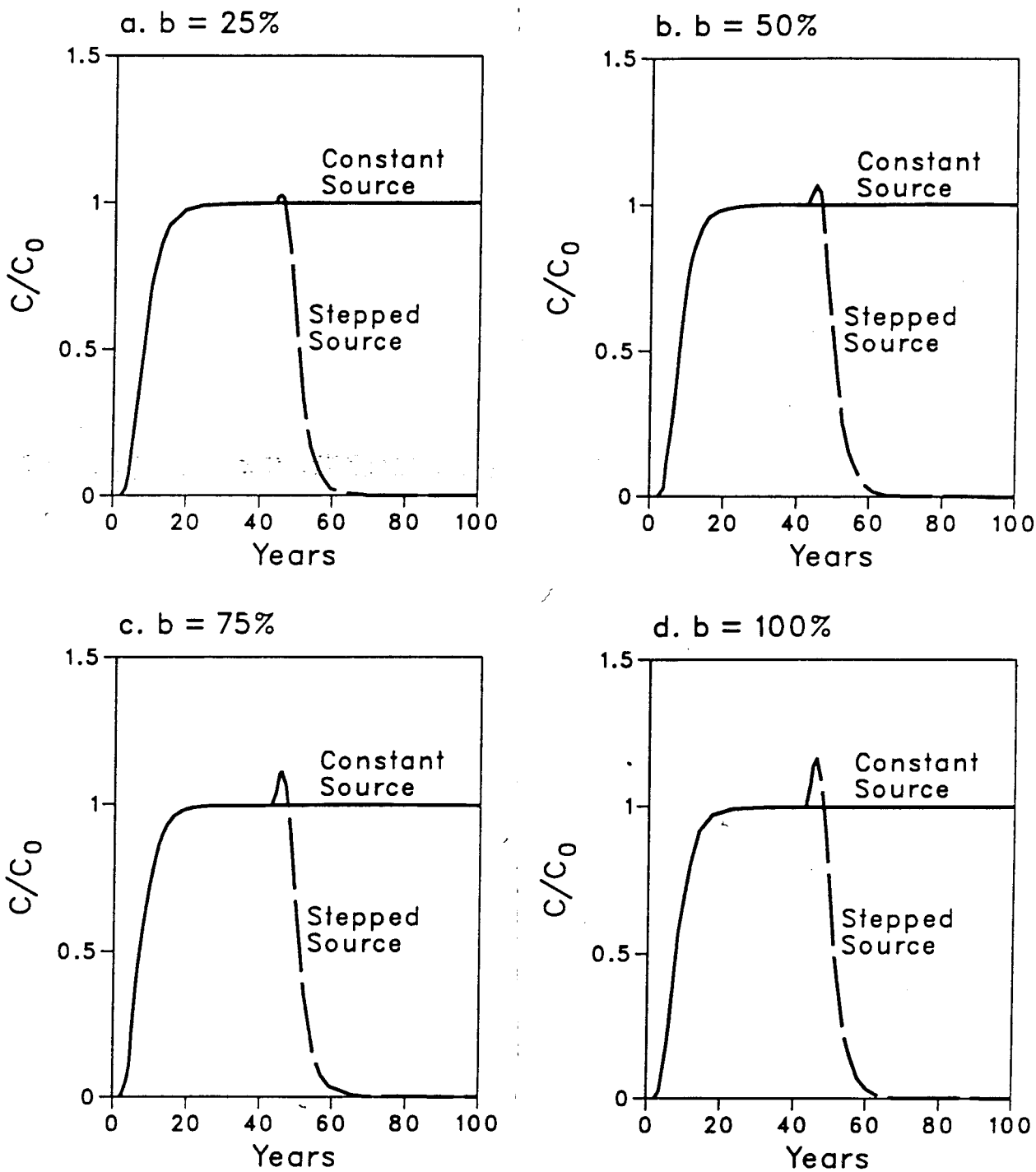

FIGURE 13 Solute Concentration as a Function of Time for Various Perturbation Amplitudes: (a) 25%, (b) 50%, (c) 75%, and (d) 100% (X = 2,500 ft, V = 300 ft/yr, D = 7.5 x 10^4 ft^2/yr, Δt_1 = 40 yr, Δt_2 = 2 yr, and R = 1)

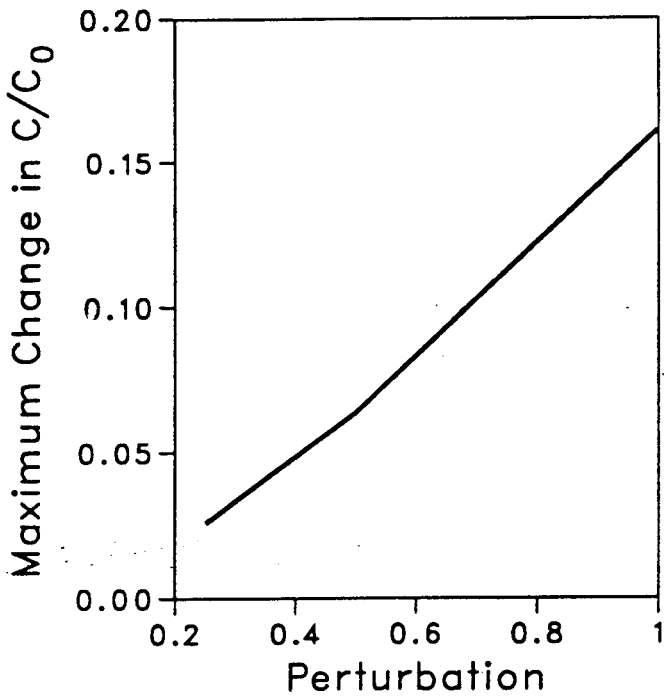

FIGURE 14 Maximum Change in C/C_0 as a Function of the Amplitude of the Source Perturbation at X = 2,500 ft

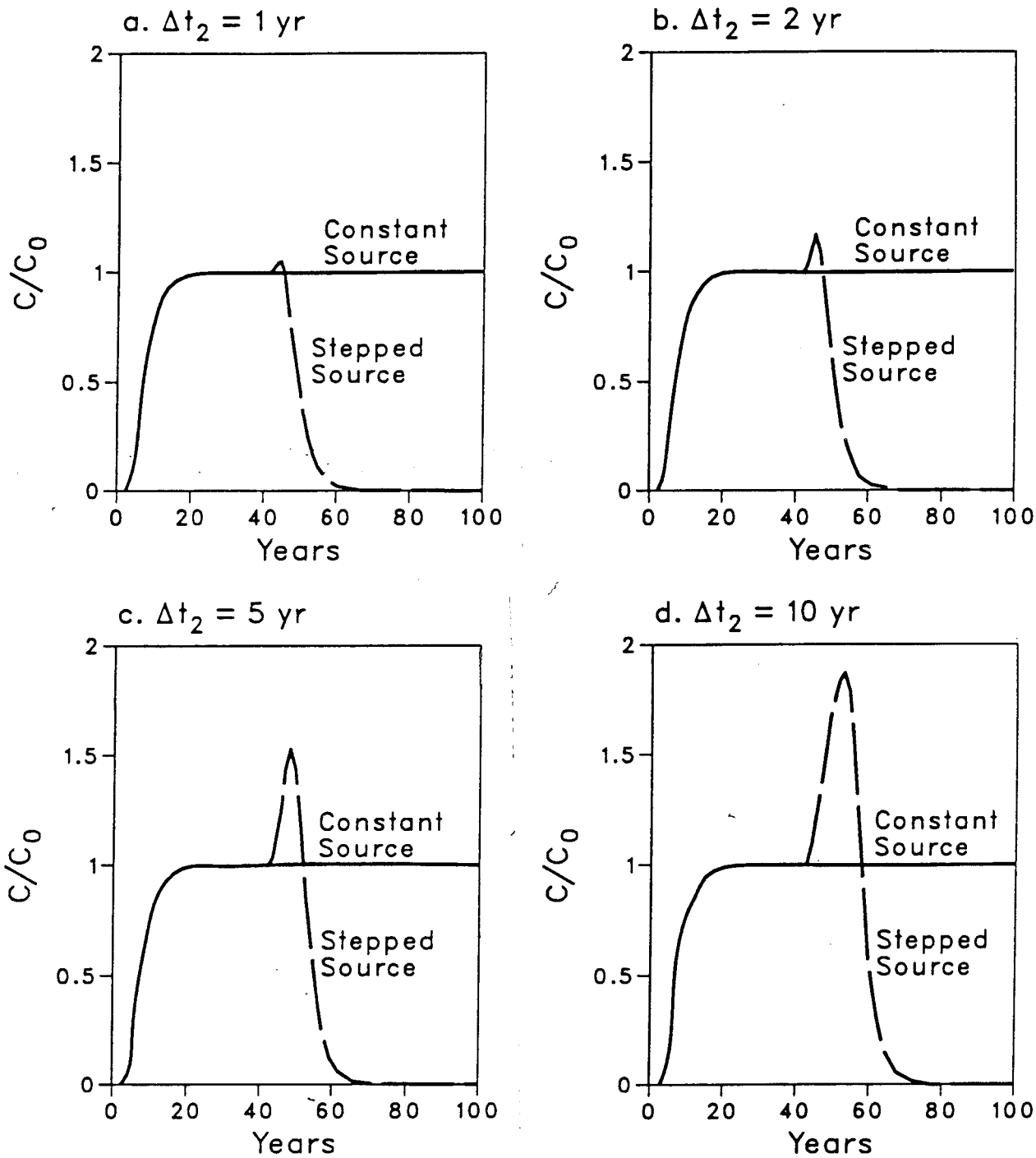

FIGURE 15 Solute Concentration as a Function of Time for Various Cleanup Durations: (a) 1 yr, (b) 2 yr, (c) 5 yr, and (d) 10 yr (X = 2,500 ft, V = 300 ft/yr, D = 7.5 x 10^4 ft^2/yr, b = 100%, Δt_1 = 40 yr, and R = 1)

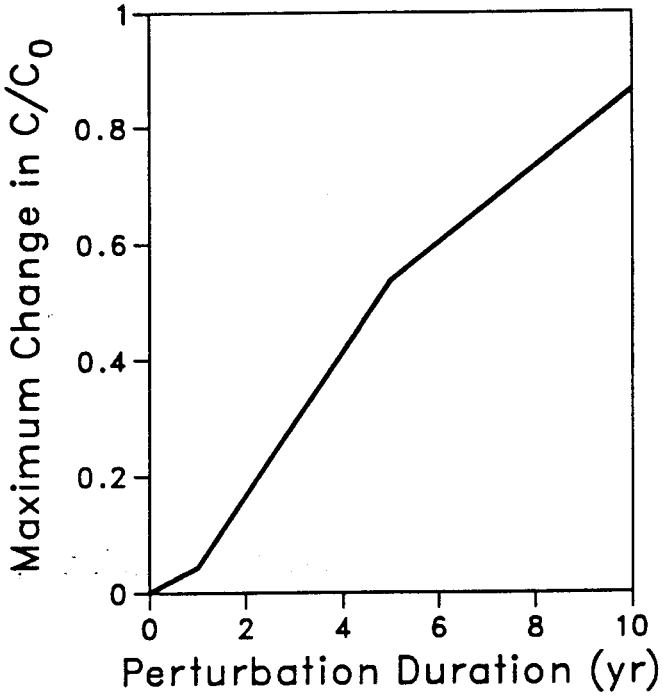

FIGURE 16 Maximum Change in C/C_0 as a Function of the Duration of the Source Perturbation at X = 2,500 ft

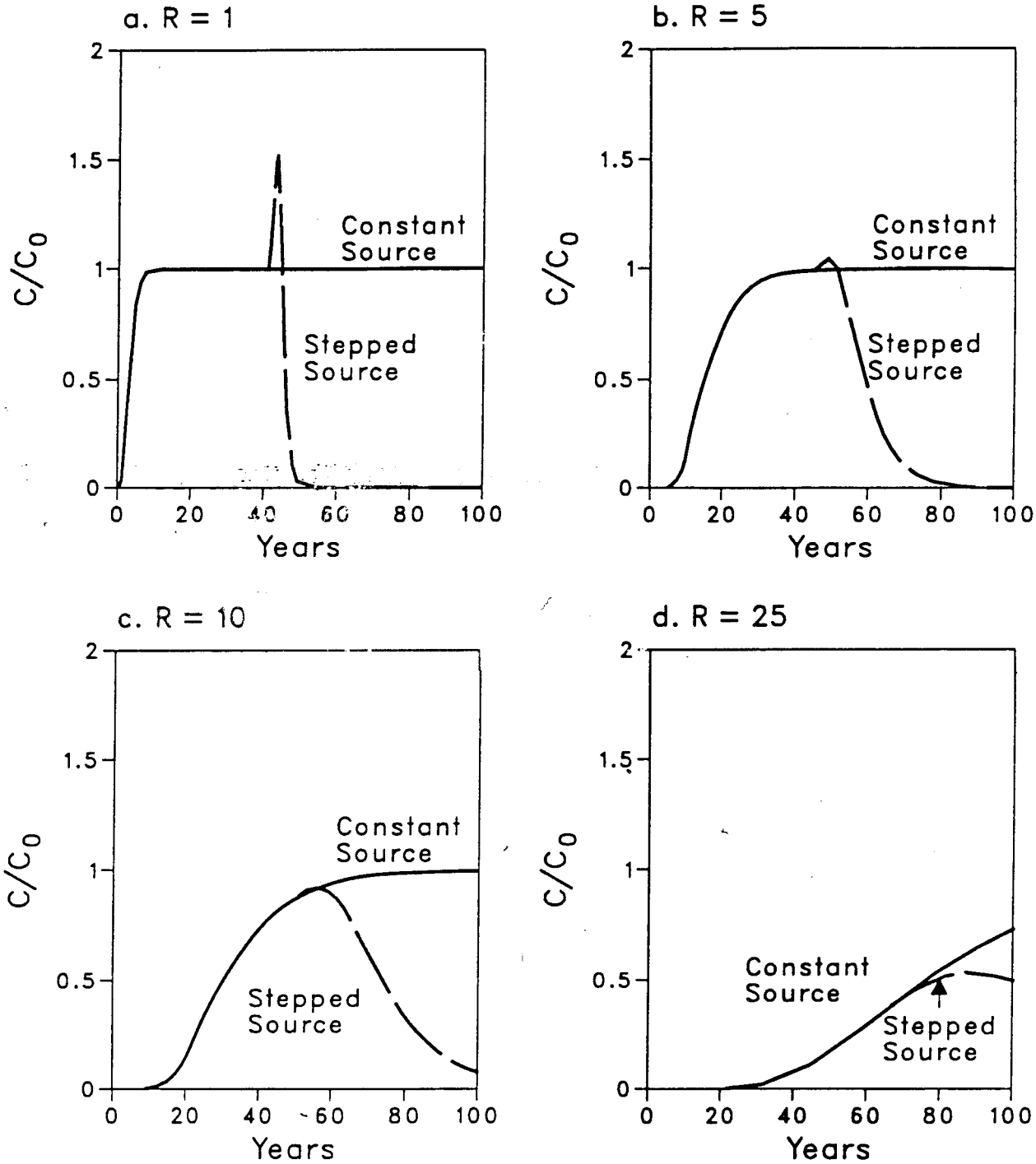

FIGURE 17 Solute Concentration as a Function of Time for Various Retardation Factors: (a) 1, (b) 5, (c) 10, and (d) R = 25 (X = 1,000 ft, V = 300 ft/yr, D = 3 x 10^4 ft^2/yr, b = 100%, Δt_1 = 40 yr, and Δt_2 = 2 yr)

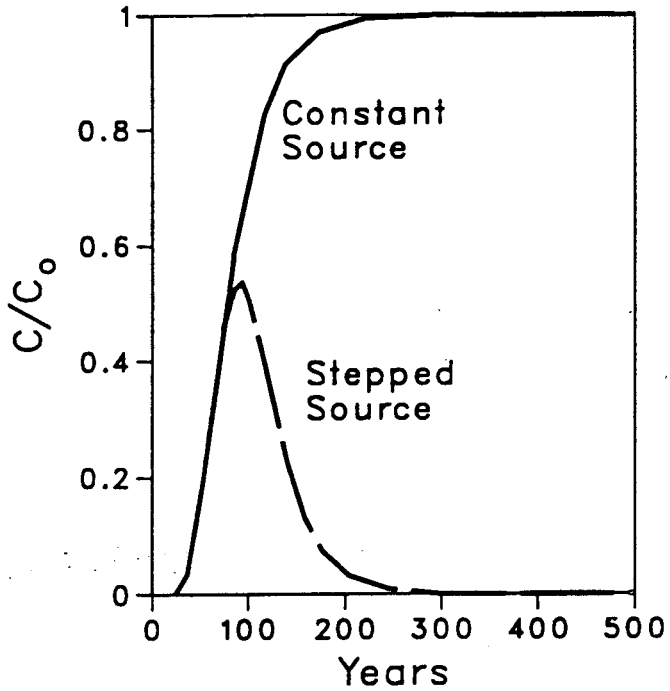

FIGURE 18 Solute Concentration as a Function of Time for 500 yr at Maximum Retardation (R = 25)

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