

AN ABSTRACT OF THE THESIS OF

Tracy D. Cork for the degree of Master of Science in Civil Engineering presented on February 26, 1988.

Title: The Fate of Hydrophobic Organic Compounds in Soil Systems: A Kinetic Model and Sensitivity Analysis.

Abstract  
Approved:

Redacted for Privacy

---

Sandra Woods

A mathematical model was developed using finite difference numerical techniques to examine the effects of kinetic parameters on the fate of hydrophobic organic compounds in soil systems. The model included advection; dispersion; bacterial metabolism; and sorption and desorption to soil solids and bacteria, and degradation by bacteria. The most important processes governing the eventual fate of organic compounds were surface sorption and degradation by soil bacteria. It was concluded that future research should be focused in these areas.

The Fate of Hydrophobic Organic Compounds  
In Soil Systems:  
A Kinetic Model and Sensitivity Analysis

by

Tracy D. Cork

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Master of Science

Completed February 26, 1988

Commencement June 1988

APPROVED:

Redacted for Privacy

---

Professor of Civil Engineering in charge of major

Redacted for Privacy

---

Head of Department of Civil Engineering

Redacted for Privacy

---

Dean of Graduate School

Date thesis is presented: February 26, 1988

## TABLE OF CONTENTS

INTRODUCTION AND OBJECTIVES	1
LITERATURE REVIEW AND THEORETICAL CONSIDERATIONS	3
SORPTION	3
BIODEGRADATION	5
MODEL DEVELOPMENT	7
TRANSPORT DUE TO ADVECTION	10
TRANSPORT DUE TO DISPERSION	10
TRANSPORT DUE TO SORPTION	14
LOSSES DUE TO BACTERIAL METABOLISM	19
RESULTS AND DISCUSSION	22
DISPERSION COEFFICIENTS AND SEEPAGE VELOCITIES	22
BATCH SYSTEM RESULTS	25
COLUMN BASE RUN WITH SORPTION AND DISPERSION	27
SURFACE SORPTION PHENOMENA ( $K_1$ , $K_2$ , AND $S_{smax}$ )	37
SOLID INTERIOR SORPTION PHENOMENA ( $K_3$ , $K_4$ , and $S_{imax}$ )	55
ANALYSIS OF THE BACTERIAL PHASE	73
BACTERIAL PHASE SORPTION AND DEGRADATION ( $K_5$ , $K_6$ , $K_b$ , AND $B_{smax}$ )	73
MONOD DEGRADATION FROM THE LIQUID PHASE ( $K_m$ AND $K_s$ )	85

SUMMARY	93
BIODEGRADATION	94
SORPTION TO SOIL SOLIDS	95
CONCLUSIONS	99
BIBLIOGRAPHY	101
APPENDIX	103

## LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
Figure 1.	Schematic of the soil column as treated using the finite difference approach.	8
Figure 2.	Schematic of the dispersion process as treated by the finite difference approach.	12
Figure 3.	Schematic representation of the soil sorption process.	15
Figure 4.	Soil column liquid concentration profile for Case 1 at several times showing the effect of combined advection and dispersion.	23
Figure 5.	Pollutant mass in the liquid ( $M_l$ ), solid surface ( $M_s$ ) and solid interior ( $M_i$ ) phases as a function of time under Case 2 conditions for a batch system.	26
Figure 6.	Soil column profile at time equals hours showing liquid, solid surface, and solid interior pollutant mass distributions.	31
Figure 7.	Soil column profile at time equals 10 hours showing liquid, solid surface, and solid interior pollutant mass distributions.	32
Figure 8.	Soil column profile at time equals 25 hours showing liquid, solid surface, and solid interior pollutant mass distributions.	33
Figure 9.	Soil column profile at time equals 50 hours showing liquid, solid surface, and solid interior pollutant mass distributions.	34

Figure 10.	Soil column profile at time equals 1,000 hours showing liquid, solid surface, and solid interior pollutant mass distributions.	35
Figure 11.	Soil column profile at time equals 10,000 hours showing liquid, solid surface, and solid interior pollutant mass distributions.	36
Figure 12.	Liquid phase profile at time equals 5 hours varying $K_1$ or $S_{smax}$ over three orders of magnitude while maintaining the remaining Case 2 parameters.	42
Figure 13.	Liquid phase profile at time equals 50 hours varying $K_1$ or $S_{smax}$ over three orders of magnitude while maintaining the remaining Case 2 parameters.	43
Figure 14.	Solid surface phase profile at time equals 5 hours varying $K_1$ or $S_{smax}$ over three orders of magnitude while maintaining the remaining Case 2 parameters.	44
Figure 15.	Solid surface phase profile at time equals 50 hours varying $K_1$ or $S_{smax}$ over three orders of magnitude while maintaining the remaining Case 2 parameters.	45
Figure 16.	Solid interior phase profile at time equals 5 hours varying $K_1$ or $S_{smax}$ over three orders of magnitude while maintaining the remaining Case 2 parameters.	46
Figure 17.	Solid interior phase profile at time equals 50 hours varying $K_1$ or $S_{smax}$ over three orders of magnitude while maintaining the remaining Case 2 parameters.	47
Figure 18.	Liquid phase profile at time equals 5 hours varying $K_2$ while maintaining the remaining Case 2 parameters.	48

Figure 19.	Liquid phase profile at time equals 25 hours varying K2 while maintaining the remaining Case 2 parameters.	49
Figure 20.	Solid surface phase profile at time equals 50 hours varying K2 while maintaining the remaining Case 2 parameters.	50
Figure 21.	Solid interior phase profile at time equals 50 hours varying K2 while maintaining the remaining Case 2 parameters.	51
Figure 22.	Liquid phase profile at time equals 500 hours varying K2 while maintaining the remaining Case 2 parameters.	52
Figure 23.	Solid surface phase profile at time equals 500 hours varying K2 while maintaining the remaining Case 2 parameters.	53
Figure 24.	Solid interior phase profile at time equals 500 hours varying K2 while maintaining the remaining Case 2 parameters.	54
Figure 25.	Liquid phase profile at time equals 25 hours varying K3 while maintaining the remaining Case 2 parameters.	59
Figure 26.	Liquid phase profile at time equals 50 hours varying K3 while maintaining the remaining Case 2 parameters.	60
Figure 27.	Solid surface phase profile at time equals 5 hours varying K3 while maintaining the remaining Case 2 parameters.	61
Figure 28.	Solid surface phase profile at time equals 50 hours varying K3 while maintaining the remaining Case 2 parameters.	62



Figure 29.	Solid interior phase profile at time equals 5 hours varying K3 while maintaining the remaining Case 2 parameters.	63
Figure 30.	Solid interior phase profile at time equals 50 hours varying K3 while maintaining the remaining Case 2 parameters.	64
Figure 31.	Liquid phase profile at time equals 25 hours varying K4 while maintaining the remaining Case 2 parameters.	65
Figure 32.	Liquid phase profile at time equals 50 hours varying K4 while maintaining the remaining Case 2 parameters.	66
Figure 33.	Liquid phase profile at time equals 500 hours varying K4 while maintaining the remaining Case 2 parameters.	67
Figure 34.	Solid surface phase profile at time equals 50 hours varying K4 while maintaining the remaining Case 2 parameters.	68
Figure 35.	Solid surface phase profile at time equals 500 hours varying K4 while maintaining the remaining Case 2 parameters.	69
Figure 36.	Solid interior phase profile at time equals 5 hours varying K4 while maintaining the remaining Case 2 parameters.	70
Figure 37.	Solid interior phase profile at time equals 50 hours varying K4 while maintaining the remaining Case 2 parameters.	71
Figure 38.	Solid interior phase profile at time equals 500 hours varying K4 while maintaining the remaining Case 2 parameters.	72

- Figure 39. Liquid phase profile at time equals 5 hours for advection, dispersion, sorption to soil solids, sorption to bacterial solids (described by  $K_5$  and  $K_6$ ) and biodegradation (described by  $K_b$ ). The Case 2 curve describes advection, dispersion and sorption to soil solids. The remaining curves reflect changes to a single variable ( $K_b$  or  $K_6$ ) from the parameters described for Case 4. 76
- Figure 40. Liquid phase profile at time equals 10 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters. 77
- Figure 41. Liquid phase profile at time equals 25 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters. 78
- Figure 42. Soil bacterial phase profile at time equals 5 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters. 79
- Figure 43. Soil bacterial phase profile at time equals 10 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters. 80
- Figure 44. Soil bacterial phase profile at time equals 25 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters. 81
- Figure 45. Soil bacterial phase profile at time equals 50 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters. 82
- Figure 46. Solid surface phase profile at time equals 50 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters. 83
- Figure 47. Solid interior phase profile at time equals 50 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters. 84

Figure 48.	Liquid phase profile at 5 hours varying $K_m$ and the solids concentration (S) while maintaining the remaining Case 5 parameters.	88
Figure 49.	Liquid phase profile at 10 hours varying $K_m$ and the solids concentration (S) while maintaining the remaining Case 5 parameters.	89
Figure 50.	Liquid phase profile at 50 hours varying $K_m$ and the solids concentration (S) while maintaining the remaining Case 5 parameters.	90
Figure 51.	Solid surface phase profile at 10 hours varying $K_m$ and the solids concentration (S) while maintaining the remaining Case 5 parameters.	91
Figure 52.	Solid interior phase profile at 10 hours varying $K_m$ and the solids concentration (S) while maintaining the remaining Case 5 parameters.	92

## LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
Table 1	Base parameter values for cases 1 through 5.	28
Table 2	Relative effect of kinetic sorption and degradation constants on pollutant fate in soil systems.	98

## LIST OF SYMBOLS

$C_l$	=	liquid phase concentration in moles/cm <sup>3</sup> liquid
$n$	=	the cell number
$T$	=	time in hours
$dT$	=	time increment in hours
$A$	=	cross sectional area of cell in cm <sup>2</sup>
$dX$	=	cell length increment in cm
$p$	=	soil porosity in cm <sup>3</sup> liquid per cm <sup>3</sup> total
$T_a$	=	transport of pollutant due to advection in moles
$u$	=	seepage velocity through the pore water in cm per hour
$D_p$	=	numerical mixing correction factor in cm <sup>3</sup> liquid per cm per hour
$T_d$	=	transport due to dispersion over one time increment in moles
$w$	=	liquid volume of water exchanged by dispersion in cm <sup>3</sup> liquid
$D$	=	dispersion coefficient in cm <sup>3</sup> liquid per cm per hour
$S_s$	=	solid surface phase available sites in mole surface sites per gram solids
$C_s$	=	pollutant bound with solid surface in mole per gram solids
$K_1$	=	forward surface sorption constant in gram solids per mole sites per hour
$K_2$	=	reverse surface desorption constant in gram solids cm <sup>3</sup> liquid per hour
$S_i$	=	solid interior phase available sites in mole interior sites per gram solids

$C_i$  = pollutant bound with solid interior in mole per gram solids  
 $K_3$  = forward surface to interior partition rate constant in gram solids per mole sites per hour  
 $K_4$  = reverse interior to surface partition rate constant in 1/hr  
 $B_s$  = bacterial phase available sites in mole bacterial sites per gram bacteria  
 $C_b$  = pollutant bound with bacterial phase in mole per gram bacteria  
 $K_5$  = forward bacterial sorption constant in gram bacteria per mole sites per hour  
 $K_6$  = reverse bacterial desorption constant in gram bacteria per  $\text{cm}^3$  liquid per hour  
 $T_{ss}$  = transport due to surface sorption and desorption in moles  
 $T_b$  = transport due to bacterial sorption and desorption in moles  
 $S_{smax}$  = maximum available surface sites on sorbate in mole sites per gram solids  
 $S_{imax}$  = maximum available interior sites in sorbate in mole sites per gram solids  
 $B_{smax}$  = maximum available sites on bacteria in mole sites per gram bacteria  
 $S$  = solids concentration in grams solids per  $\text{cm}^3$  total  
 $B$  = bacteria concentration in grams bacteria per  $\text{cm}^3$  total  
 $R_{su}$  = substrate utilization rate in moles  $\text{cm}^3$  liquid per hour  
 $K_m$  = maximum substrate utilization rate constant in moles per gram bacteria per hour  
 $K_s$  = half velocity constant in moles per  $\text{cm}^3$  liquid

T<sub>bm</sub> = transport due to degradation from bacterial phase in moles

K<sub>b</sub> = first order rate constant in moles degraded per mole present per hour

The Fate of Hydrophobic Organic Compounds  
in Soil Systems:  
A Kinetic Model and Sensitivity Analysis

INTRODUCTION AND OBJECTIVES

The environmental fate of toxic hydrophobic organic chemicals in soil systems has recently received increasing attention. In attempts at both greater understanding and prediction, researchers have developed mathematical models of this complex process. Presently, several models are available to predict the fate of toxic compounds in soil systems using a wide variety of assumptions [1,2].

One of the most common assumptions is that local equilibrium exists between the aqueous and solid phases. In some cases this assumption may be valid and reasonable; however, recent research has shown that the equilibrium assumption may be valid only over a limited range of certain parameters such as pore flow velocity and the sorption coefficients of various chemicals.

Another important factor often neglected in soil system models is bacterial degradation and sorption to bacteria. Most often these sinks are considered as separate problems and are not incorporated in sorption models because so little is known about degradation in natural soil systems. The process of bacterial



sorption and degradation are often difficult to separate from one another in natural systems and the disappearance of a compound may be due to either or both mechanisms.

The purpose of this research was to develop a mathematical computer model to study the fate of organic pollutants in natural soil systems. The model considers the kinetic processes of sorption and desorption to soil solids, sorption and desorption to bacteria in the soil, and bacterial degradation of a model compound. The specific objectives were:

1. To develop a kinetic model for the analysis of the environmental fate of organic compounds in soil systems that includes sorption and desorption to soil and bacteria, bacterial degradation, advective transport and diffusion of a model compound;
2. To perform a sensitivity analysis of the kinetic parameters considered in the model and identify the most critical mechanisms controlling fate and transport; and
3. To recommend areas for future research to quantify parameters identified as most important.

## LITERATURE REVIEW AND THEORETICAL CONSIDERATIONS

This study considers several facets of fate and transport modeling of hydrophobic pollutants using finite-difference techniques [4]. The mathematical development of the model is given in the following section.

The following phenomena occurring in natural soil systems are considered in this model:

1. Advection of the pollutant through the soil column;
2. Diffusion of the pollutant due to turbulent mixing in the column;
3. Reversible and latent sorption to the soil;
4. Reversible sorption to bacteria present in the soil;
5. Bacterial degradation from the liquid phase; and
6. Bacterial degradation from that fraction sorbed to the bacteria.

### SORPTION

Significant work in the area of modeling in soil systems has been done by many researchers. Gschwend [1] described some typical approaches to kinetic modeling of sorption and also developed an alternative approach based on diffusion of the sorbate into the interior of the sorbent. One-box and two-box models similar to the those described by Gschwend were used in this treatment due to their simplicity and

conceptual representation of the sorption process. The development of these models are described in the following section. The diffusion approach used by Gschwend is capable of reducing the number of parameters required to fit experimental data; however, its application to flow-through systems is extremely difficult to implement using the techniques employed in this model.

Several researchers have reported what has been termed a "solids effect" at high solids concentrations. This effect leads to reduced values of the equilibrium partition coefficient as the solids concentration increases. This phenomena raises questions about the application of constants determined in the laboratory to natural soil systems. Theories explaining this observed solids effect include increased particle interaction at high solids concentrations [12], and the presence of "micro particles" that may influence partition coefficients [13].

As an example of this phenomena, Dolan [11] observed a time dependant solids effect in experiments using 2,4-dichlorophenol and cellulose triacetate as the sorbate in batch tests. However, he found that at longer time periods, the chemical and the sorbate approached a "true" equilibrium condition. The kinetic equations used to describe the sorption

process in this work are identical to those used by Dolan to fit his experimental results.

An excellent review of recent sorption models is given by Valocchi [3] in which he described the conditions under which local equilibrium assumptions are valid. Valocchi discussed two important assumptions often used in kinetic models: physical and chemical nonequilibrium. In the physical nonequilibrium approach, modelers assume that the liquid inside the porous media is stagnant. This separates the liquid phase into a mobile phase and an immobile stagnant phase. Sorption occurs in both phases, but at different rates related to the seepage velocity and several other factors. In the chemical nonequilibrium approach, no distinction is made between the mobile and stagnant liquid regions and first order sorption processes are usually assumed. The model used for this study is of the chemical nonequilibrium type and considers reversible and latent sorption to soil [5].

#### BIODEGRADATION

Metabolism of potentially hazardous compounds has been observed by several researchers. McCarty [6] observed biodegradation of simple nonbranched chlorinated aliphatic organic compounds during rapid infiltration of secondary wastewater to soil.

Degradation of chlorinated nitrobenzenes [7], chlorinated phenols [8], and several other organic compounds have also been documented.

The mechanisms behind the processes remain controversial. Traditionally, degradation is assumed to take place from the liquid phase according to Monod or first-order kinetics [9]. The presence of high solid concentrations and significant fractions of the compound bound to the soil and bacterial solids may affect availability of the pollutant as compared to an aqueous phase solution. For this reason the model considers both Monod degradation from the liquid phase and first order degradation from the fraction of the pollutant sorbed to bacteria.

MODEL DEVELOPMENT

The technique and assumptions used to model the flow, sorption, and bacterial processes in a soil system are described below. The technique uses the concept of mass balance on a finite cell volume over a discrete time interval. A schematic of a model soil column that helps to visualize the modeling process is shown in Figure 1. The mass balance equation can be described as:

$$\begin{array}{l}
 \text{The mass of} \\
 \text{pollutant in cell} \\
 \text{n at the end} \\
 \text{of the time} \\
 \text{increment}
 \end{array}
 =
 \begin{array}{l}
 \text{The mass in} \\
 \text{cell n at} \\
 \text{the beginning} \\
 \text{of the time} \\
 \text{increment}
 \end{array}
 +
 \begin{array}{l}
 \text{The net mass} \\
 \text{transport into cell n} \\
 \text{over the time} \\
 \text{increment}
 \end{array}
 \quad (1)$$

The cell length and cross sectional area are represented by  $dx$  and  $A$  and are assumed to be constant over the length of the column. The liquid concentration in cell  $n$  at time  $T$ ,  $C_l(n,T)$ , and at  $T + dT$ ,  $C_l(n,T+dT)$ , are:

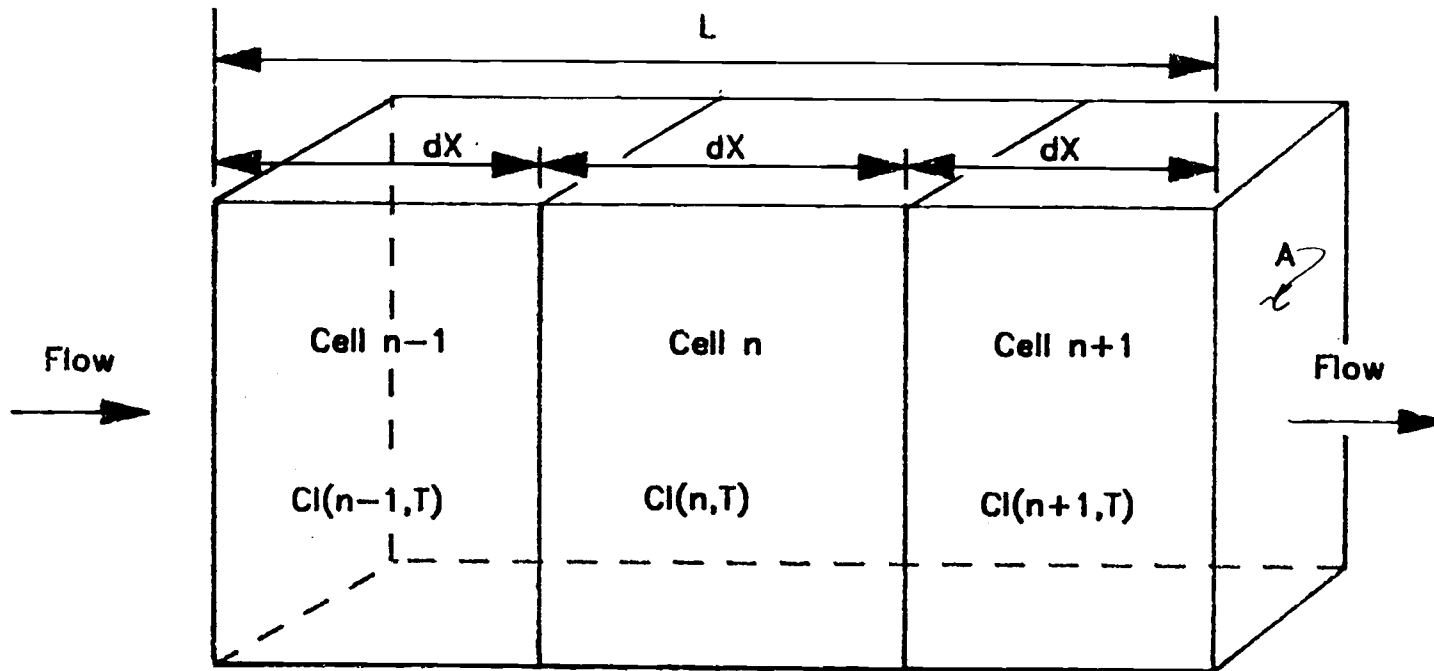


Figure 1. Schematic of the soil column as treated using the finite difference approach.

$$C_l(n, T+dT) A \, dX \, p = C_l(n, T) A \, dX \, p + \text{the net transport of pollutant into cell } n \text{ over } dT. \quad (2)$$

where:

$C_l$  = liquid phase concentration in moles/cm<sup>3</sup> liquid,  
 $n$  = the cell number,  
 $T$  = time in hours,  
 $dT$  = time increment in hours,  
 $A$  = cross sectional area of cell in cm<sup>2</sup>,  
 $dX$  = cell length increment in cm, and  
 $p$  = soil porosity in cm<sup>3</sup> liquid per cm<sup>3</sup> total.

The transport term in Equation 2 is due to; 1) the flow through the cell due to percolation, 2) dispersion due to turbulent mixing, 3) sorption and desorption to and from the solid and bacterial phase, and 5) bacterial degradation. Thus:

$$C_l(T+dT) A \, dX \, p = C_l(n, T) A \, dX \, p + T_a + T_d + T_{ss} + T_b + T_{bm} \quad (3)$$

where:

$T_a$  = transport of pollutant due to advection in moles,  
 $T_d$  = transport due to dispersion over one time increment in moles,  
 $T_{ss}$  = transport due to surface sorption and desorption in moles,  
 $T_b$  = transport due to bacterial sorption and desorption in moles,  
 $T_{bm}$  = transport due to metabolism from the bacterial phase in moles.



### TRANSPORT DUE TO ADVECTION

Flow or advection through the interstitial pore water is assumed to be at a constant seepage velocity through a fully saturated column with negligible headwater over the column. The transport of pollutant due to advection through the cell is represented as:

$$T_a = u A p dT [C_l(n-1,T) - C_l(n,T)] \quad (4)$$

where:

$u$  = seepage velocity through the pore water in cm total/hr.

Equation 4 is subject to certain restrictions. The volume of water transferred can not exceed the volume of the cell. This is represented by the expression:

$$u A dT p \leq A dX p \quad (5)$$

or,

$$u dT \leq dX \quad (6)$$

### TRANSPORT DUE TO DISPERSION

Another phenomena that must be addressed is a numerical mixing error when  $u * dT$  does not equal  $dX$ . This mathematical mixing can be used to model dispersion in the column but, for the sake of simplicity, dispersion is treated as a separate term in this formulation. A correction factor that

compensates for the numerical dispersion is applied to the desired dispersion coefficient. The correction factor is calculated as:

$$D_p = (u \cdot p / 2) / (dT u - dx) \quad (7)$$

where:

$$D_p = \text{Numerical mixing correction factor in cm}^3 \text{ liquid per cm total hour.}$$

The transport due to dispersion is one of the more complicated terms to derive. Figure 2 is used to help visualize the dispersion process for the following discussion.

At the beginning of the time increment, equal volumes of water,  $w$ , are exchanged between cells  $n$  and  $n+1$  and between cells  $n$  and  $n-1$ . Assuming all individual cells are completely mixed, the mass of pollutant leaving cell  $n$  during this exchange is:

$$w C_l(n, T) + w C_l(n, T).$$

The mass entering the cell  $n$  during the exchange is,

$$w C_l(n-1, T) + w C_l(n+1, T).$$

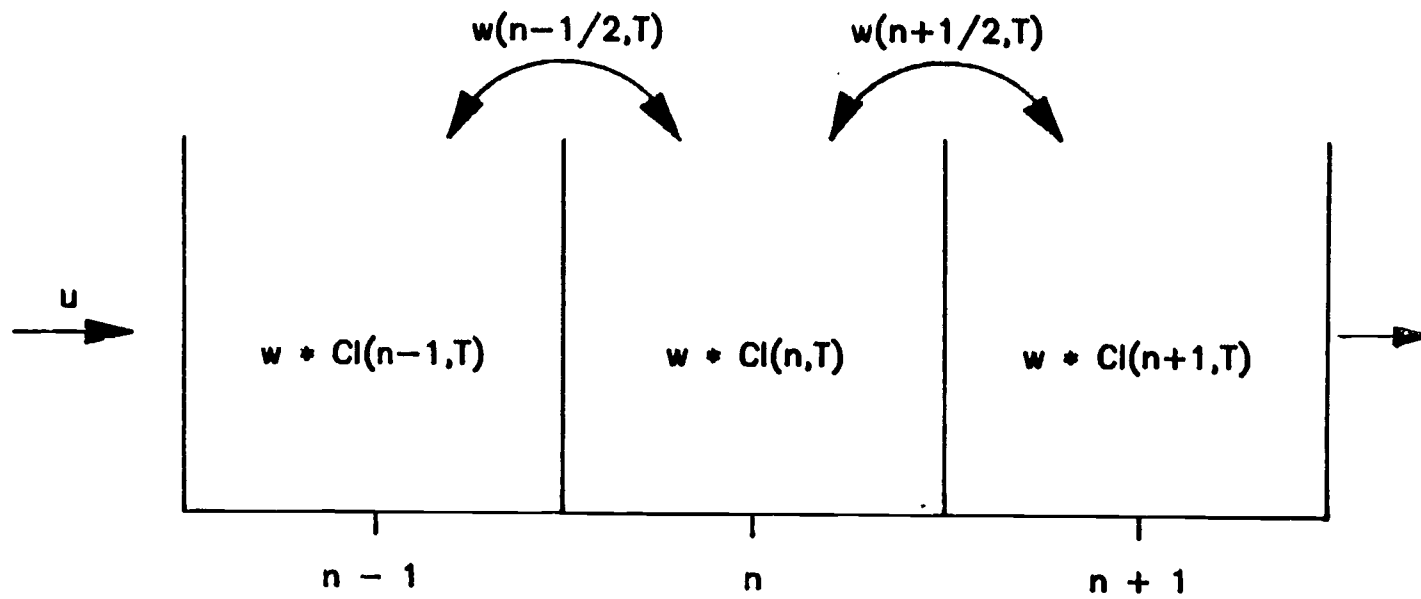


Figure 2. Schematic of the dispersion process as treated by the finite difference approach.

The mass transport of pollutant due to dispersion is the mass entering from cells  $n-1$  and  $n+1$  minus the mass leaving from cell  $n$ .

$$T_d = w [C_l(n-1, T) + C_l(n+1, T) - 2 C_l(n, T)] \quad (8)$$

where:

$w$  = volume of water exchanged by dispersion in  $\text{cm}^3$  liquid.

The dispersion coefficient,  $D$ , is the amount of water exchanged over a time increment.

$$D = w \, dX / A \, dT \quad (9)$$

where:

$D$  = dispersion coefficient in  $\text{cm}^3$  liquid per  $\text{cm}$  per hour.

Solving Equation 9 for  $w$  and substituting into equation 8, the transport due to dispersion over a time increment is equal to:

$$T_d = D \, A \, dT/dX \quad * [C_l(n-1, T) + C_l(n+1, T) - 2 C_l(n, T)] \quad (10)$$

The restriction on the dispersion equation is also fairly obvious. The total volume of water exchanged can not exceed the volume present in the cell.

$$2 w \leq A dx p \quad (11)$$

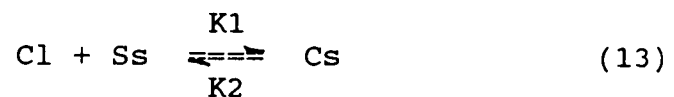
In terms of the dispersion coefficient,

$$D dT / dx^2 p \leq 1/2 \quad (12)$$

Equation 10 is subject to the restrictions given in Equations 11 and 12 is incorporated into the final transport equation used in the model.

#### TRANSPORT DUE TO SORPTION

The model for sorption to the solids in the soil can be represented as a two compartment model as shown in Figure 3 [1]. Sorption from the liquid phase to the solid surface phase is represented by a first order reversible chemical process is:



where:

- Ss = solid surface phase available sites in mole surface sites per gram solids,
- Cs = pollutant bound with solid surface in mole per gram solids,
- K1 = forward surface sorption constant in gram solids per mole sites per hour and,
- K2 = reverse surface desorption constant in gram solids per cm<sup>3</sup> liquid per hour.

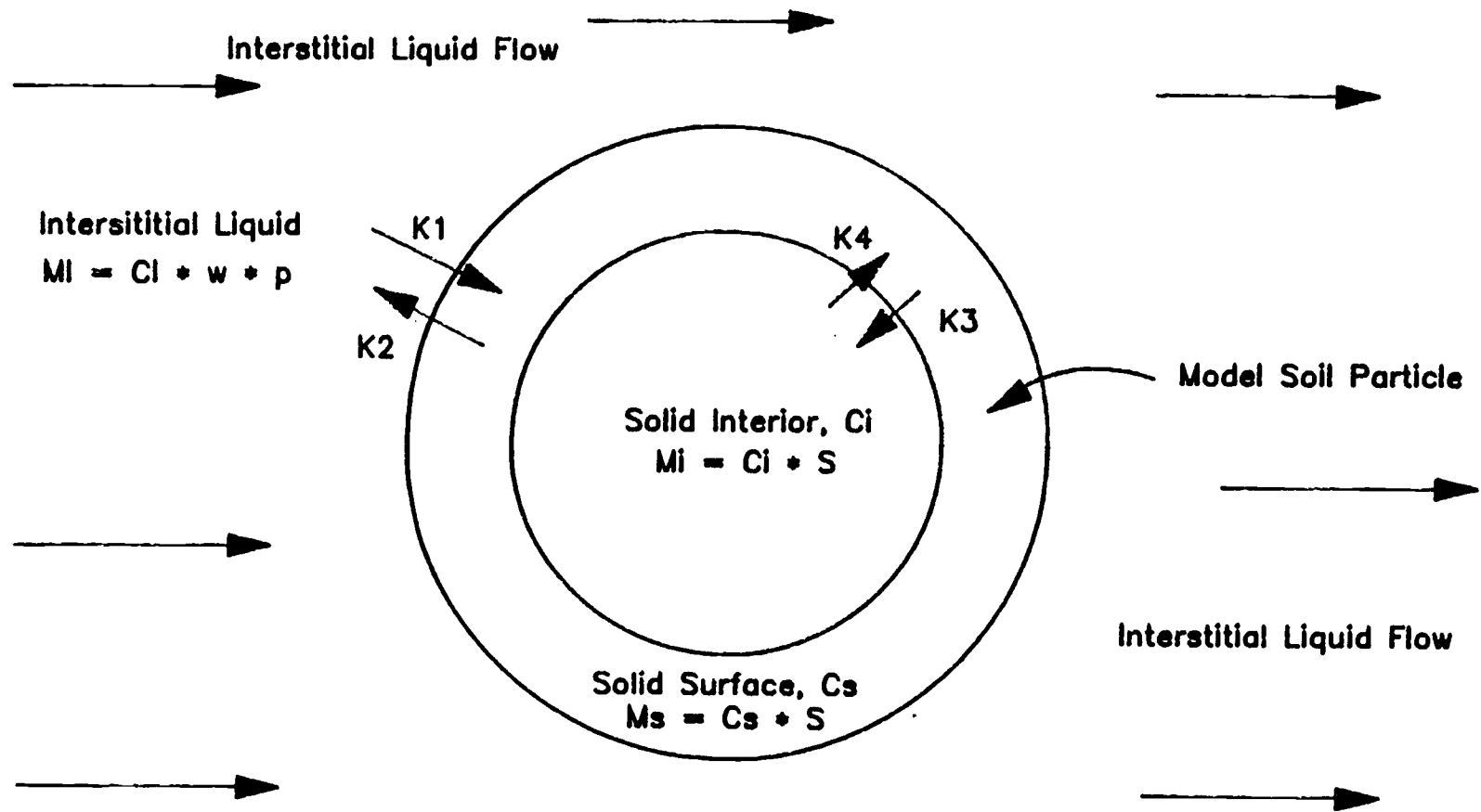
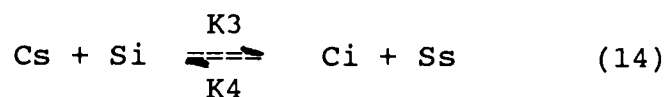


Figure 3. Schematic representation of the soil sorption process.

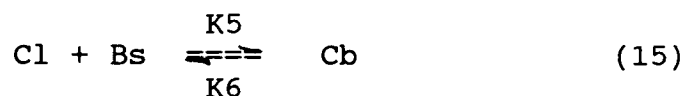
This process is followed by partitioning of the sorbate into the interior phase by a first order reversible chemical process.



where:

- Si = solid interior phase available sites in mole interior sites per gram solids,
- Ci = pollutant bound with solid interior in mole per gram solids,
- K3 = forward surface to interior partition rate constant in gram solids per mole sites per hour, and
- K4 = reverse interior to surface partition rate constant in 1/hour.

Sorption to the bacterial phase is treated as a one compartment model. The derivation and assumptions are identical to those for the solid surface phase sorption model with the following notation.



where:

- Bs = bacterial phase available sites in mole bacterial sites per gram bacteria,
- Cb = pollutant bound with bacterial phase in mole per gram bacteria,
- K5 = forward bacterial sorption constant in gram bacteria per mole sites per hour, and
- K6 = reverse bacterial desorption constant in gram bacteria per cm<sup>3</sup> liquid per hour.

While the one compartment model may be too simple to represent the processes involved in bacterial

sorption, too little is known about the metabolism and sorption mechanisms to justify a more complex approach. The one box model provides adequate representation of the processes involved and provides insight regarding which parameters or mechanisms may be important.

The transport due to the various sorption and desorption processes is modeled by additions and subtractions from each respective compartment over the time increment  $dT$ . The net pollutant transport into and out of the liquid phase due to sorption is the sum of the transport from sorption and desorption to the solid surface phase and the bacterial phase. The transport to the solid surface phase and bacterial phase are,

$$T_{ss} = A \, dX \, p \, dT$$

$$* [C_s(n,T) K_2 - C_l(n,T) K_1 S_s(n,T)] \quad (16)$$

$$T_b = A \, dX \, p \, dT$$

$$* [C_b(n,T) K_6 - C_l(n,T) K_5 B_s(n,T)] \quad (17)$$

The mass of pollutant in the liquid phase at time  $T+dT$  is the mass in the liquid phase at time  $T$  plus the transport over the time increment  $dT$  due to advection ( $T_a$ ), dispersion ( $T_d$ ), sorption processes



( $T_{ss}$  and  $T_b$ ). Combining Equations 4, 10, 16, and 17 and solving for the liquid concentration at  $T + dT$ :

$$\begin{aligned}
 Cl(n, T+dT) = & Cl(n, T) \\
 & + u \, dT/dX [Cl(n-1, T) - Cl(n, T)] \\
 & + D \, dT/(dX^2) [Cl(n-1, T) + Cl(n+1, T) \\
 & \quad - 2 \, Cl(n, T)] \\
 & + dT [Cs(n, T) K_2 - Cl(n, T) K_1 Ss(n, T)] \\
 & + dT [Cb(n, T) K_6 - Cl(n, T) K_5 Bs(n, T)] \quad (18)
 \end{aligned}$$

$S_s$ ,  $S_i$ , and  $B_s$  represent the available surface sites at a given time on the solid surface, solid interior, and bacterial phase, respectively. These values are calculated by subtracting the concentrations in the respective phases at a given time from the maximum available sites,  $S_{smax}$ ,  $S_{imax}$ , and  $B_{smax}$  as follows shown below.

$$S_s(n, T) = S_{smax} - C_s(n, T) \quad (19)$$

$$S_i(n, T) = S_{imax} - C_i(n, T) \quad (20)$$

$$B_s(n, T) = B_{smax} - C_b(n, T) \quad (21)$$

where:

- $S_{smax}$  = maximum available surface sites on sorbate in mole sites per gram solids,
- $S_{imax}$  = maximum available interior sites in sorbate in mole sites per gram solids, and
- $B_{smax}$  = maximum available sites on bacteria in mole sites per gram bacteria.

The solid surface, solid interior and bacterial phase concentrations are calculated by the same method used to calculate the liquid phase concentration.

Assuming that the solid and bacterial phases are immobile, the resulting expressions are:

$$\begin{aligned} C_s(n, T+dT) &= C_s(n, T) \\ &+ dT \frac{p}{S} [C_l(n, T) K_1 S_s(n, T) - C_s(n, T) K_2] \\ &+ dT [C_i(n, T) K_4 - C_s(n, T) K_3 S_i(n, T)] \end{aligned} \quad (22)$$

$$\begin{aligned} C_i(n, T+dT) &= C_i(n, T) \\ &+ dT [C_s(n, T) K_3 S_i(n, T) \\ &- C_i(n, T) K_4] \end{aligned} \quad (23)$$

$$\begin{aligned} C_b(n, T+dT) &= C_b(n, T) \\ &+ dT \frac{p}{B} [C_l(n, T) K_5 B_s(n, T) \\ &- C_b(n, T) K_6] \end{aligned} \quad (24)$$

where:

- S = solids concentration in grams solids per cm<sup>3</sup> total, and
- B = bacteria concentration in grams bacteria per cm<sup>3</sup> total.

### LOSSES DUE TO BACTERIAL METABOLISM

Two possible sources of the pollutant for bacterial metabolism are included in the model. They are 1) degradation of pollutant dissolved in the liquid phase and 2) degradation of pollutant absorbed to the bacteria. Degradation from the liquid phase has a direct effect on the liquid phase transport of the pollutant. Bacterial phase degradation must be preceded by sorption of the compound to the bacteria. Both mechanisms represent ultimate destruction of the pollutant.

#### Liquid Phase Degradation

Monod kinetics are used to predict metabolism from the liquid phase [9,10]. A constant mass of bacteria is assumed for all spatial cells in the column such that the bacterial population is assumed constant with depth and time. Bacterial growth or decay are not considered.

Given the Monod constants,  $K_m$  and  $K_s$ , and a bacterial population,  $B$ , a substrate utilization rate,  $R_{su}$ , is calculated for a given liquid concentration in each cell.

$$R_{su}(n,T) = [K_m (B/p) C_l(n,T)] / [K_s + C_l(n,T)] \quad (25)$$

where:

- $R_{su}$  = substrate utilization rate in moles per  $\text{cm}^3$  per hour,
- $K_m$  = maximum substrate utilization rate constant in moles per gram bacteria per hour, and
- $K_s$  = half velocity constant in moles per  $\text{cm}^3$  liquid.

Equation 25 is then incorporated into Equation 18.

$$\begin{aligned} C_l(n,T+dT) = & C_l(n,T) \\ & + u \, dT/dX [C_l(n-1,T) - C_l(n,T)] \\ & + D \, dT/dX^2/p [C_l(n-1,T) + C_l(n+1,T) \\ & \quad - 2 C_l(n,T)] \\ & + dT [C_s(n,T) K_2 - C_l(n,T) K_1 S_s(n,T)] \\ & + dT [C_b(n,T) K_6 - C_l(n,T) K_5 B_s(n,T)] \\ & - R_{su}(n,T) \, dT \end{aligned} \quad (26)$$

### Bacterial Phase Degradation

Degradation from the bacterial phase is assumed

to be first order. The resulting transport term for the bacterial phase is simply:

$$T_{bm} = - C_b(n,T) K_b dT \quad (27)$$

where:

$K_b$  = first order rate constant in moles substrate degraded per mole present.

This transport term is then incorporated in Equation 24 as:

$$\begin{aligned} C_b(n,T+dT) = & C_b(n,T) \\ & + dT p/B [C_l(n,T) K_5 B_s(n,T) - C_b(n,T) K_6] \\ & - C_b(n,T) K_b dT \end{aligned} \quad (28)$$

A complete listing of the Fortran program that was developed to implement this model is given in Appendix A. Equations 19 through 23, 25, 26, and 28 are the final algorithms used in the model to predict the eventual fate of a given pollutant.

## RESULTS AND DISCUSSION

In the following sections, the results of a sensitivity analysis of the model are discussed. Soil column porosity, seepage velocity, and the concentration of active soil bacteria were chosen to represent a plausible "insitu" soil column and these parameters were held constant for all analyses. The parameters of primary concern were those related to sorption and degradation because of their uncertainty.

### DISPERSION COEFFICIENTS AND SEEPAGE VELOCITIES

The dispersion coefficient was chosen for the model soil column based on typical values reported by Valocchi [3] and on experiments performed by Patrier [11]. For organic compounds, typical dispersion coefficients,  $D$ , range from about 0.012 to 0.094 cm<sup>3</sup> liquid per cm per hour [3] when adjusted for a soil column porosity of 20 percent. Based on mathematical stability constraints, a seepage velocity,  $u$ , of 1.0 cm total per hour and a dispersion coefficient,  $D$ , of 0.07 cm<sup>3</sup> liquid per cm total per hour was chosen. The liquid concentration profiles with advection of 1.0 cm per hour using a dispersion coefficient of 0.07 cm<sup>2</sup>/hr are shown in Figure 4.

The effect of increasing the dispersion coefficient,  $D$ , was to spread out the pollutant spike

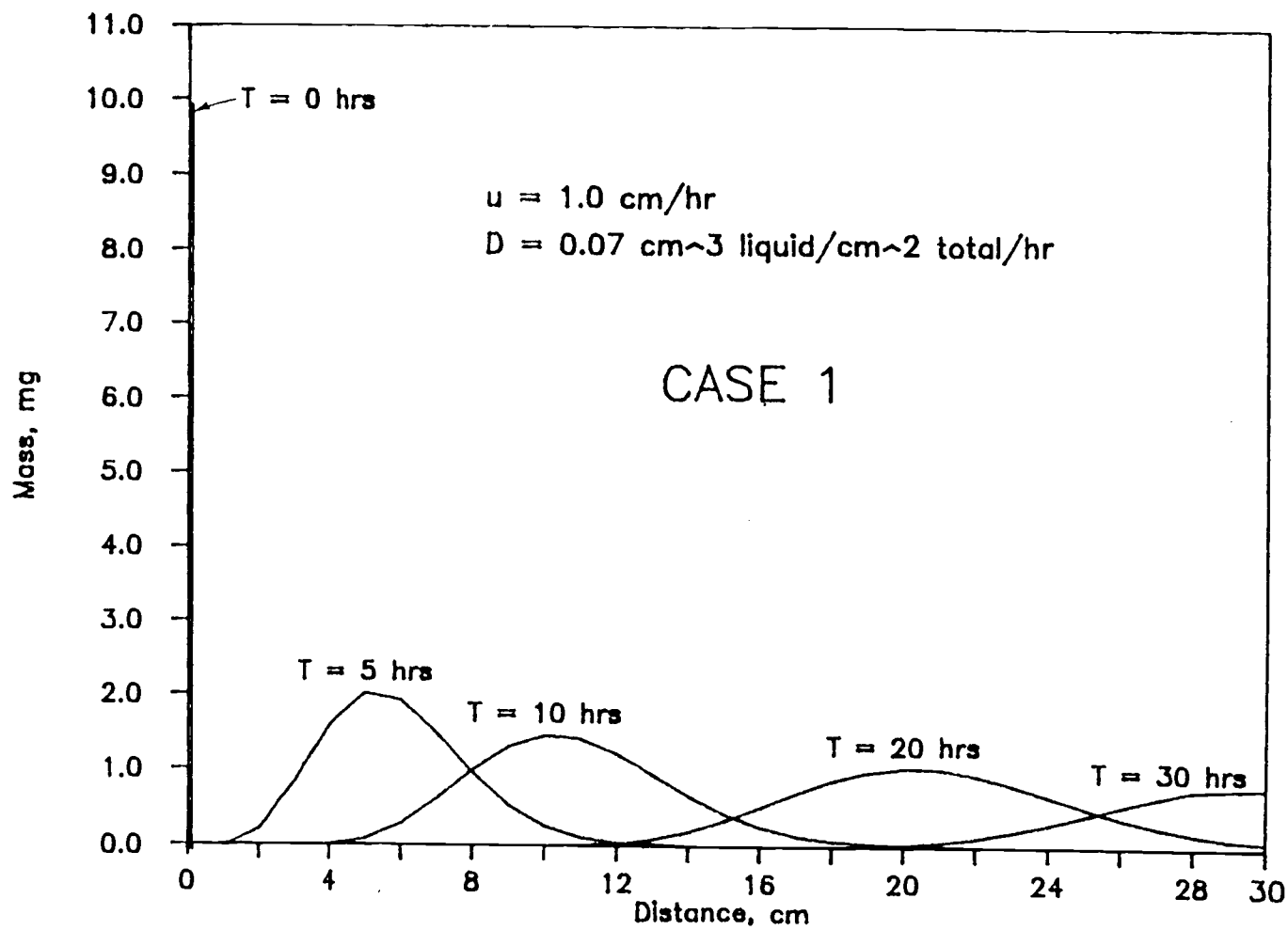


Figure 4. Soil column liquid concentration profile for Case 1 at several times showing the effect of combined advection and dispersion.

as it moved through the column. The decrease in the peak liquid phase mass of the pollutant reduces the driving force for sorption and degradation at the center of the spike. However, dispersion results in a greater volume of soil subjected to the pollutant at any given time. Eventually, the spike passed completely through the column. While the center of the plume will leave the column at the same time ( $u \cdot X$  for constant velocity,  $u$ ) for any dispersion coefficient,  $D$ , larger values of  $D$  tend to keep the trail of the pollutant plume in the column longer. Mathematically, the centroid of the plume moves through the column at the same speed in either case.

### BATCH SYSTEM RESULTS

Experimental results from a batch sorption experiment performed by Dolan [11] were modeled using the constants for sorption reported therein. Modeling the batch system was accomplished by setting  $u$  and  $D$  equal to zero and setting  $dX$  equal to  $X$ . The assumptions behind any individual cell are identical to those made for a chemostat if  $u$  is nonzero, or a batch reactor if  $u$  equals zero.

The results of the batch analysis are shown in Figure 5. The liquid concentration decreased sharply over the first 10 hours with a corresponding rise in the surface sorption to the solids. As the surface site availability is reduced, the rate of sorption from the liquid phase slowed and begins to mimic the slope of the surface sorption curve. The solid interior began to control sorption at about 15 hours and quickly became the rate limiting process. As the pollutant was transferred from the surface to the interior, more sites became available for sorption from the liquid phase, but at a steadily decreasing rate. Theoretically, these processes will reach a dynamic equilibrium at some time after 150 hours.



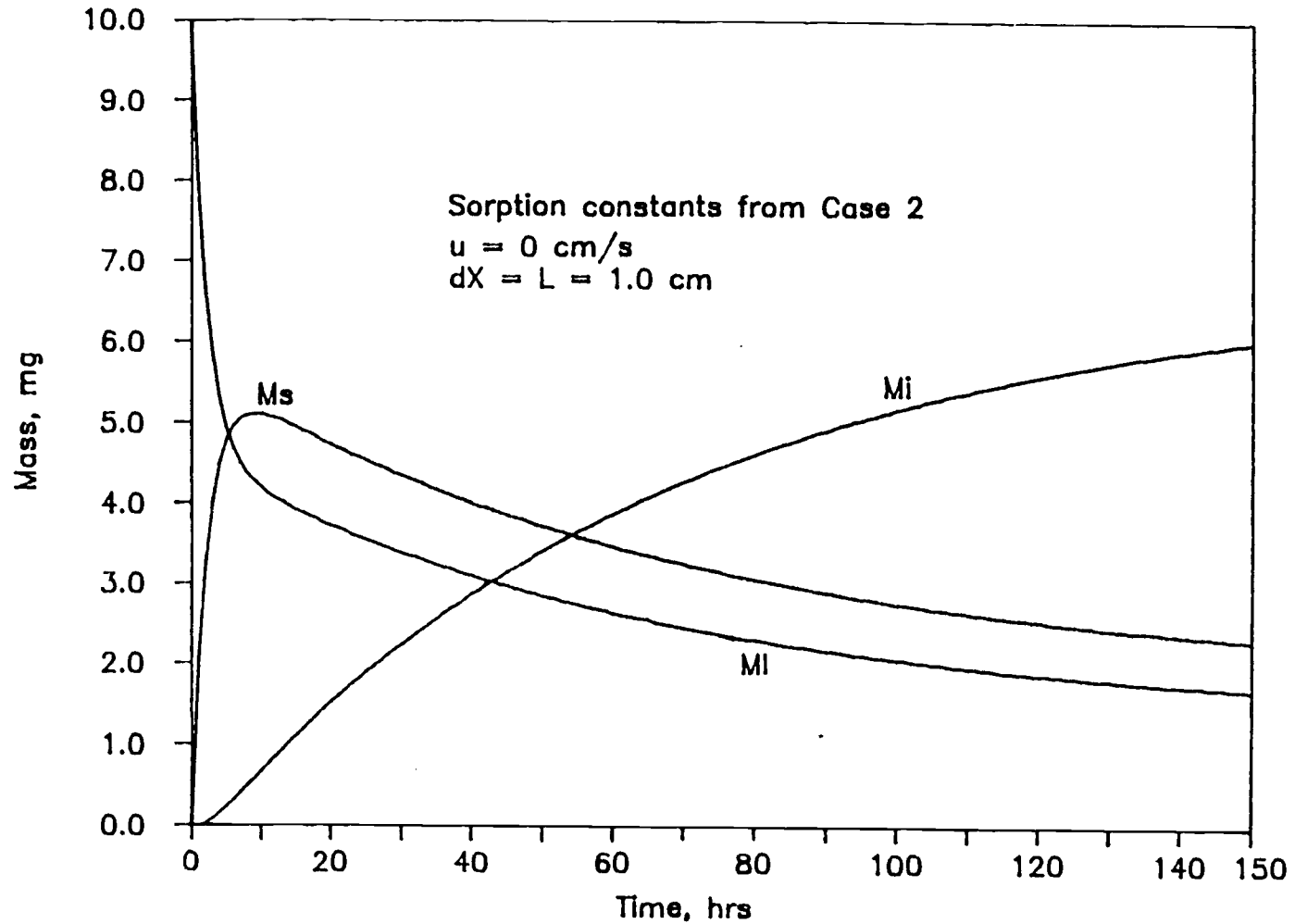


Figure 5. Pollutant mass in the liquid (M<sub>l</sub>), solid surface (M<sub>s</sub>) and solid interior (M<sub>i</sub>) phases as a function of time under Case 2 conditions for a batch system.

COLUMN BASE RUN WITH SORPTION AND DISPERSION

To examine the sensitivity of mass transport in a soil column to constants describing sorption and dispersion, a base set of parameters was established. Sorption constants reported by Dolan [11] for 2,4-dichlorophenol sorbing to a model organic sorbent, cellulose triacetate, were used. Constants describing biodegradation and sorption to bacterial cells were set equal to zero to evaluate the effects of sorption and dispersion alone (see Table 1, Case 2). A seepage velocity of 1 cm/hr and a dispersion coefficient of  $0.07 \text{ cm}^2/\text{hr}$  were used in all runs. A column length of 30 cm was used. This length was adequate to show the various processes taking place, but still allows for a relatively short computation time for each run. these values are held constant and are referred to as Case 2.

The liquid, solid surface, and solid interior profile along the length of the column at various times using the Case 2 base constant values are shown in Figures 6 through 11. As time progresses, the peak amount of pollutant in the liquid phase was reduced by dispersion and sorption processes. The effect of sorption on the liquid phase was revealed by comparison of Figure 4 with Figures 6 through 11. The peak liquid phase mass decreased by over half of the values for the dispersion only case (Case 1) at 5

Case	Name	S gm	B gm	K1 $\frac{\text{gm s.}}{\text{mole hr}}$	K2 $\frac{\text{gm s.}}{\text{cm}^3 \text{ hr}}$	K3 $\frac{\text{gm s.}}{\text{mole hr}}$	K4 1/hr	K5 $\frac{\text{gm b.}}{\text{mole hr}}$	K6 $\frac{\text{gm b.}}{\text{mole hr}}$	Kb $\frac{\text{mole}}{\text{mole-hr}}$	Km $\frac{\text{mole}}{\text{g b. hr}}$	Ks $\frac{\text{mole}}{\text{cm}^3}$	S <sub>max</sub> $\frac{\text{mole}}{\text{g s.}}$	S <sub>imox</sub> $\frac{\text{mole}}{\text{g s.}}$	B <sub>max</sub> $\frac{\text{mole}}{\text{g b.}}$
1	Dispersion Only	2.08	1.0 E-5	0	0	0	0	0	0	0	0	1.0	4.6 E-5	6.14 E-4	1.0 E-4
2	Dispersion Soil Sorption	2.08	1.0 E-5	4352	1.4 E-3	29.3	5.0 E-3	0	0	0	0	1.0	4.6 E-5	6.14 E-4	1.0 E-4
3	Dispersion Soil Sorption Bocteriol Sorption	2.08	1.0 E-5	4352	1.4 E-3	29.3	5.0 E-3	4352	1.4 E-3	0	0	1.0	4.6 E-5	6.14 E-4	1.0 E-4
4	Dispersion Soil Sorption Bocteriol Sorption Degradation	2.08	1.0 E-5	4352	1.4 E-3	29.3	5.0 E-3	435210	0	3.0 E-2	0	1.0	4.6 E-5	6.14 E-4	1.0 E-4
5	Dispersion Soil Sorption Monod Degradation	2.08	1.0 E-5	4352	1.4 E-3	29.3	5.0 E-3	0	0	0	3.0 E-3	1.5 E-7	4.6 E-5	6.14 E-4	1.0 E-4

Table 1. Base parameter values for cases 1 through 5.

hours (Figure 6) and by two orders of magnitude at 25 hours (Figure 8). Desorption may contribute somewhat to the apparent widening of the peak, but most of spreading was due to dispersion as the spike travels along the column.

Surface sorption was highly dependent on the concentration gradient that exists between the surface and liquid phase. Most of the sorption that takes place was in the first six to eight centimeters of the soil where the liquid concentration was relatively undiluted and has not been exposed to the entire soil column. At 10 hours (Figure 7), the surface phase mass in the first few centimeters was already decreasing due to sorption into the interior and desorption to the liquid phase.

The fraction of pollutant present in the solid interior phase showed steady increase for 50 hours at which time it was almost identical to the solid surface phase profile. After 50 hours (Figure 9), essentially no pollutant was present in the liquid phase from the initial spike and the fraction in the solid surface phase was beginning to decrease due to migration of the pollutant into the interior. After 1000 hours (Figure 10), the processes of desorption begin to become apparent and the interior concentration begins to decrease slowly. Over the period of 1000 to 10,000 hours (about 40 to 400 days),

the peak mass present in the solid interior decreases slightly (Figures 10 and 11). The solid surface mass showed a proportional decrease indicating that desorption was the dominant phenomena.

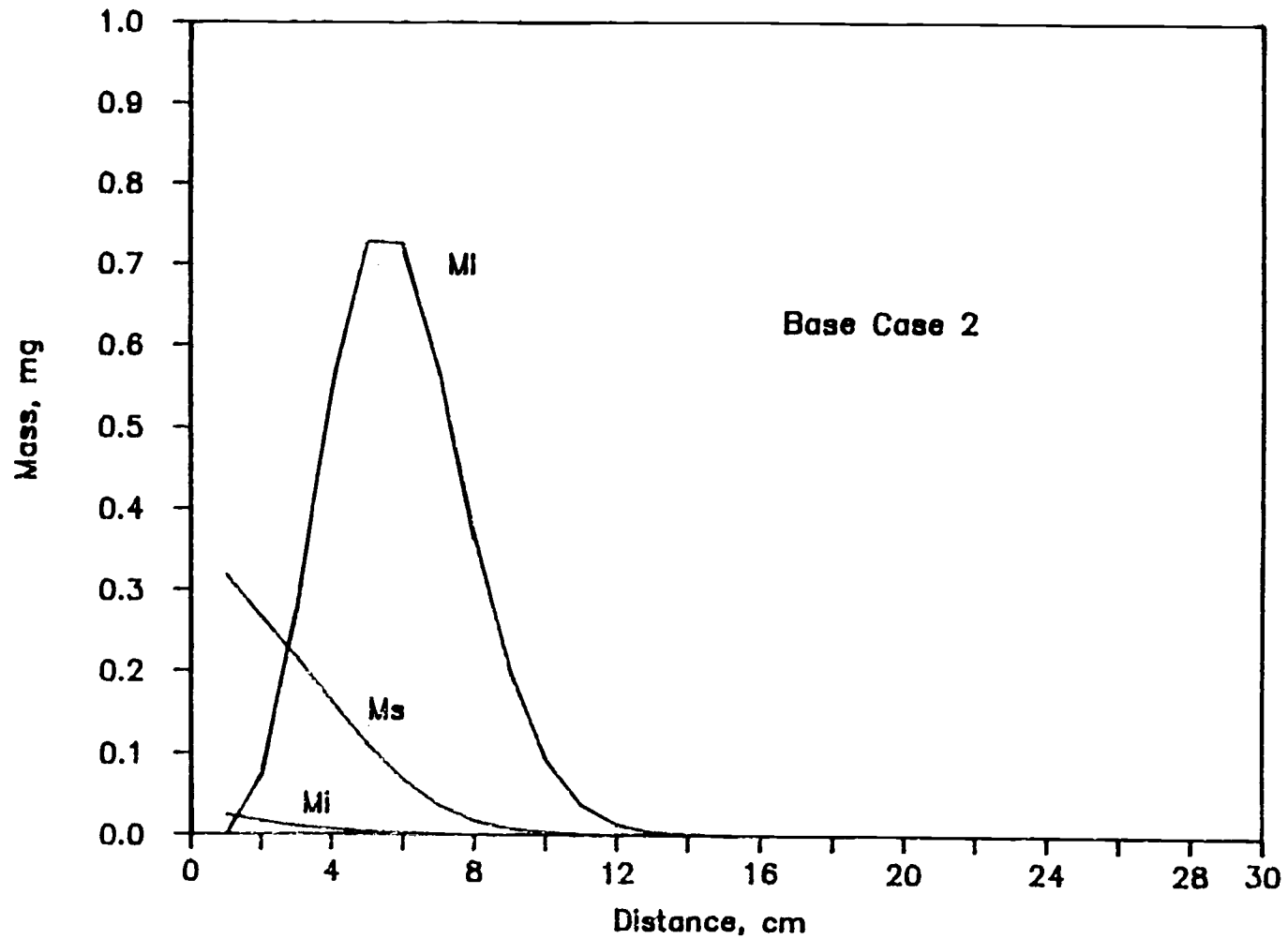


Figure 6. Soil column profile at time equals 5 hours showing liquid, solid surface, and solid interior pollutant mass distributions.

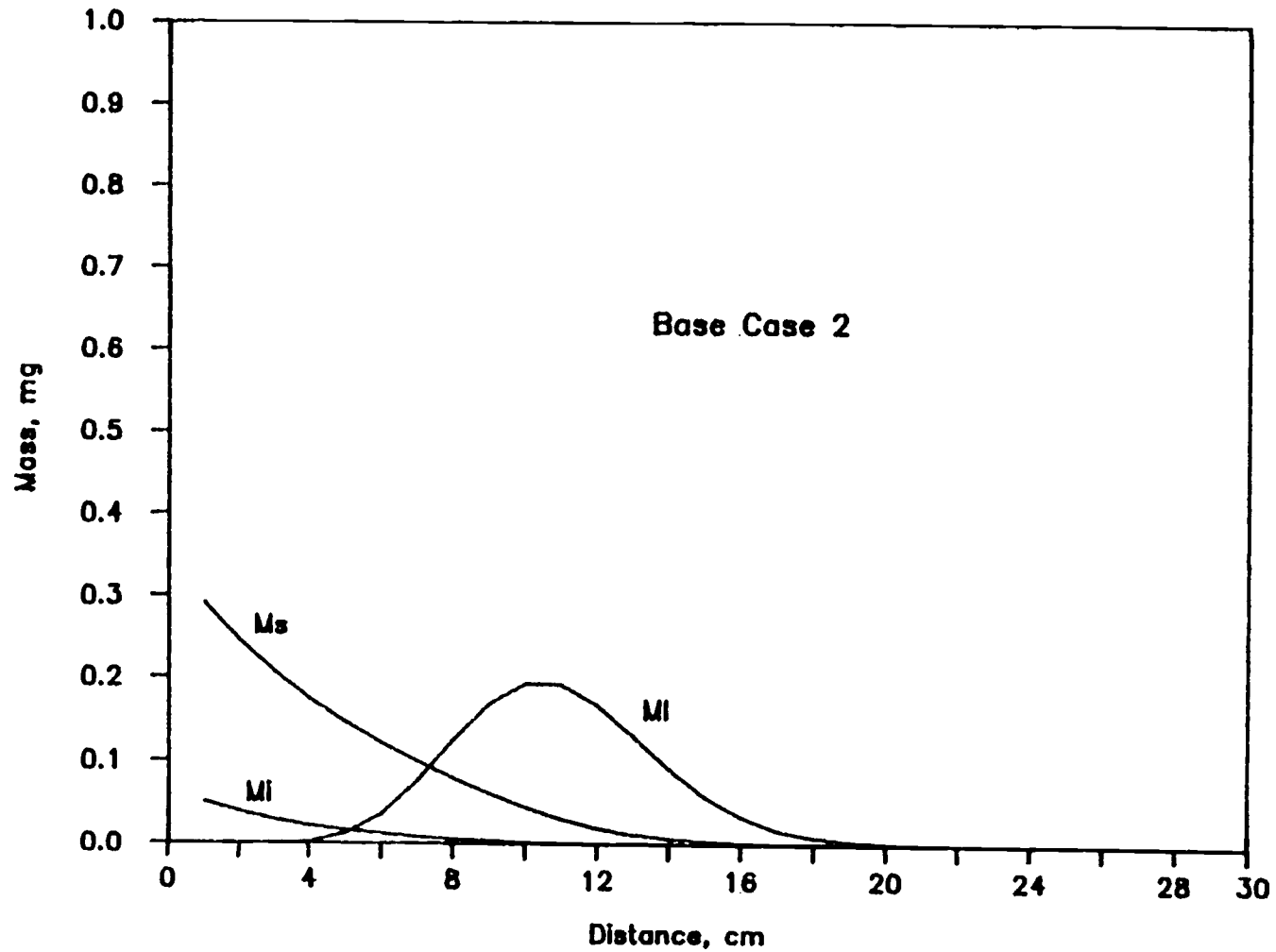


Figure 7. Soil column profile at time equals 10 hours showing liquid, solid surface, and solid interior pollutant mass distributions.

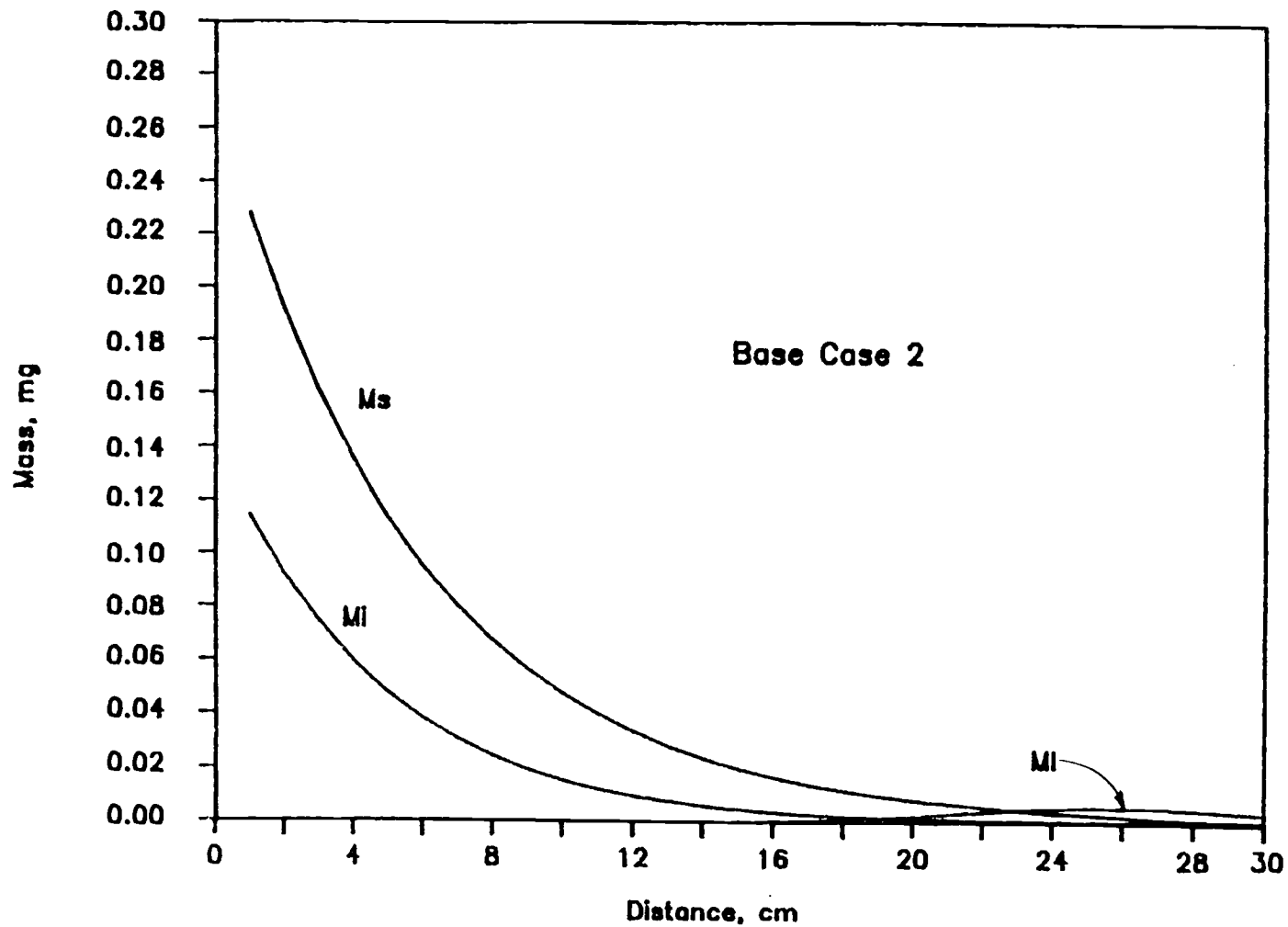


Figure 8. Soil column profile at time equals 25 hours showing liquid, solid surface, and solid interior pollutant mass distributions.



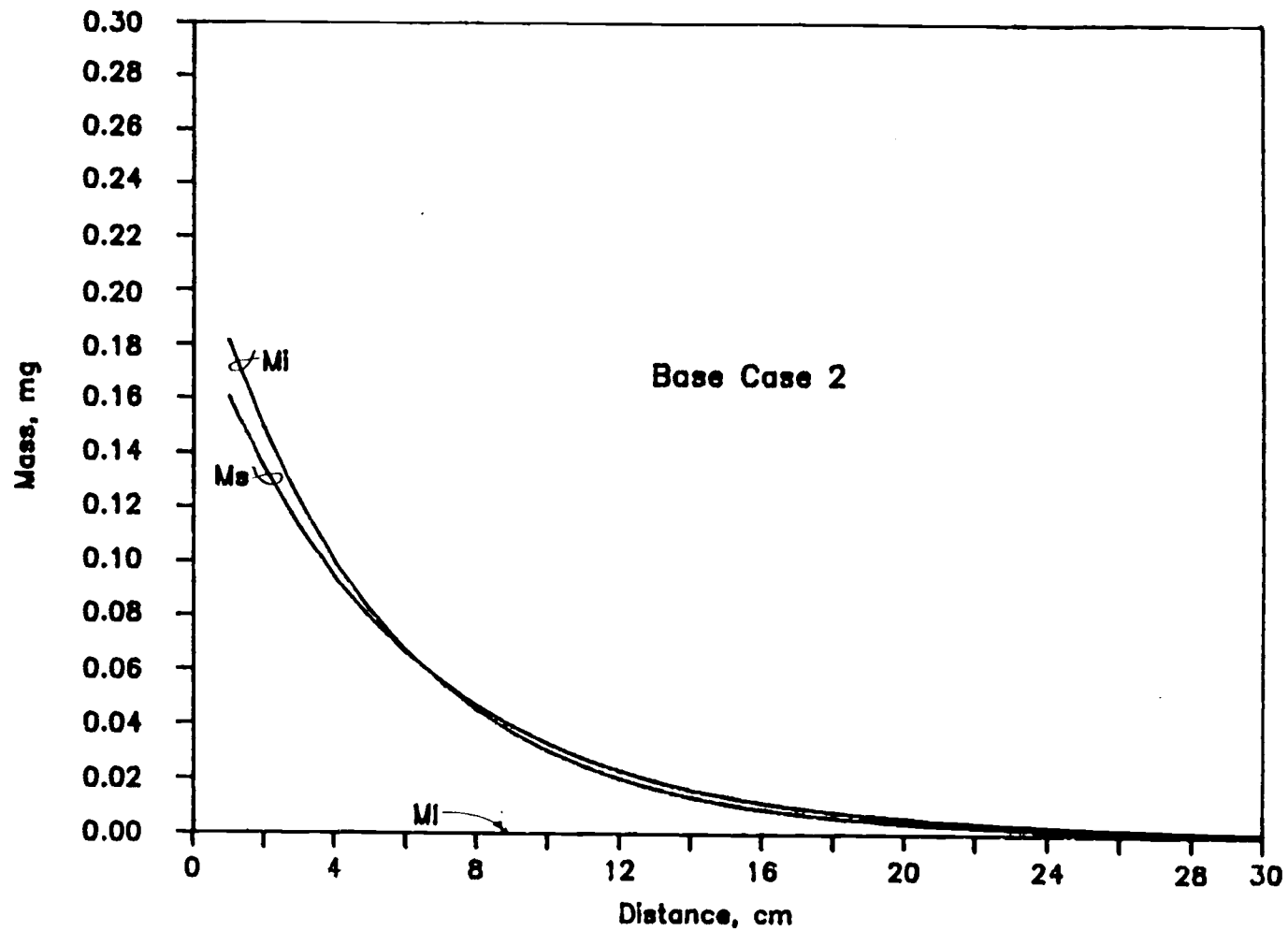


Figure 9. Soil column profile at time equals 50 hours showing liquid, solid surface, and solid interior pollutant mass distributions.

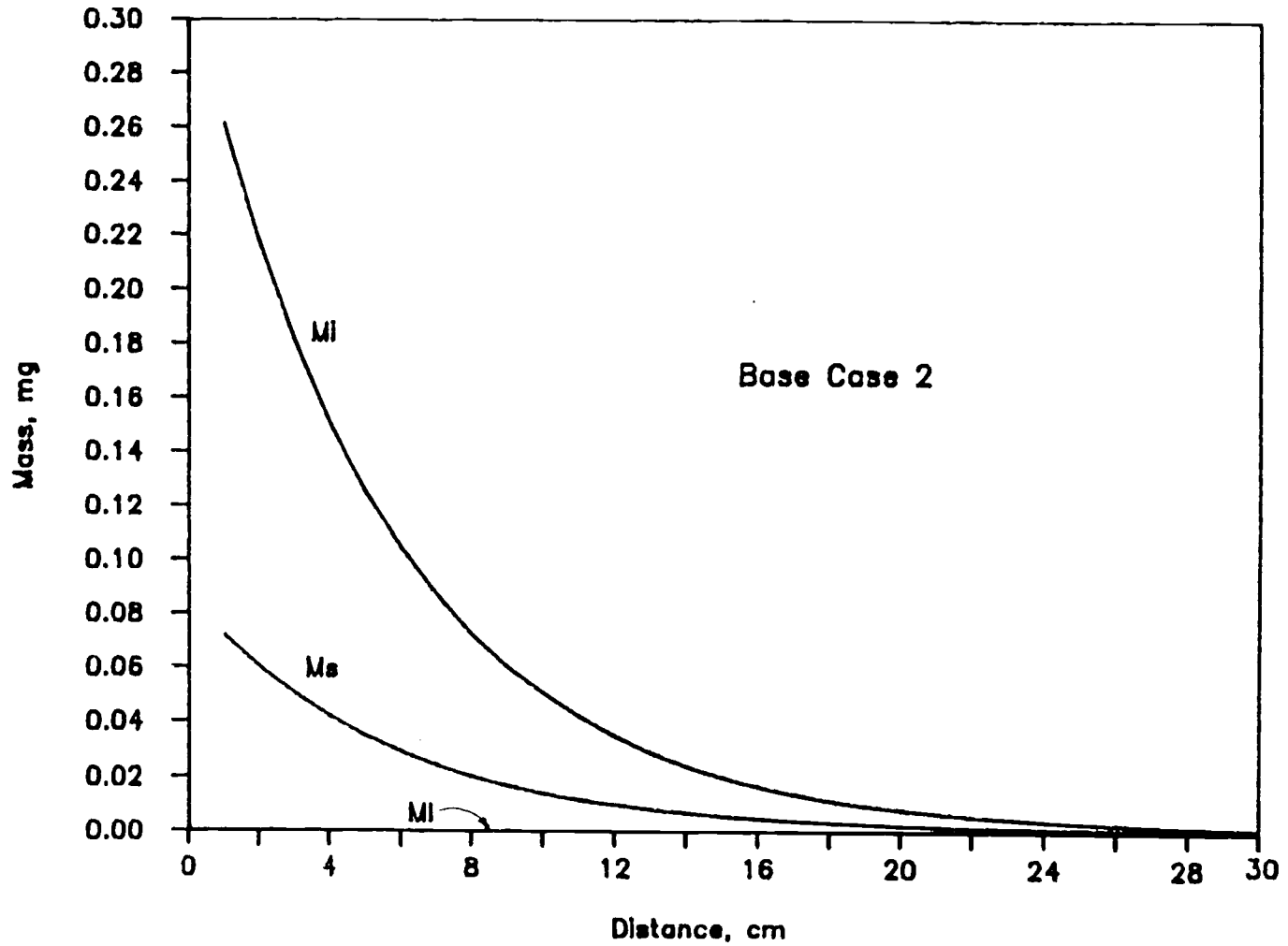


Figure 10. Soil column profile at time equals 1,000 hours showing liquid, solid surface, and solid interior pollutant mass distributions.

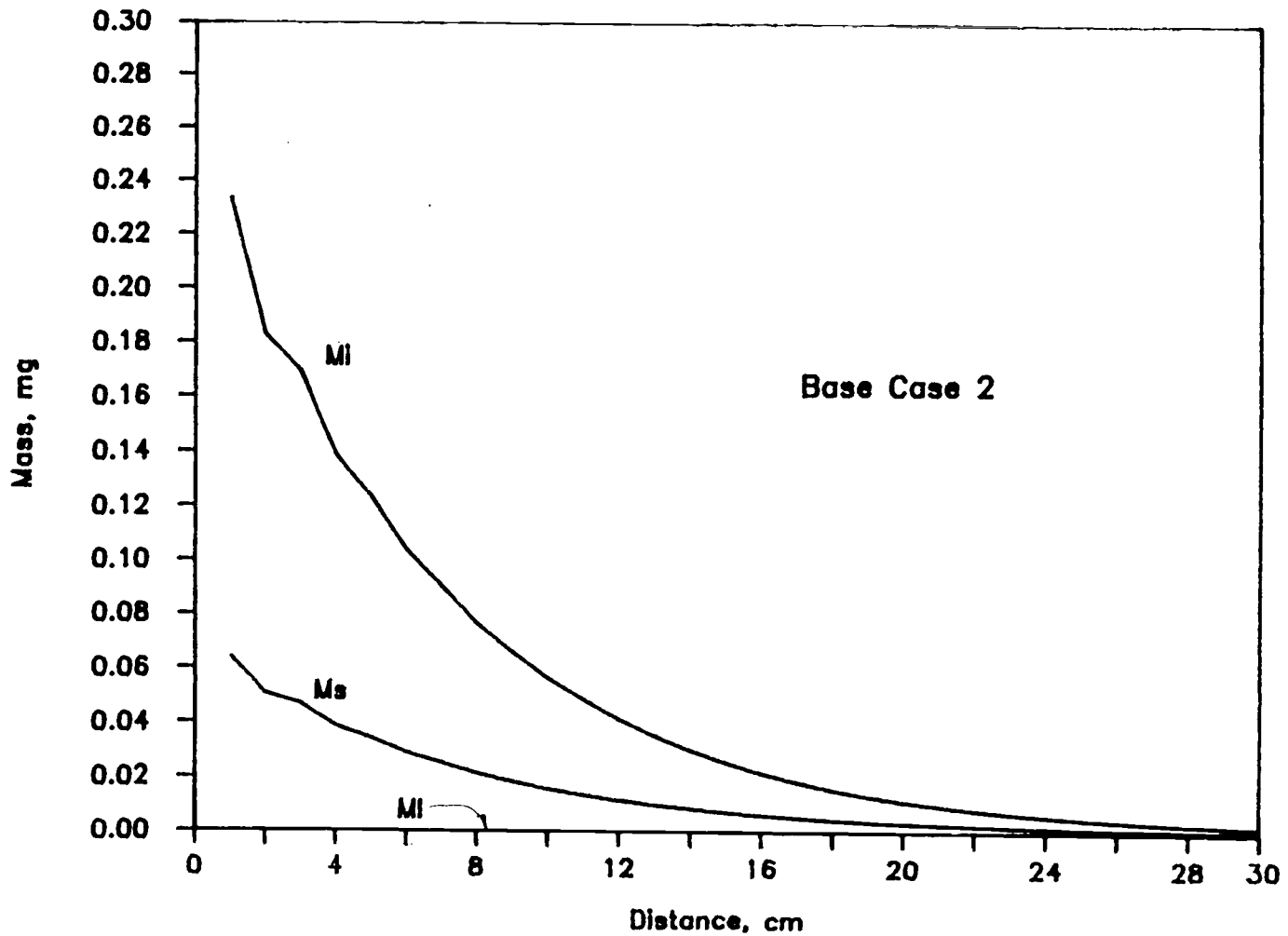


Figure 11. Soil column profile at time equals 10,000 hours showing liquid, solid surface, and solid interior pollutant mass distributions.

SURFACE SORPTION PHENOMENA ( $K_1$ ,  $K_2$ , AND  $S_{smax}$ )

Both the solid surface site availability and the sorption rate constant affect the liquid concentration in a similar manner. As shown in Equation 26,  $K_1$  and  $S_{smax}$  are each present in the same terms and, therefore, varying either parameter by the same multiple has the same result. Physically, however,  $K_1$  and  $S_{smax}$  represent entirely different processes.  $K_1$  is a property of the compound, while the maximum available surface sites,  $S_{smax}$ , is a property of the sorbent surface. A high surface availability would represent a sorbent like activated carbon, while a low surface availability would be represented by glass beads or clean sand.

The effects of varying  $K_1$  or  $S_{smax}$  over 5 orders of magnitude on  $M_l$ ,  $M_s$ , and  $M_i$  are shown in Figures 12 through 17. The early liquid profiles are very sensitive to the magnitude of  $K_1$  and  $S_{smax}$ . At  $K_1$  or  $S_{smax}$  of one order of magnitude less than the base values, the peak liquid phase mass increases from 0.7 mg to near 2.0 mg (Figure 12). By decreasing  $K_1$  or  $S_{smax}$  by another order of magnitude, a much smaller relative increase in the liquid profile occurs, nearing the case where no sorption takes place. Increasing  $K_1$  or  $S_{smax}$  by one order of magnitude sharply drops the mass solubilized in the liquid phase. Variations of even 10% from the base values

shifts the curve up or down significantly as shown in Figure 12.

For a constant desorption rate, increasing  $K_1$  values are associated with more hydrophobic compounds with higher equilibrium partition coefficients. Lower  $K_1$  values tends to represent less hydrophobic compounds. Compounds that have high  $K_1$  values would tend to be sorbed onto the solid surface fraction in the first several centimeters of a natural soil column. These compounds then would be subjected to a high initial rate of sorption to the solid interior due to the steep gradient existing between the surface and the interior. This buildup in the interior phase increases the residence time of the compound in the soil column because the compound must pass through the surface phase before being solubilized to the liquid phase. Since the desorption process is often very slow, the long term concentration in the pore water is much lower because of the less favorable gradient driving desorption back into the liquid phase.

This extremely slow process of desorption back into the liquid phase is typical of the processes observed in spills of hydrophobic organic chemicals. The chemicals are present in extractable quantities for many years after the initial contamination. Depending on the amount initially spilled, the leaching process can be a source of significant

amounts of toxic material to the ground water. The positive aspect of this phenomena is that the contaminated area could be cleaned up by removing the top layer of soil. The remaining pollutant would be slowly released at relatively low concentrations and be subjected to other dilution processes. On the other hand, the soil removed still may represent a large volume of waste that must be treated or disposed of in some manner. If the contaminated soil is not removed, a long term source of potentially hazardous chemicals will remain.

A property that has an significant effect on the fate of the solute is the fraction of organic carbon present in a natural soil. A mixture composed of sand and powdered activated carbon could be adequately modeled by considering only the activated carbon. To accomplish this, one would estimate an appropriate value of  $S_{max}$  for activated carbon and then set the solids concentration equal to the amount of activated carbon in the column. The sand could be safely neglected because of its low sorption capacity. The example can be extended by considering only the organic fraction of the soil in the sorption analysis. Peat and loam type soils would have very high solids concentrations, while sands with a low percentage of organic compounds would have a very low solids concentrations.

Desorption from the solid surface represents the only major source of pollutant to the interstitial pore water after the initial pollutant spike has passed through the column. Figures 18 through 24 show the results of varying the surface desorption rate constant ( $K_2$ ) over five orders of magnitude.

At earlier time intervals, there was very little effect of varying  $K_2$ . Sorption to the solid surface ( $K_1$ ) was the major process involved and was the most important sorption mechanism during the first five hours as shown in Figure 18. At 25 hours (Figure 19), the effect of sorption became less important because of lower liquid phase mass in the upper soil layers. Higher values of  $K_2$  showed a marked increase in liquid phase mass over the base run. Note that the Y-scale in Figure 19 is about two orders of magnitude less than in Figure 18. Solid surface and interior phase masses did not differ significantly from the base run except for the highest value of  $K_2$  at 50 hours as shown in Figures 20 and 21.

After the pulse passes through the column length, the effect of  $K_2$  became much more pronounced. At times greater than 50 hours, increased values of  $K_2$  showed larger increases in liquid phase mass over the base Case 1 values as shown in Figure 22. The effect grew more pronounced as  $K_2$  was increased indicating

that desorption occurs faster than sorption at longer times for larger desorption coefficients.

The solid surface fraction profile tended to flatten out over the column length as  $K_2$  is increased. Peak liquid phase masses were in direct correlation with this phenomenon. The surface fraction was eventually reduced to very low values as time progresses to 1000 hours for high values of  $K_2$ . The interior fraction profile emulated the surface profile. Without the significant buildup of pollutant in the surface phase creating a gradient favorable to rapid interior phase sorption, large fractions of pollutant in the interior phase will not occur.



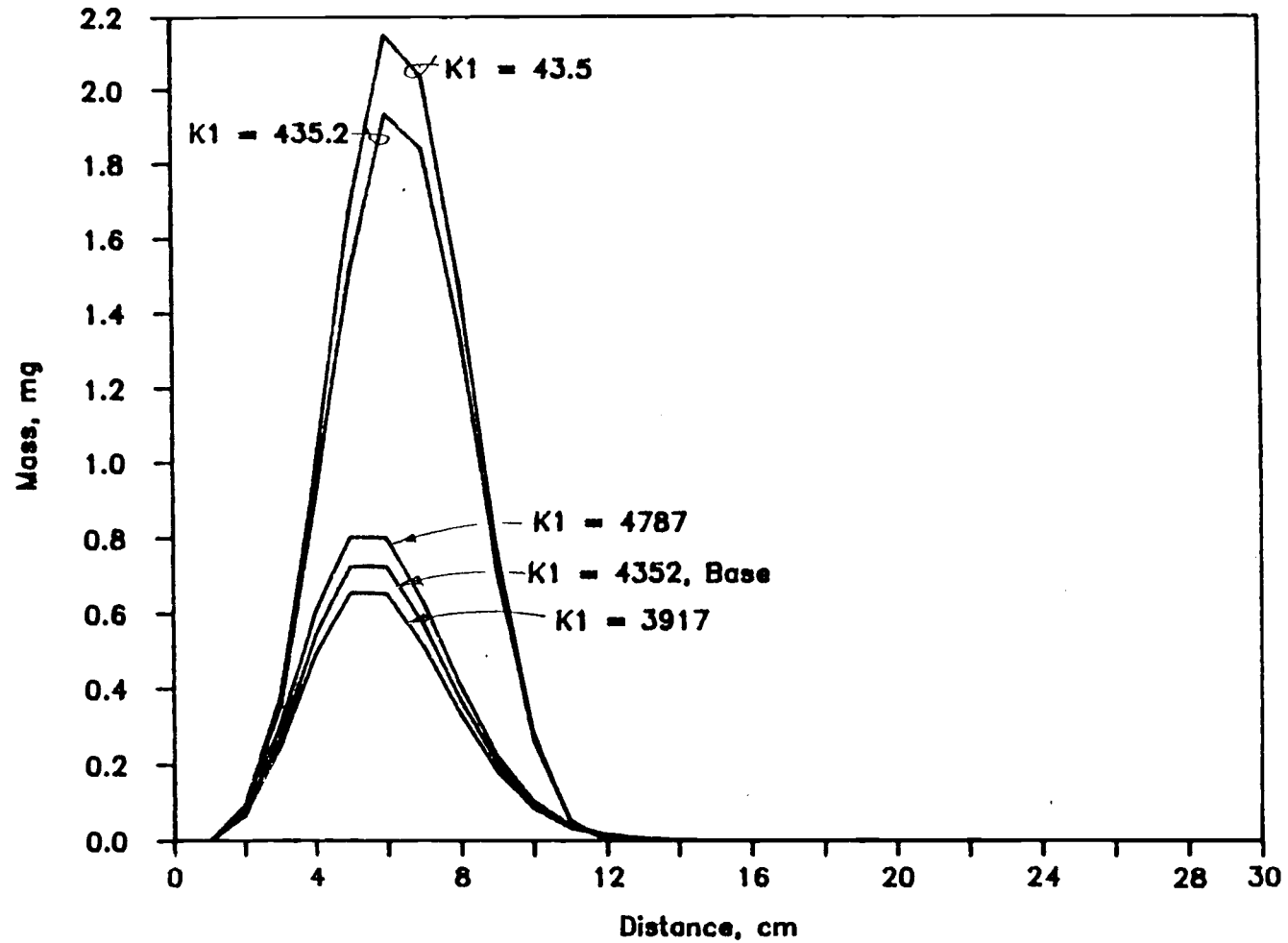


Figure 12. Liquid phase profile at time equals 5 hours varying K1 or Ssm<sub>ax</sub> over three orders of magnitude while maintaining the remaining Case 2 parameters.

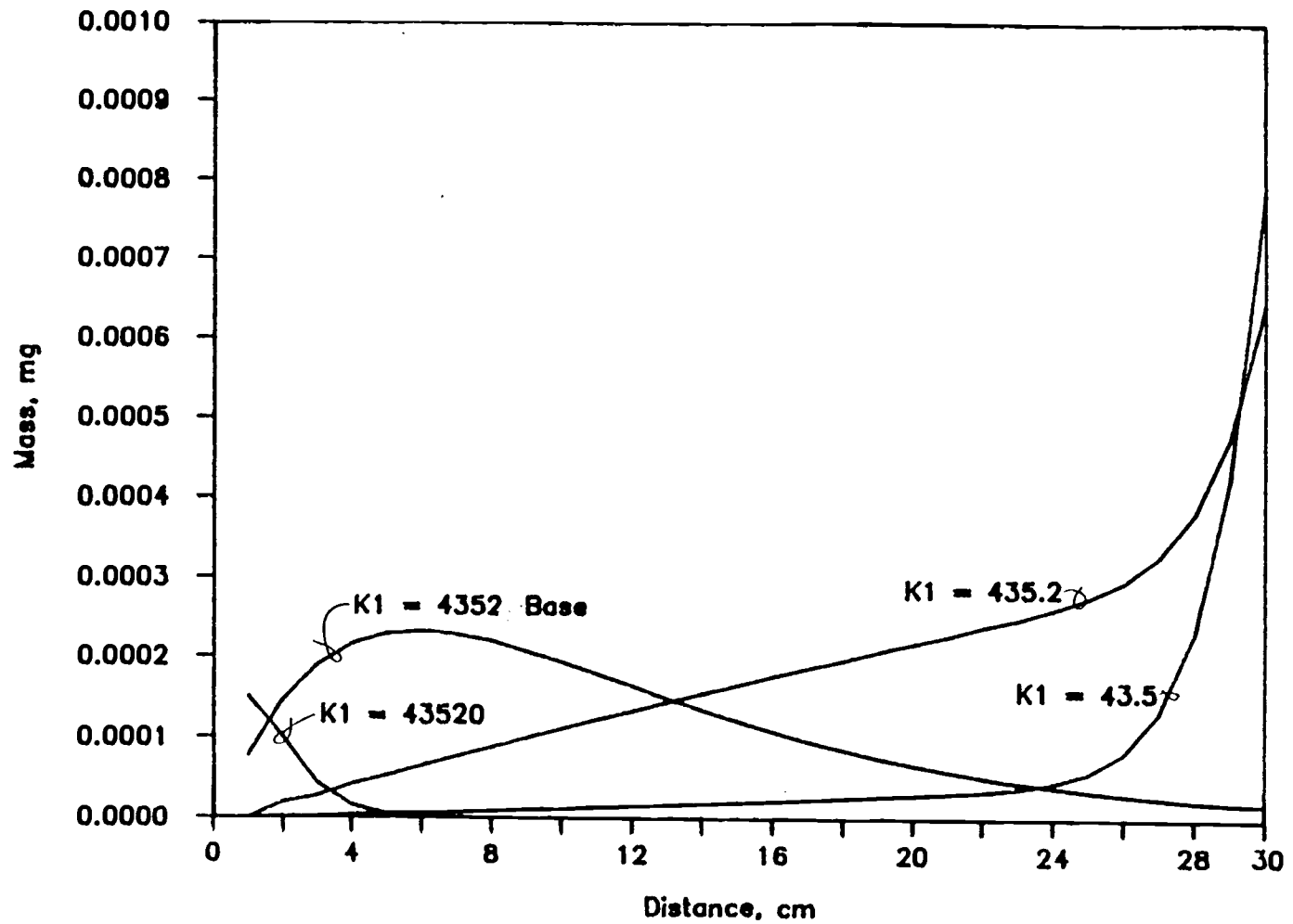


Figure 13. Liquid phase profile at time equals 50 hours varying  $K_1$  or  $S_{smax}$  over three orders of magnitude while maintaining the remaining Case 2 parameters.

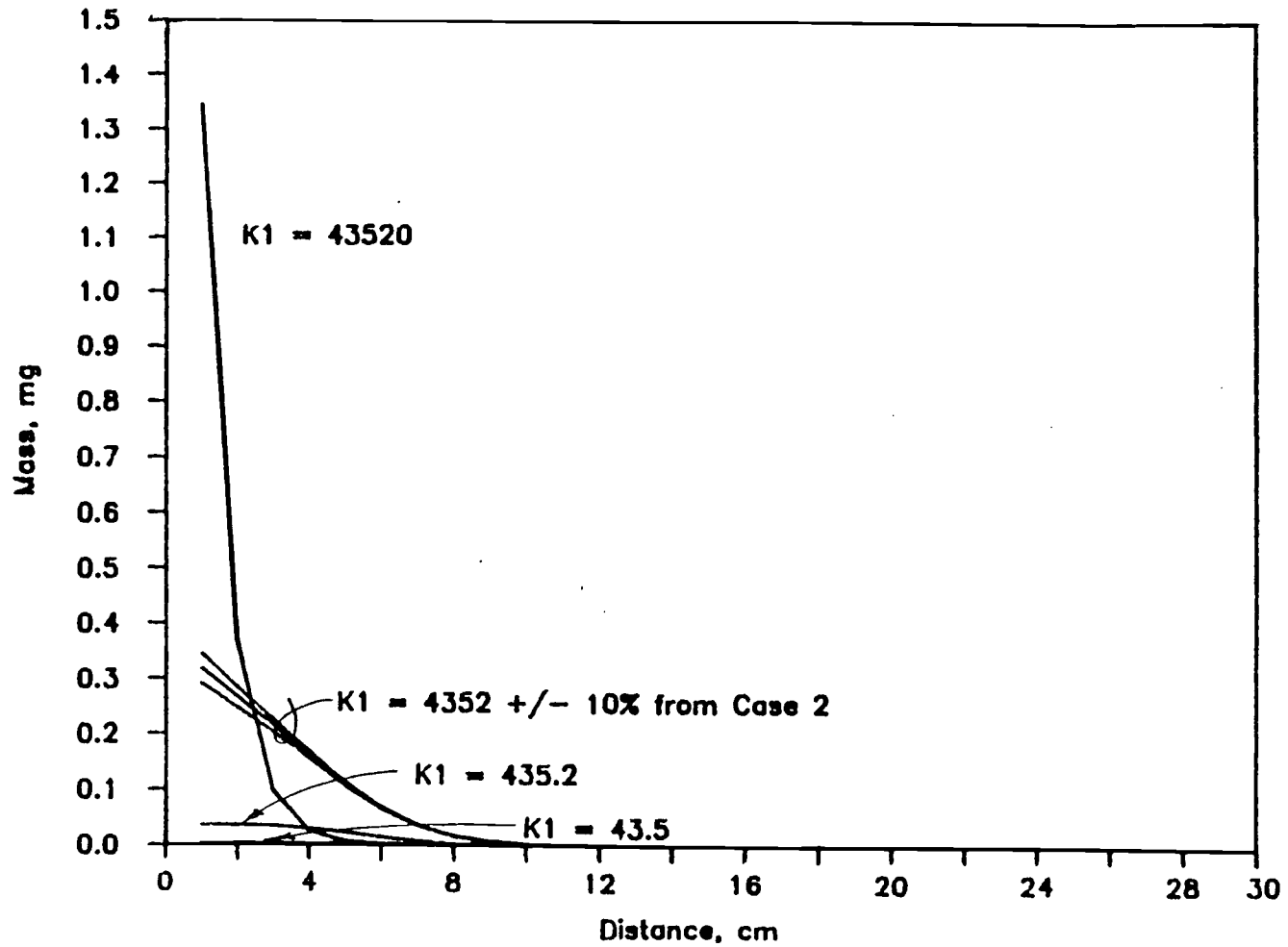


Figure 14. Solid surface phase profile at time equals 5 hours varying K1 or Ssmax over three orders of magnitude while maintaining the remaining Case 2 parameters.

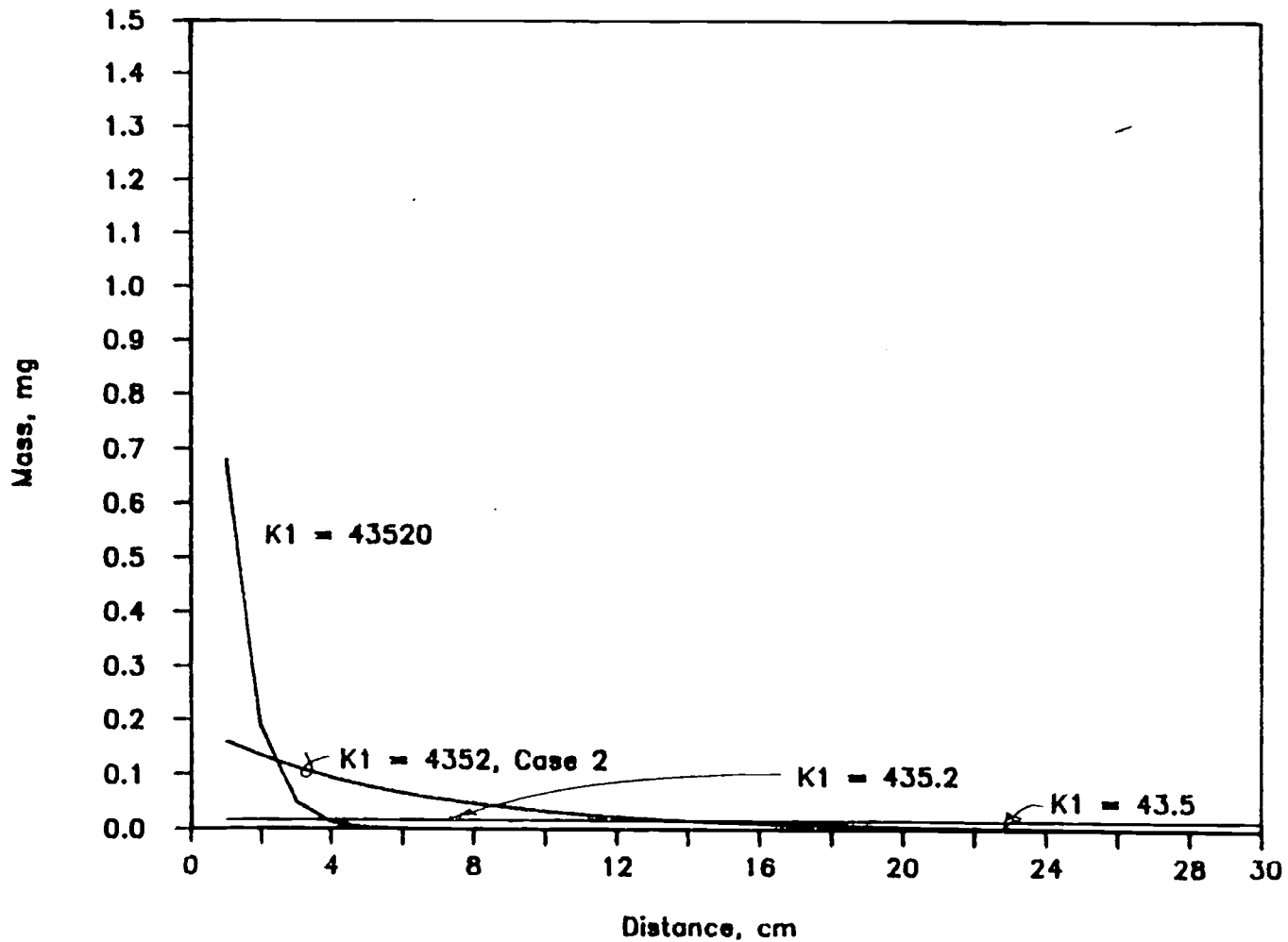


Figure 15. Solid surface phase profile at time equals 50 hours varying  $K_1$  or  $S_{smax}$  over three orders of magnitude while maintaining the remaining Case 2 parameters.

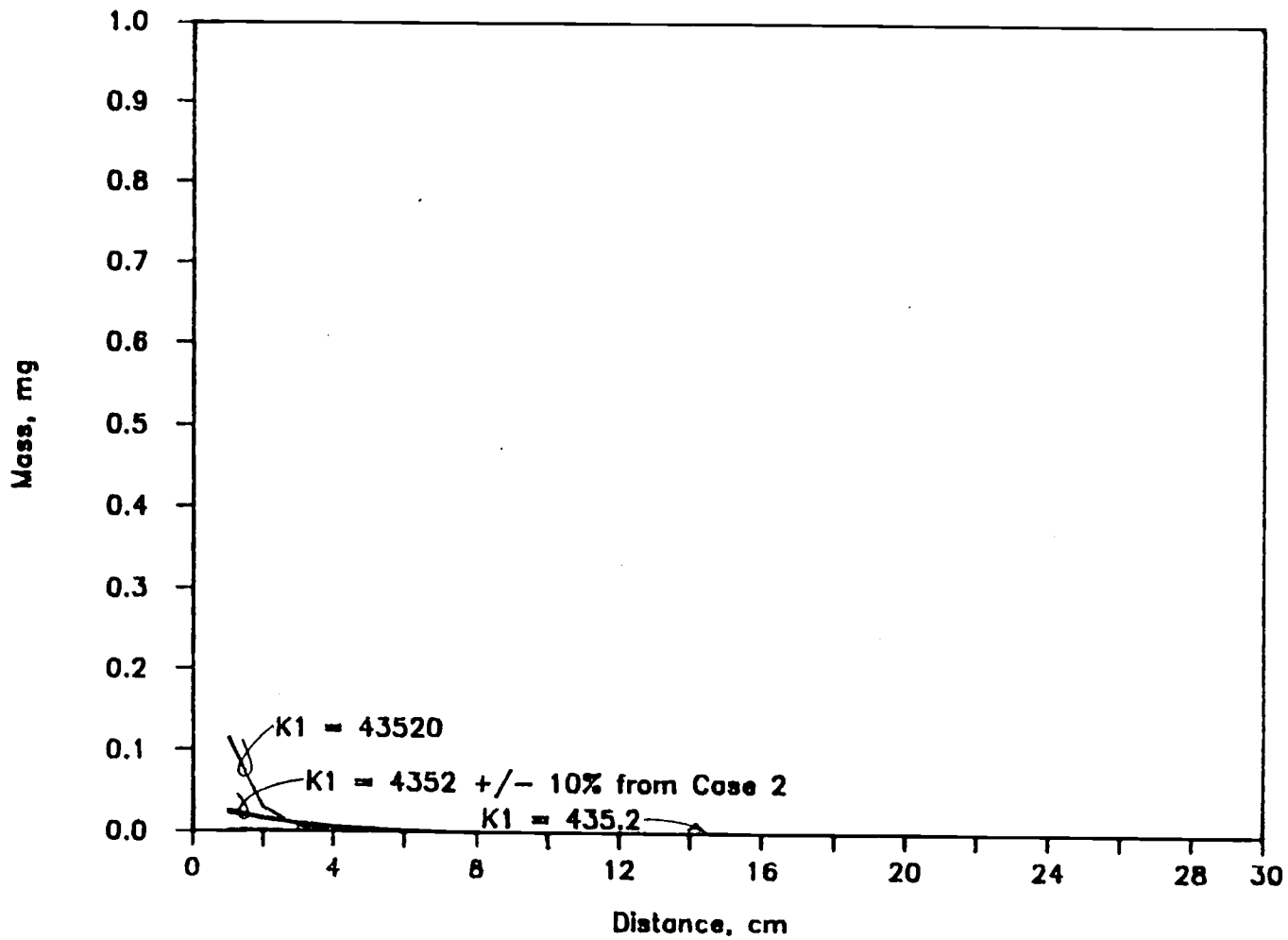


Figure 16. Solid interior phase profile at time equals 5 hours varying  $K_1$  or  $S_{smax}$  over three orders of magnitude while maintaining the remaining Case 2 parameters.

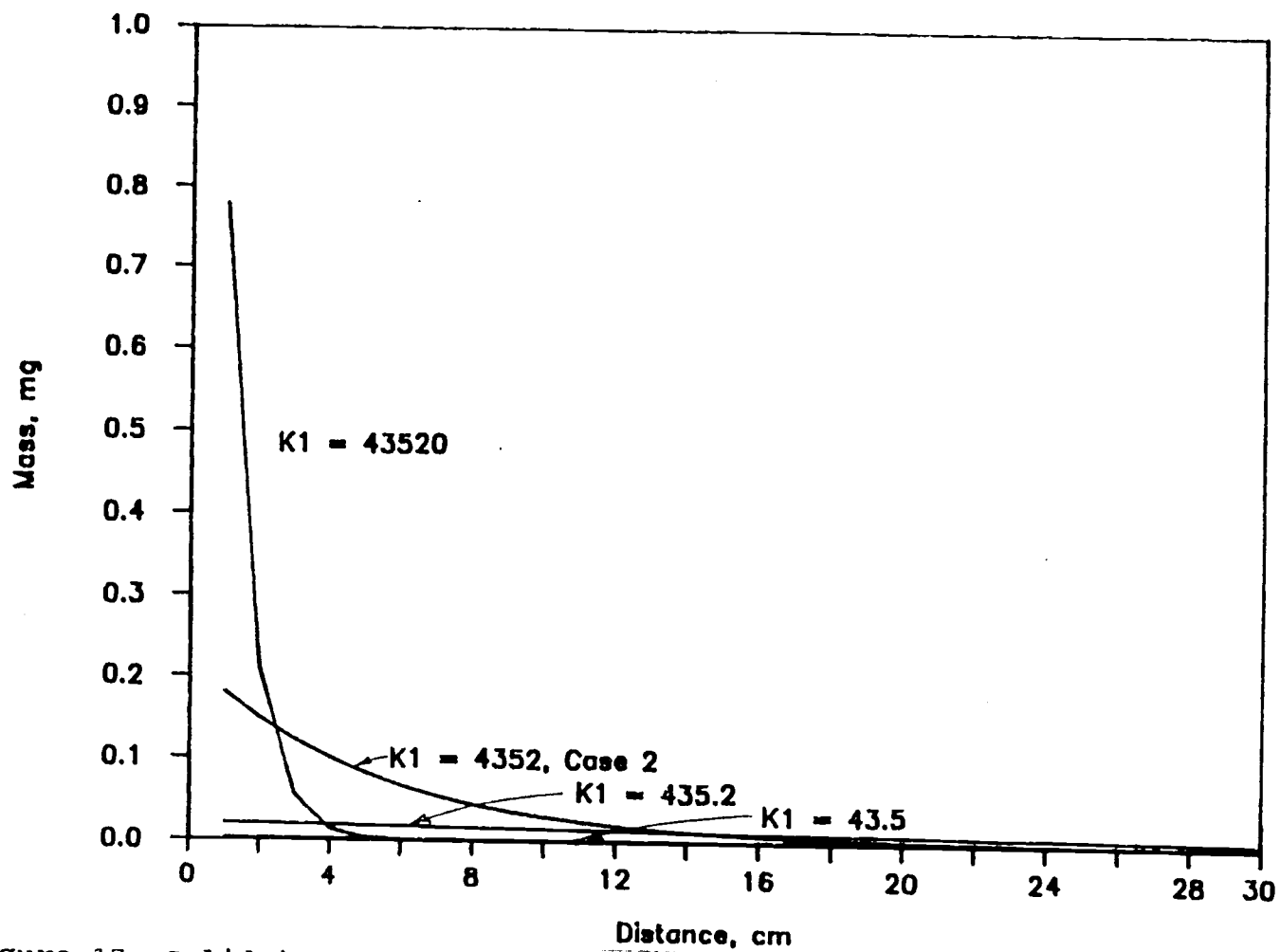


Figure 17. Solid interior phase profile at time equals 50 hours varying  $K1$  or  $S_{max}$  over three orders of magnitude while maintaining the remaining Case 2 parameters.

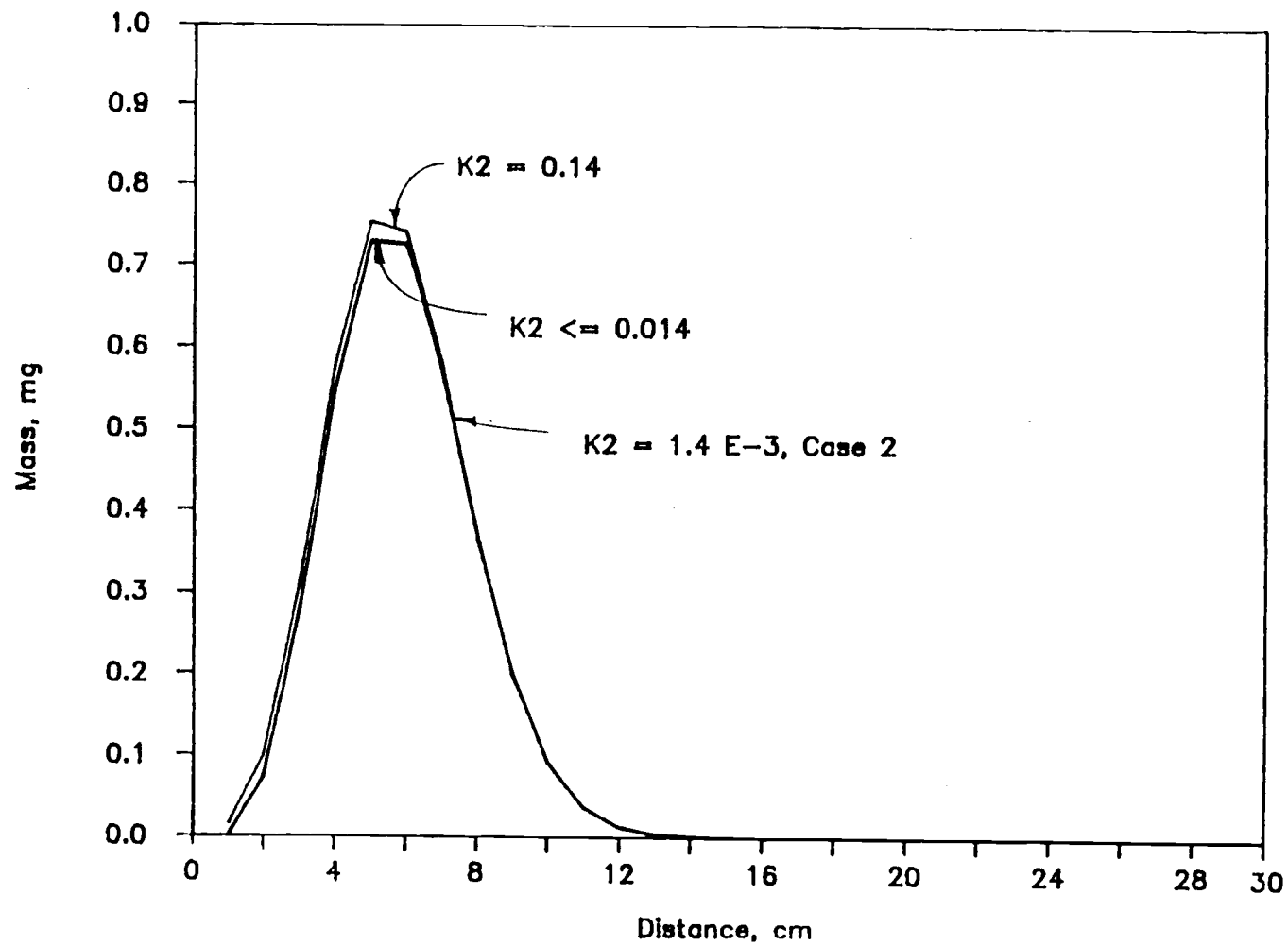


Figure 18. Liquid phase profile at time equals 5 hours varying  $K_2$  while maintaining the remaining Case 2 parameters.

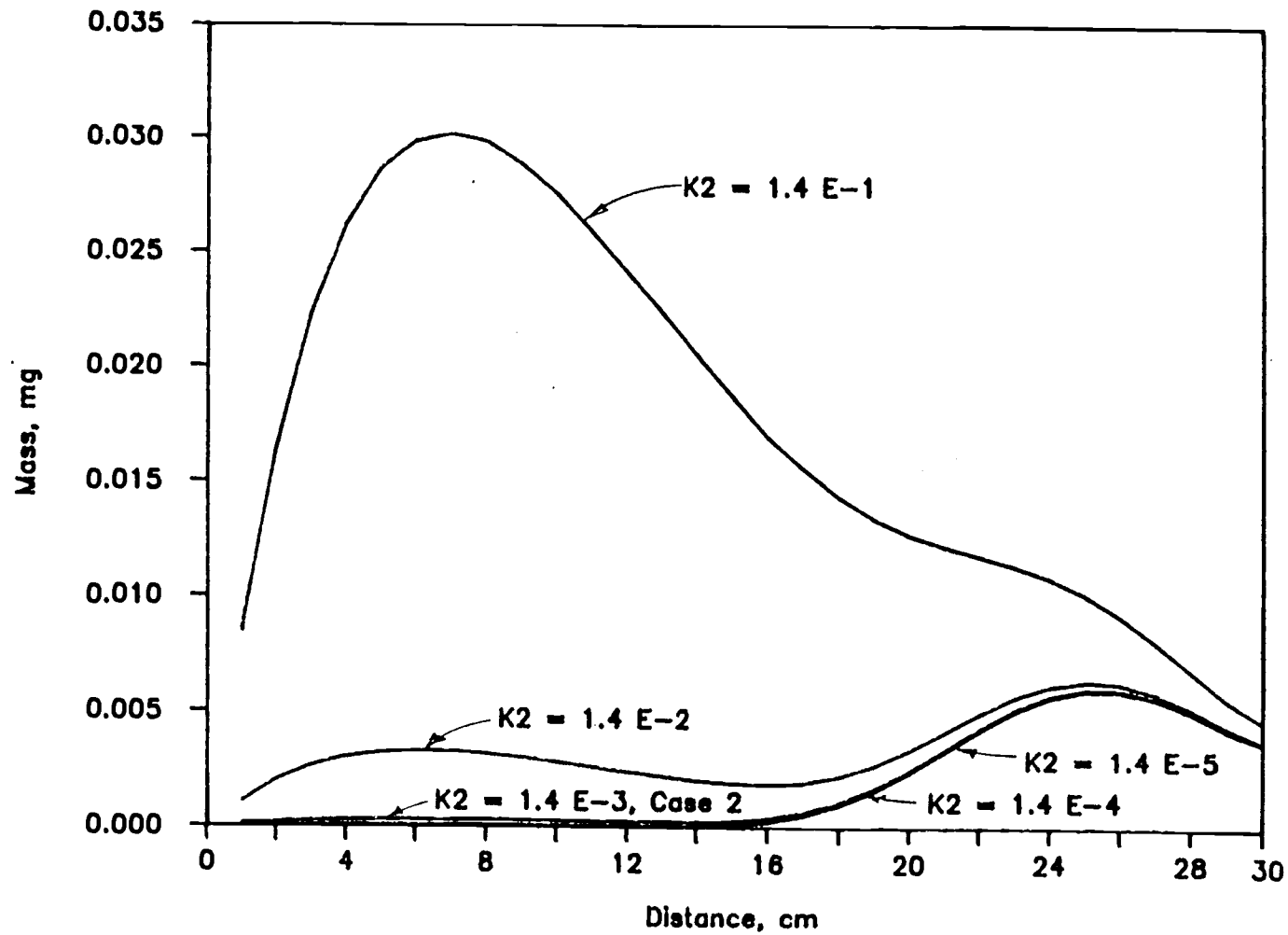


Figure 19. Liquid phase profile at time equals 25 hours varying  $K_2$  while maintaining the remaining Case 2 parameters.



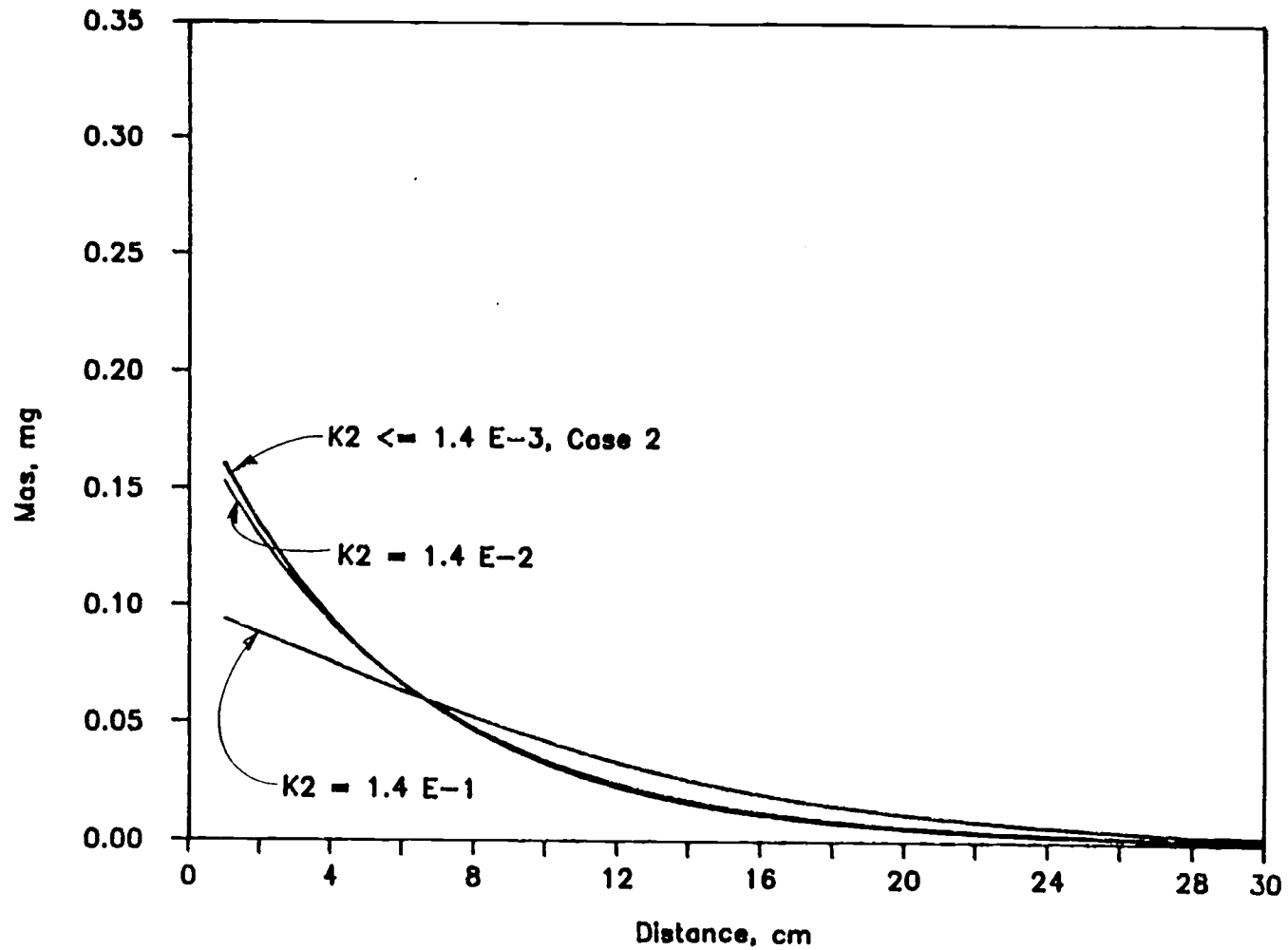


Figure 20. Solid surface phase profile at time equals 50 hours varying  $K_2$  while maintaining the remaining Case 2 parameters.

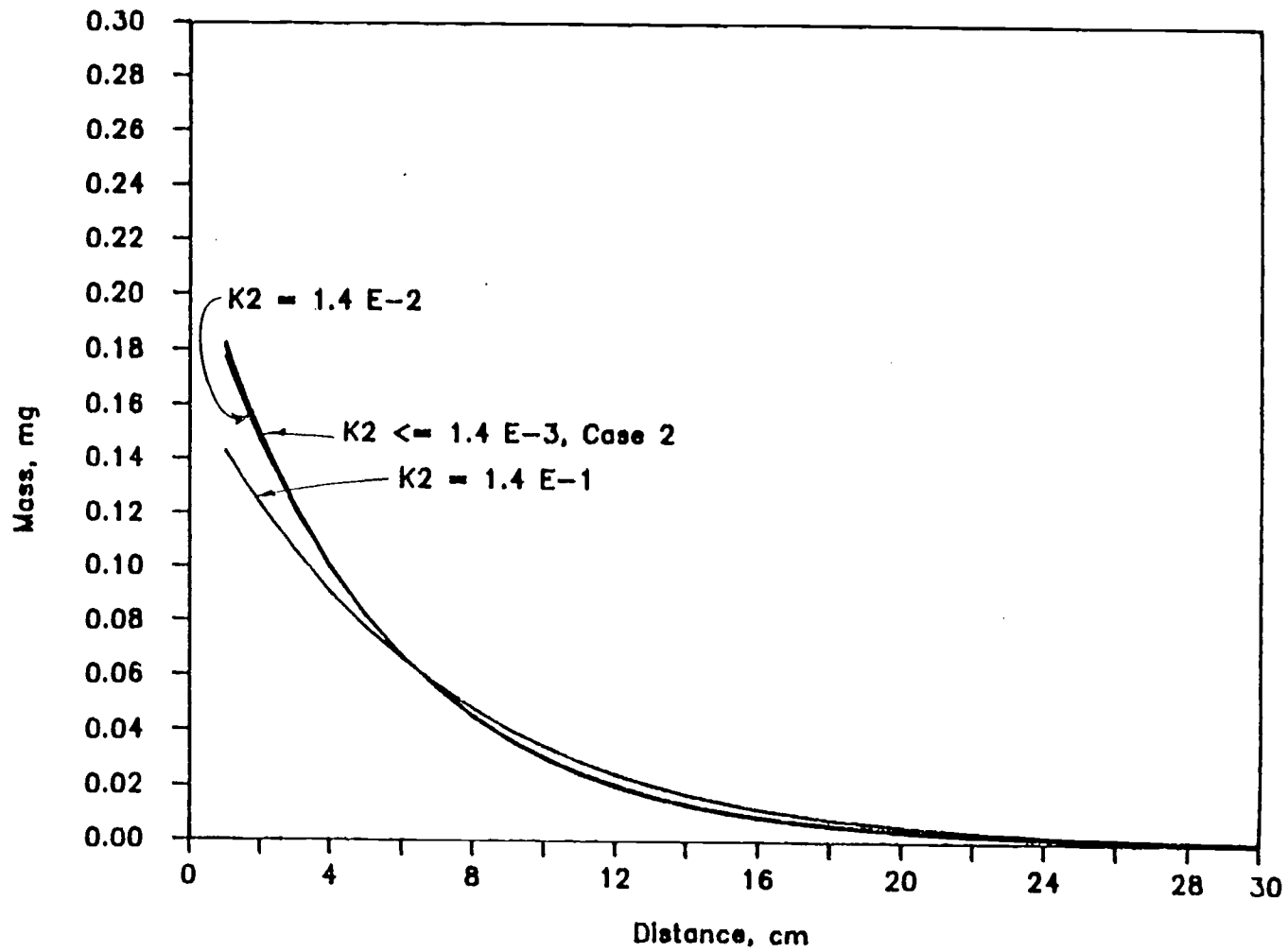


Figure 21. Solid interior phase profile at time equals 50 hours varying  $K_2$  while maintaining the remaining Case 2 parameters.

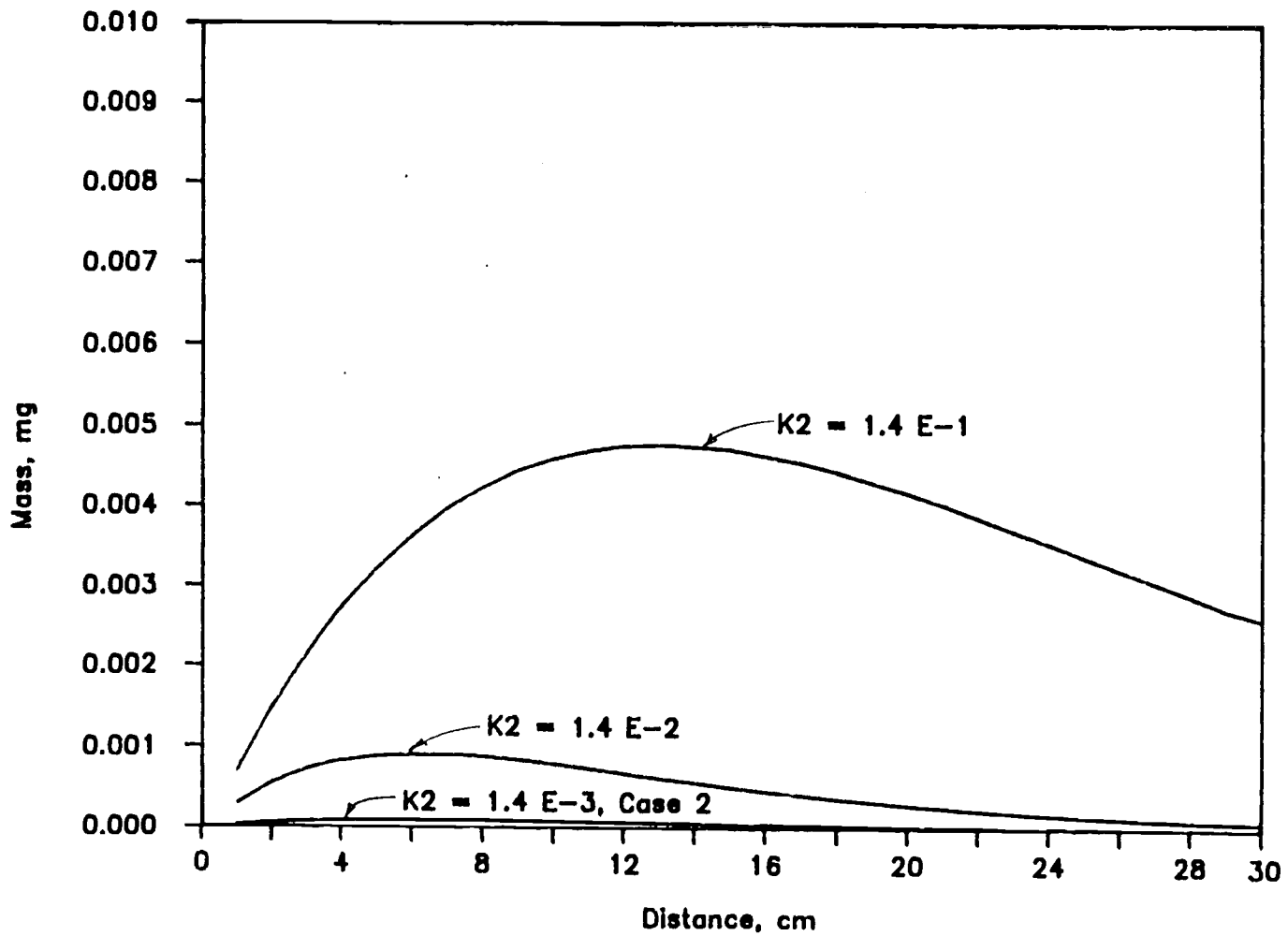


Figure 22. Liquid phase profile at time equals 500 hours varying  $K_2$  while maintaining the remaining Case 2 parameters.

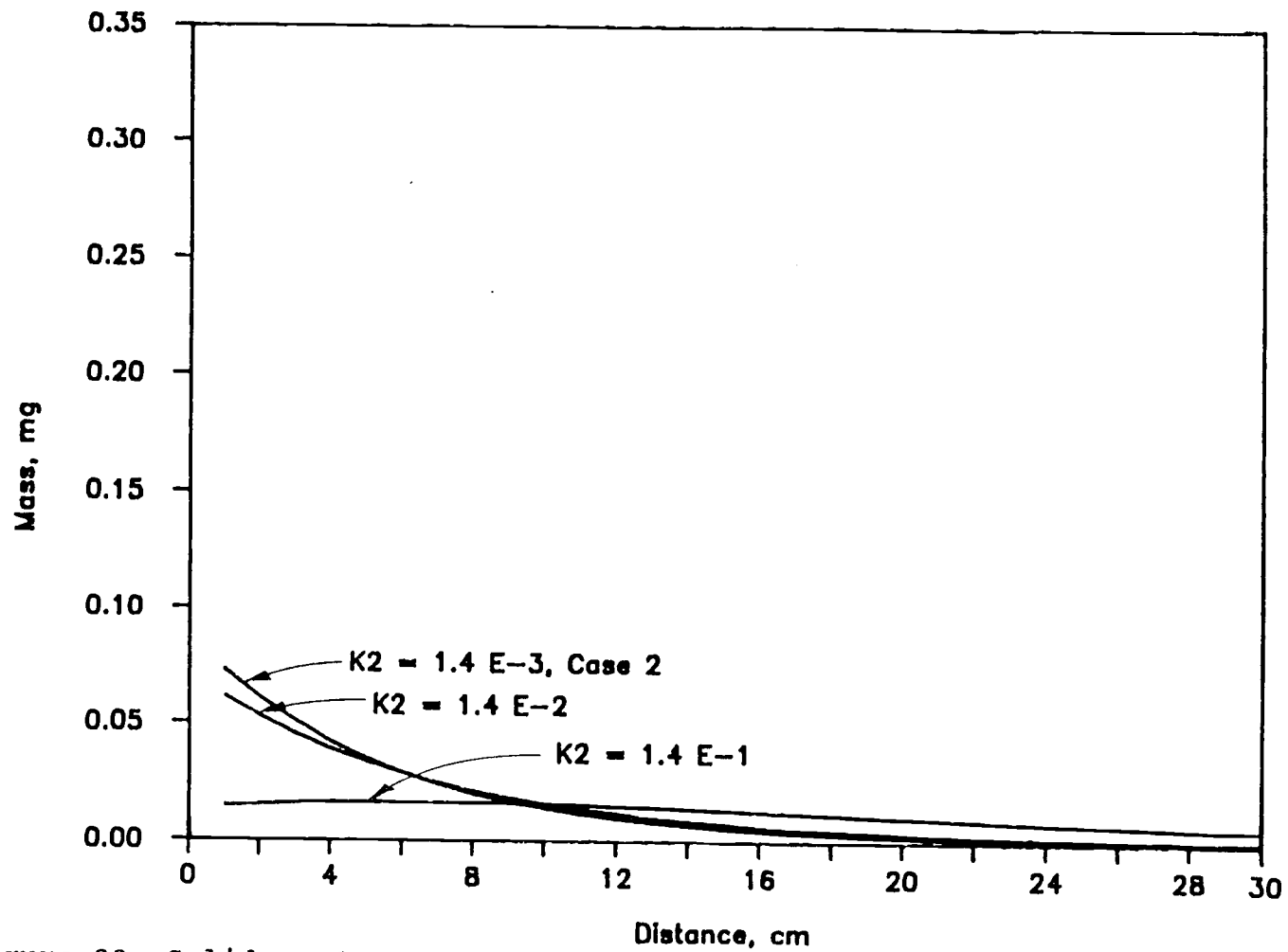


Figure 23. Solid surface phase profile at time equals 500 hours varying  $K_2$  while maintaining the remaining Case 2 parameters.

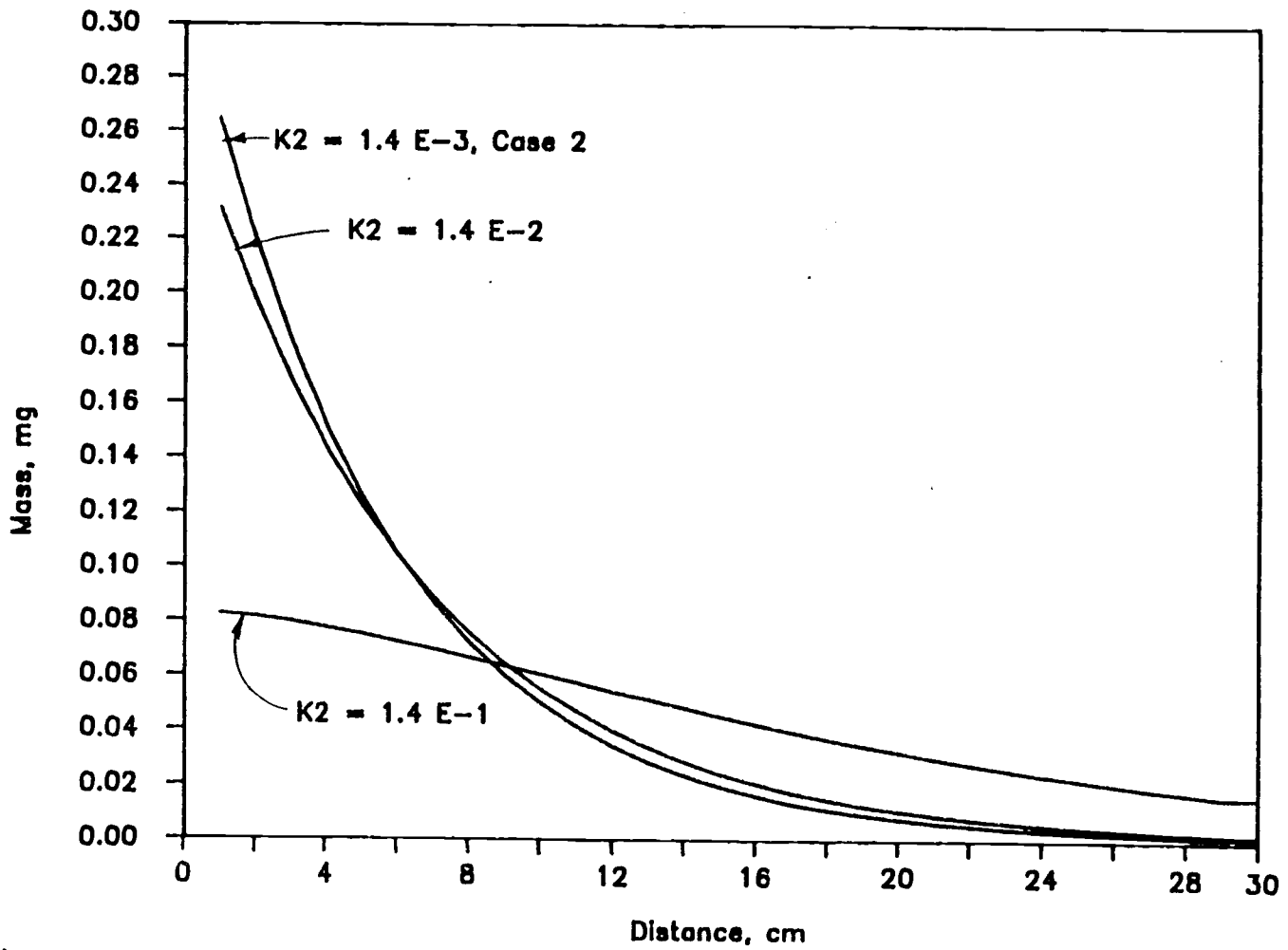


Figure 24. Solid interior phase profile at time equals 500 hours varying K2 while maintaining the remaining Case 2 parameters.

SOLID INTERIOR SORPTION PHENOMENA (K3, K4, and Simax)

As with K1 and S<sub>max</sub>, the interior sorption constant (K3), and the maximum available interior sites (Simax), show identical effects since they occur together in all equations used in the program. The results of varying K3 or Simax over 5 orders of magnitude are shown in Figures 25 through 30. The effects of K3 or Simax on the liquid phase are almost unnoticeable until after 25 hours (Figure 25). At this time, a decrease in the sorption rate (K3) or the available sites (Simax) allows the desorption processes (K2 and K4) to become evident.

At 50 hours (Figure 28), the solid surface became nearly saturated for smaller values of K3 and Simax and the liquid phase mass was quite low (Figures 26). This produced a gradient favorable for desorption. If K3 was small, then the desorption rate (K4) became more important. Since the solid surface was nearly saturated, rapid exchange takes place between the surface and the liquid phase as shown the 50 hour profile of the surface and liquid phase profiles (Figure 26 and 28). If the surface interior capacity is small, the solid has limited capacity to trap the compound in the non-labile interior phase. The dominating process was surface sorption and follows the concentration gradient

induced by the initial pollutant spike passing through the column.

If  $K_3$  was large, a high rate of interior and surface sorption was apparent. The compound was transferred almost immediately from the solid surface to the solid interior. This also creates a larger gradient between the liquid and solid surface phase enabling more total mass of the compound to sorb.

The physical processes represented by  $K_3$  and  $S_{\text{imax}}$  are also similar to those represented by  $K_1$  and  $S_{\text{smax}}$ .  $K_3$  is dependent on the sorbate-sorbent system, while  $S_{\text{imax}}$  is a function entirely of the sorbate. A low value of  $S_{\text{imax}}$  could be visualized as a sand with a coating of organic material. This type of soil may have a moderate to high surface capacity, but almost no internal capacity. One would expect the non-labile process to be relatively unimportant. It follows that residence times for hydrophobic organic compounds would be much shorter for this type of soil because desorption from the surface begins to be important after the initial spike has passed through the column and the driving force is greatest toward the liquid phase.

Interior desorption was controlled by the magnitude of the interior desorption rate constant ( $K_4$ ). The results of varying  $K_4$  over 5 orders of magnitude are shown in Figures 31 through 37. Because

of the time required for sorption to the solid interior, varying  $K_4$  has little effect on the liquid phase mass for the first 25 or more hours (Figure 31). At 50 hours (Figure 32), a slight increase in the liquid phase mass was observed for higher values of  $K_4$  in the upper layers after the pollutant spike has left the column. Decreasing  $K_4$  by one or two orders of magnitude has little effect on the liquid phase at 50 hours as shown in Figure 32.

The interior desorption constant ( $K_4$ ) had significant effects on the liquid phase mass at longer times periods. Compounds having high interior desorption values tend to leach out of the soil more quickly and at higher liquid concentrations than those with a low desorption constant.  $K_3$  and  $K_4$  represent a measure of the compound's affinity for the sorbate on an intermediate term basis. Comparing Figures 22 and 33, the effect of increasing  $K_4$  on the liquid phase was shown to be similar to that of increasing  $K_2$ . The trend was less evident when  $K_4$  was increased by one order of magnitude and almost identical when increased by two orders of magnitude.

The effect of  $K_4$  on the surface phase was more pronounced. An increase of two orders of magnitude in  $K_4$  leads to a much steeper surface phase profile with higher peak liquid phase masses at relatively early times (Figure 34). This was due to the high rate of



exchange between the solid surface and interior. As the supply in the interior was exhausted, the profile begins to flatten and eventually approaches low values. An increase in one order of magnitude follows the same trend, but over a much longer time span (Figure 35). Decreasing  $K_4$  had little effect on the surface profile.

The interior phase profile mimics the surface phase profile at any given time because of its dependence on the concentration gradient that exists between surface and interior. Over time the profile of the interior phase begins to flatten out and move toward lower levels at high  $K_4$  values due to the increased rate of desorption (Figure 36 and 37). Decreasing  $K_4$  had little effect on the interior profile.

The results from this analysis indicate that desorption from the interior and surface are extremely slow processes for even slightly hydrophobic compounds. This indicates a long residence time in the upper layers of the soil column and slow leaching at low concentrations into the liquid phase. Most of the compound moves a short distance and is resorbed tending to equalize the distribution of the compound at ever decreasing levels, but it may take decades for this process to occur for some highly hydrophobic compounds.

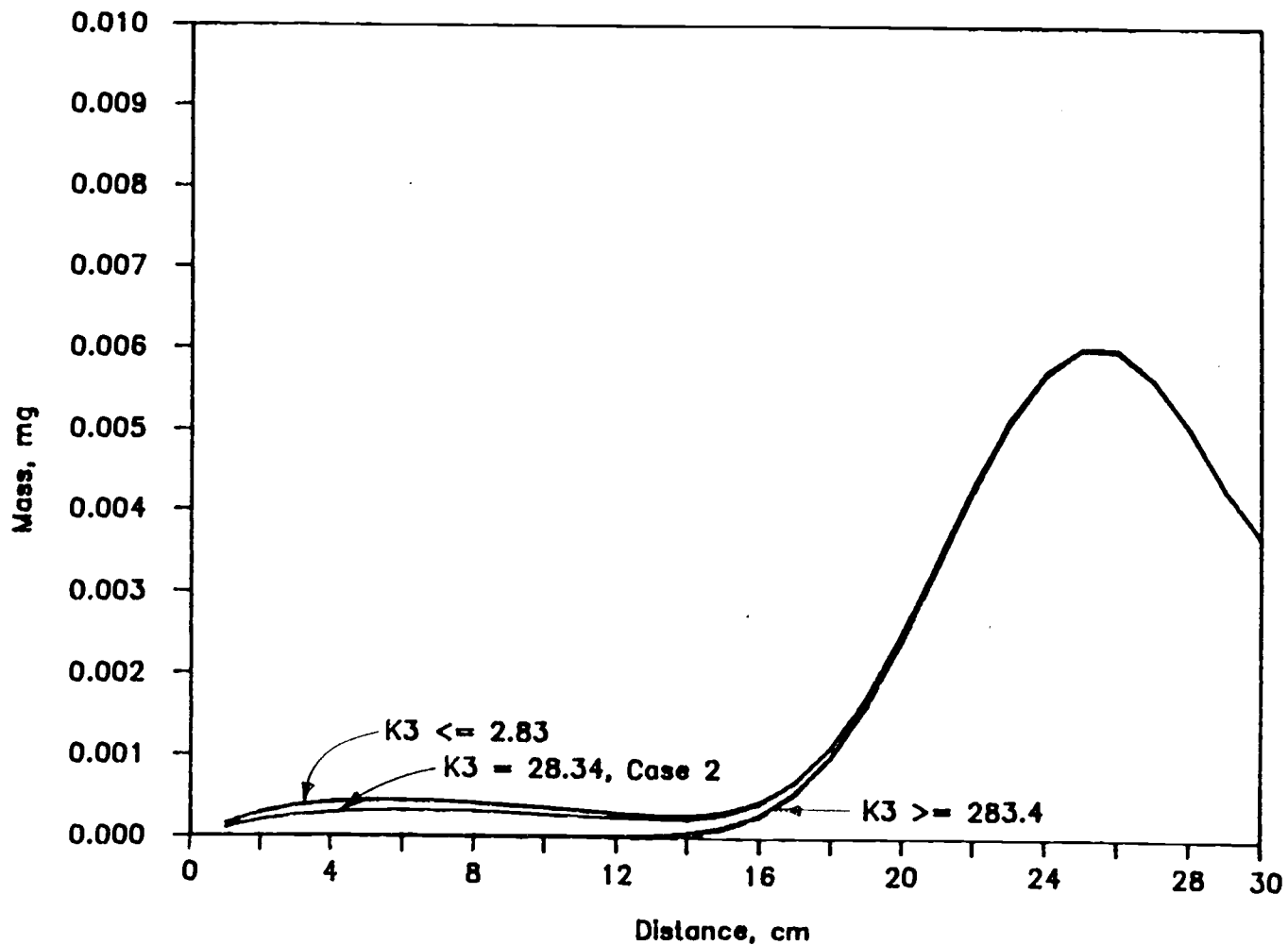


Figure 25. Liquid phase profile at time equals 25 hours varying K3 while maintaining the remaining Case 2 parameters.

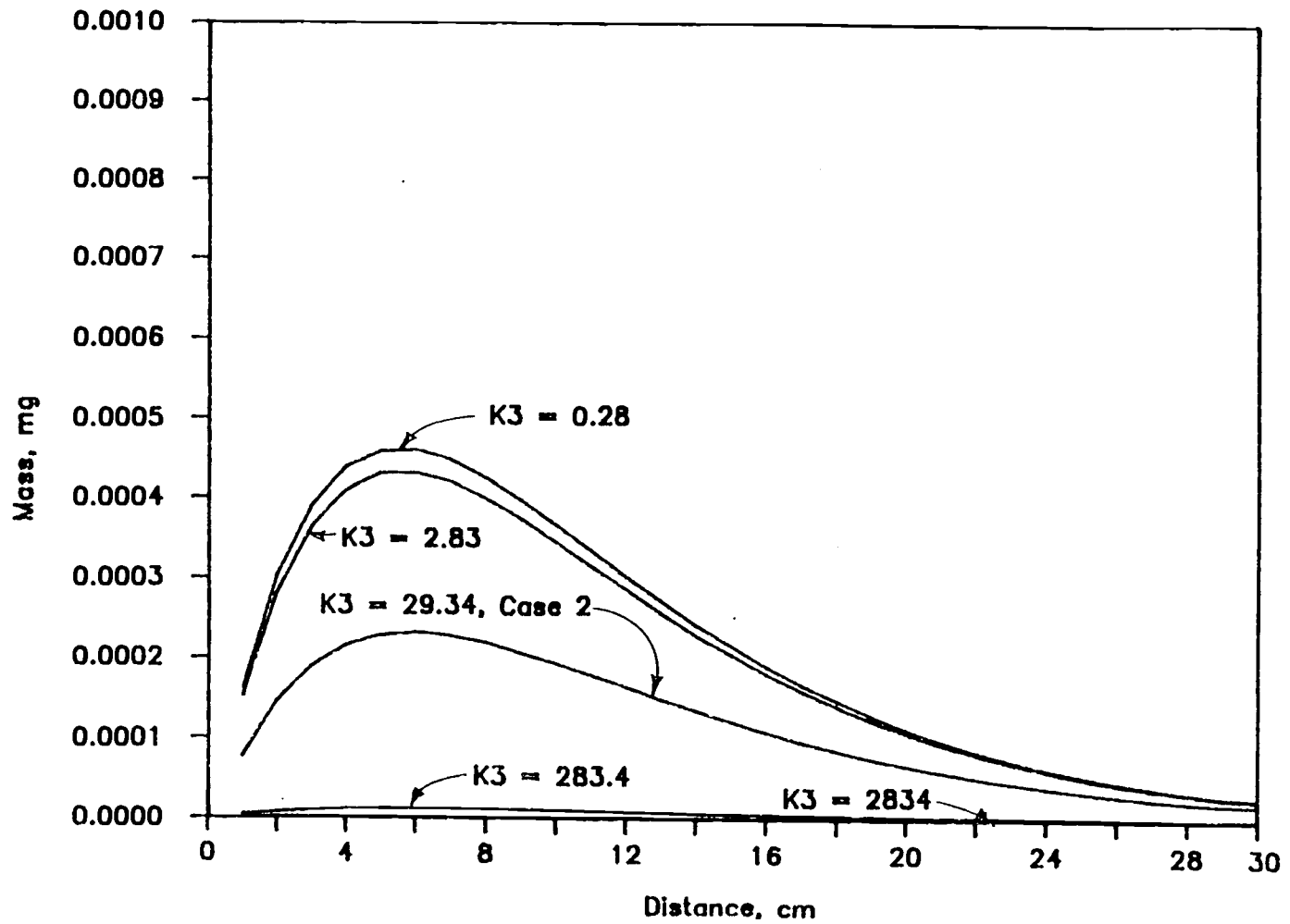


Figure 26. Liquid phase profile at time equals 50 hours varying  $K3$  while maintaining the remaining Case 2 parameters.

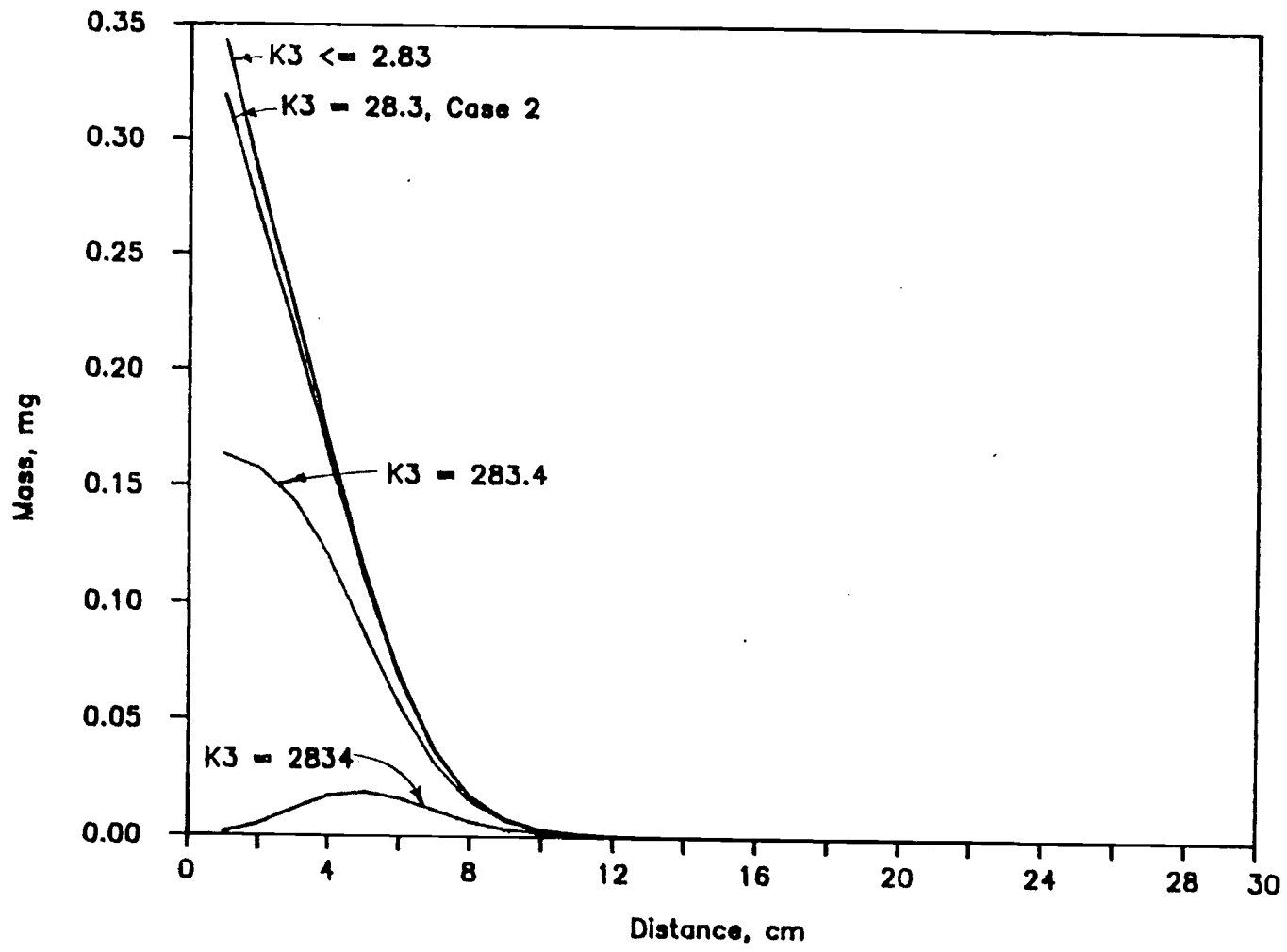


Figure 27. Solid surface phase profile at time equals 5 hours varying  $K3$  while maintaining the remaining Case 2 parameters.

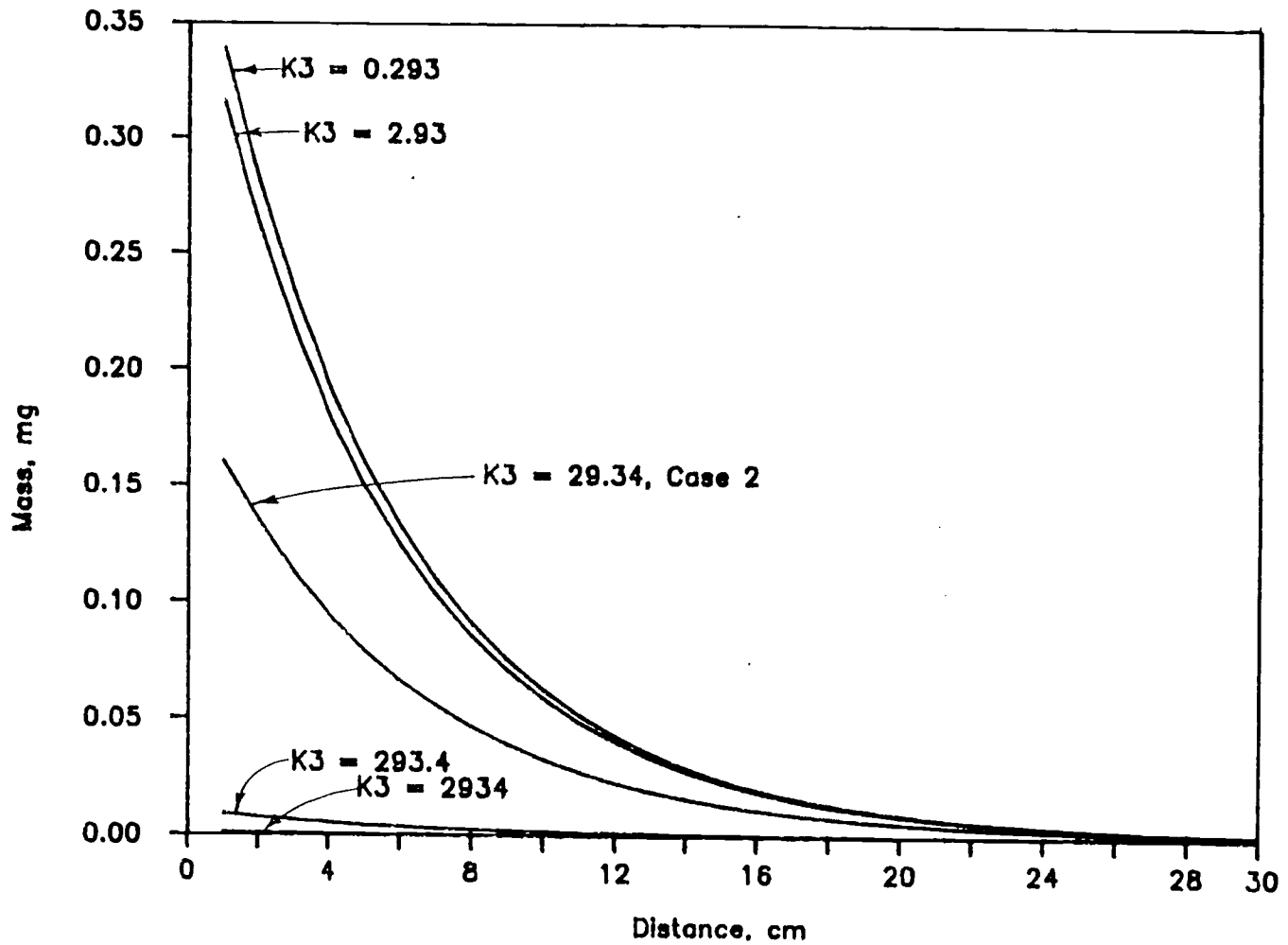


Figure 28. Solid surface phase profile at time equals 50 hours varying  $K3$  while maintaining the remaining Case 2 parameters.

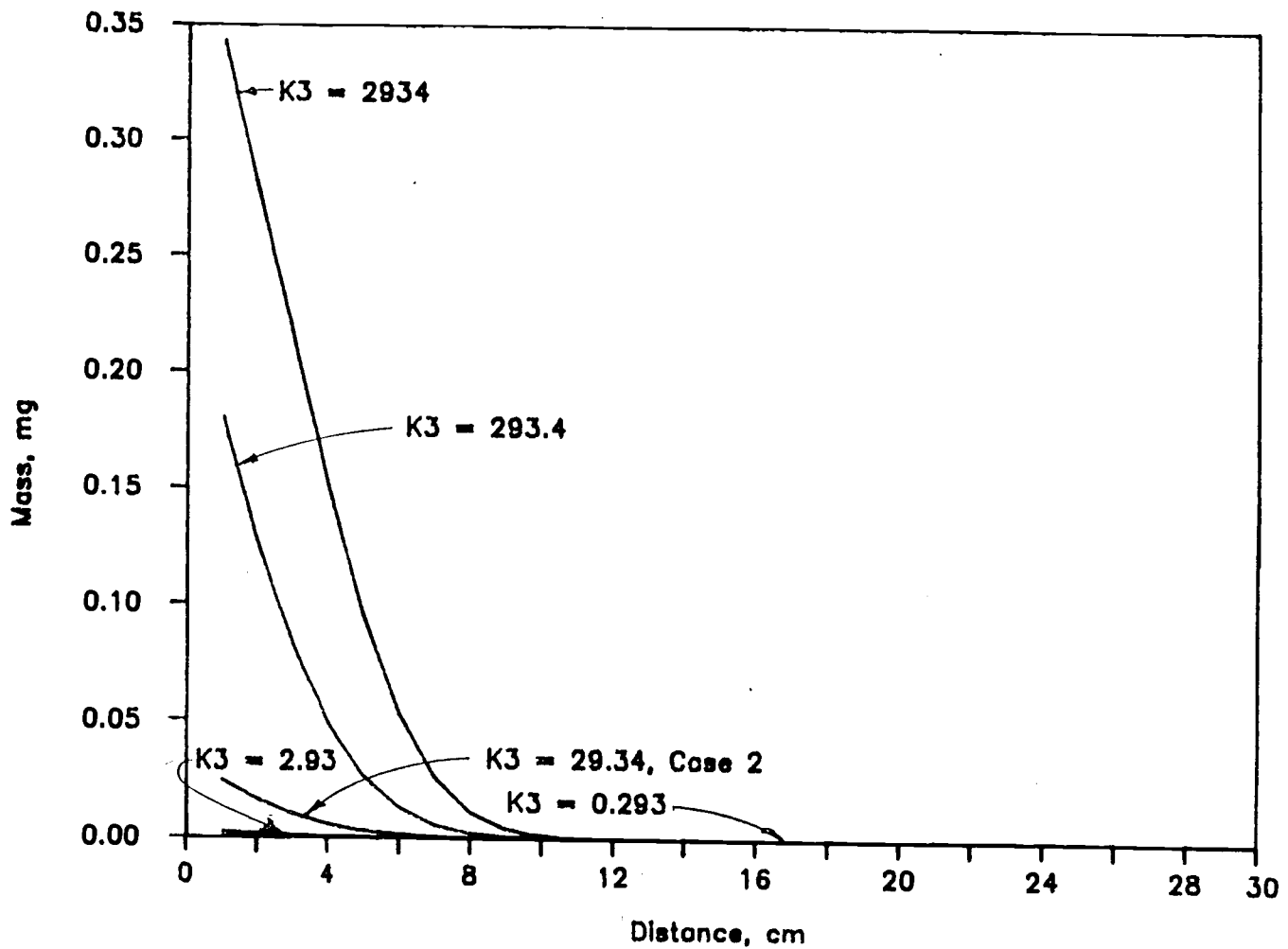


Figure 29. Solid interior phase profile at time equals 5 hours varying  $K3$  while maintaining the remaining Case 2 parameters.

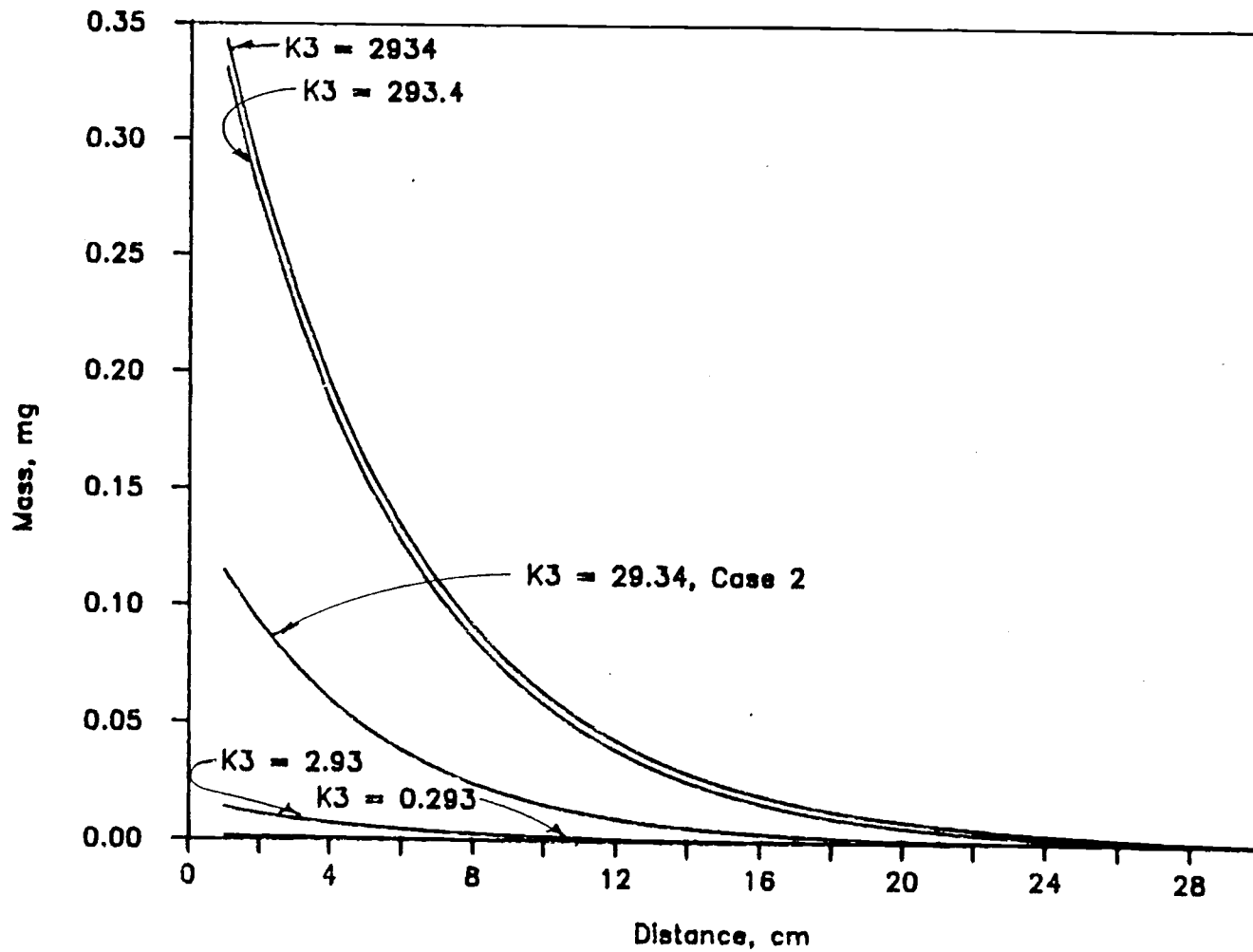


Figure 30. Solid interior phase profile at time equals 50 hours varying  $K3$  while maintaining the remaining Case 2 parameters.

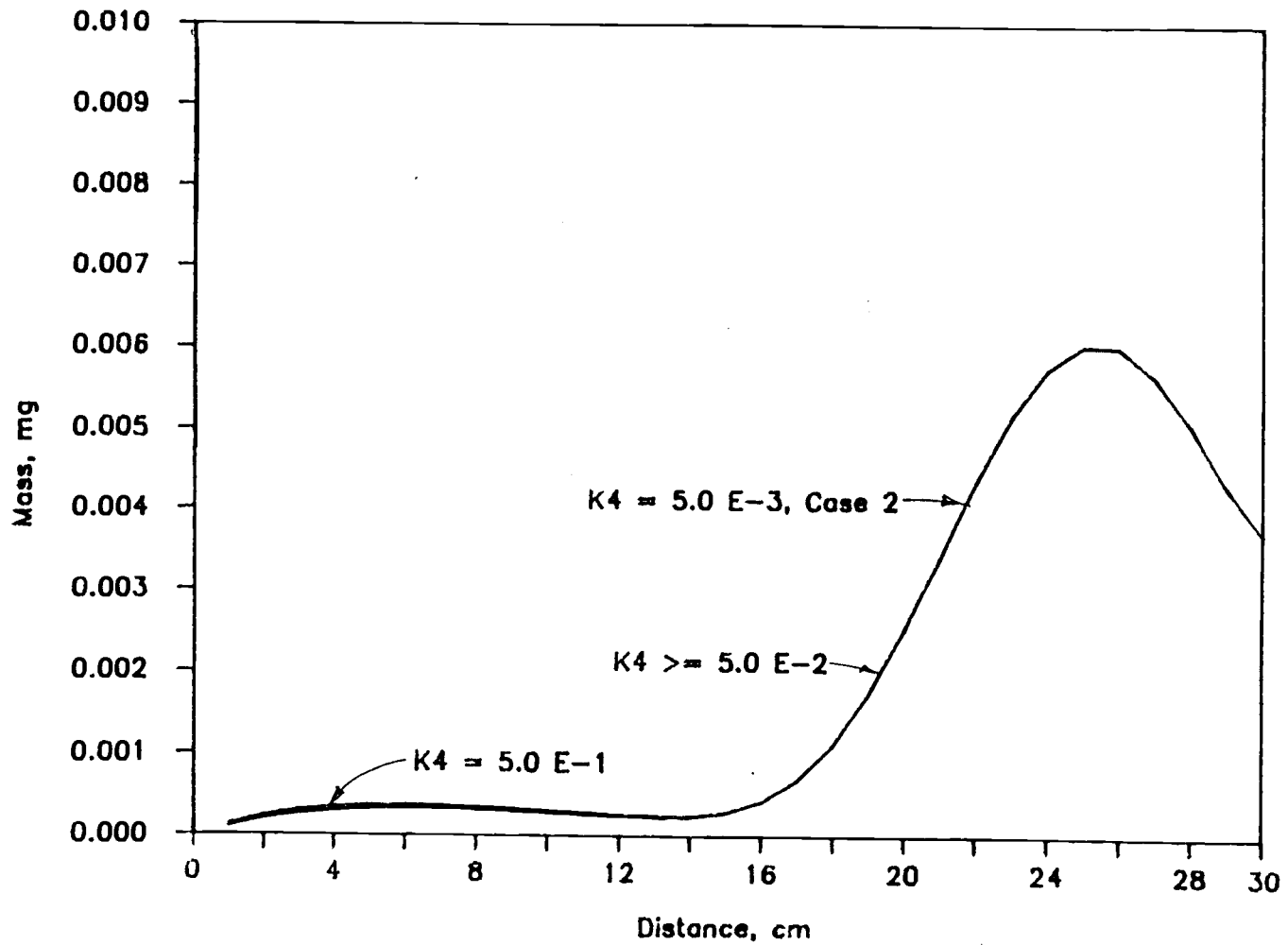


Figure 31. Liquid phase profile at time equals 25 hours varying  $K_4$  while maintaining the remaining Case 2 parameters.



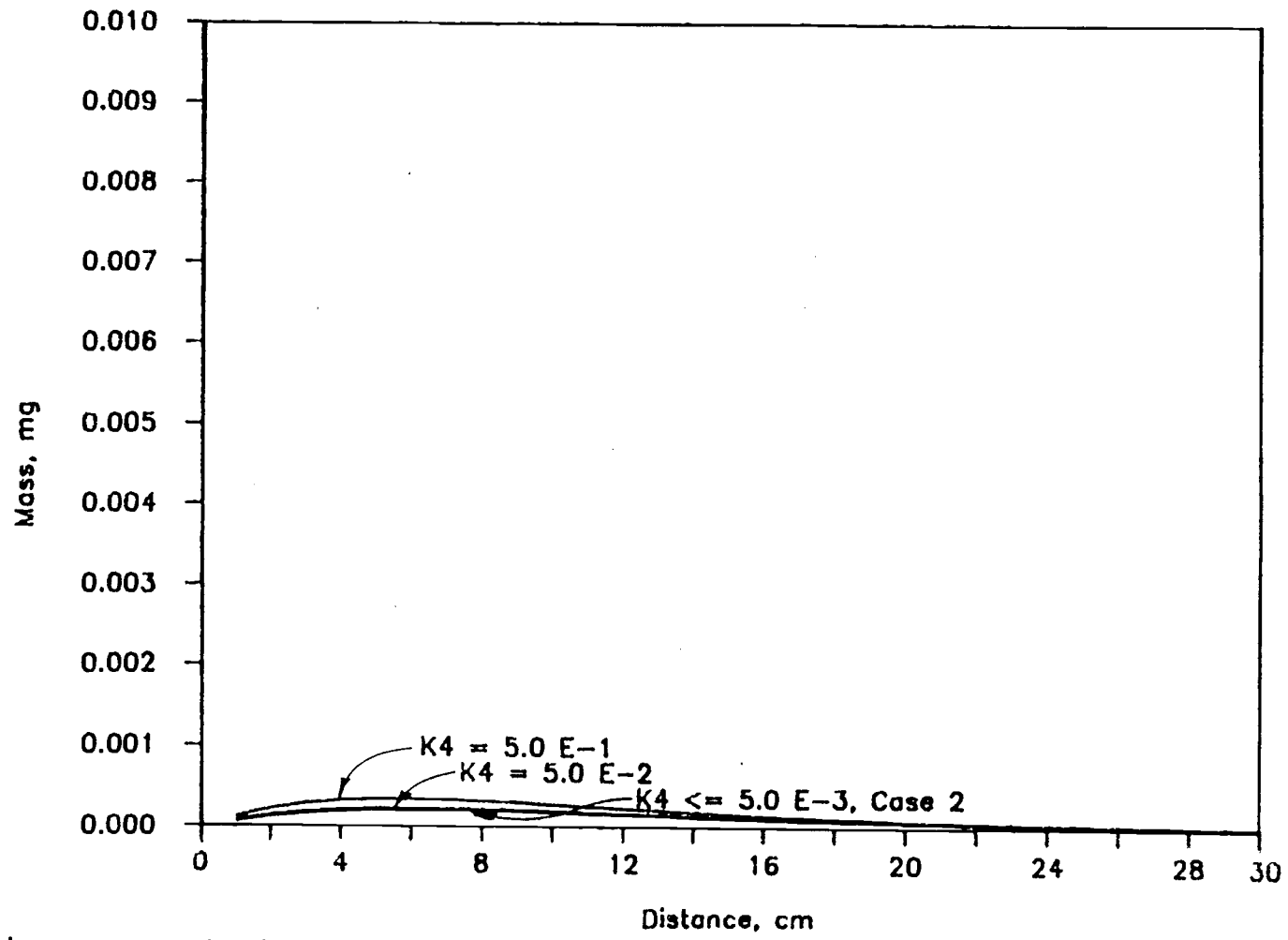


Figure 32. Liquid phase profile at time equals 50 hours varying  $K4$  while maintaining the remaining Case 2 parameters.

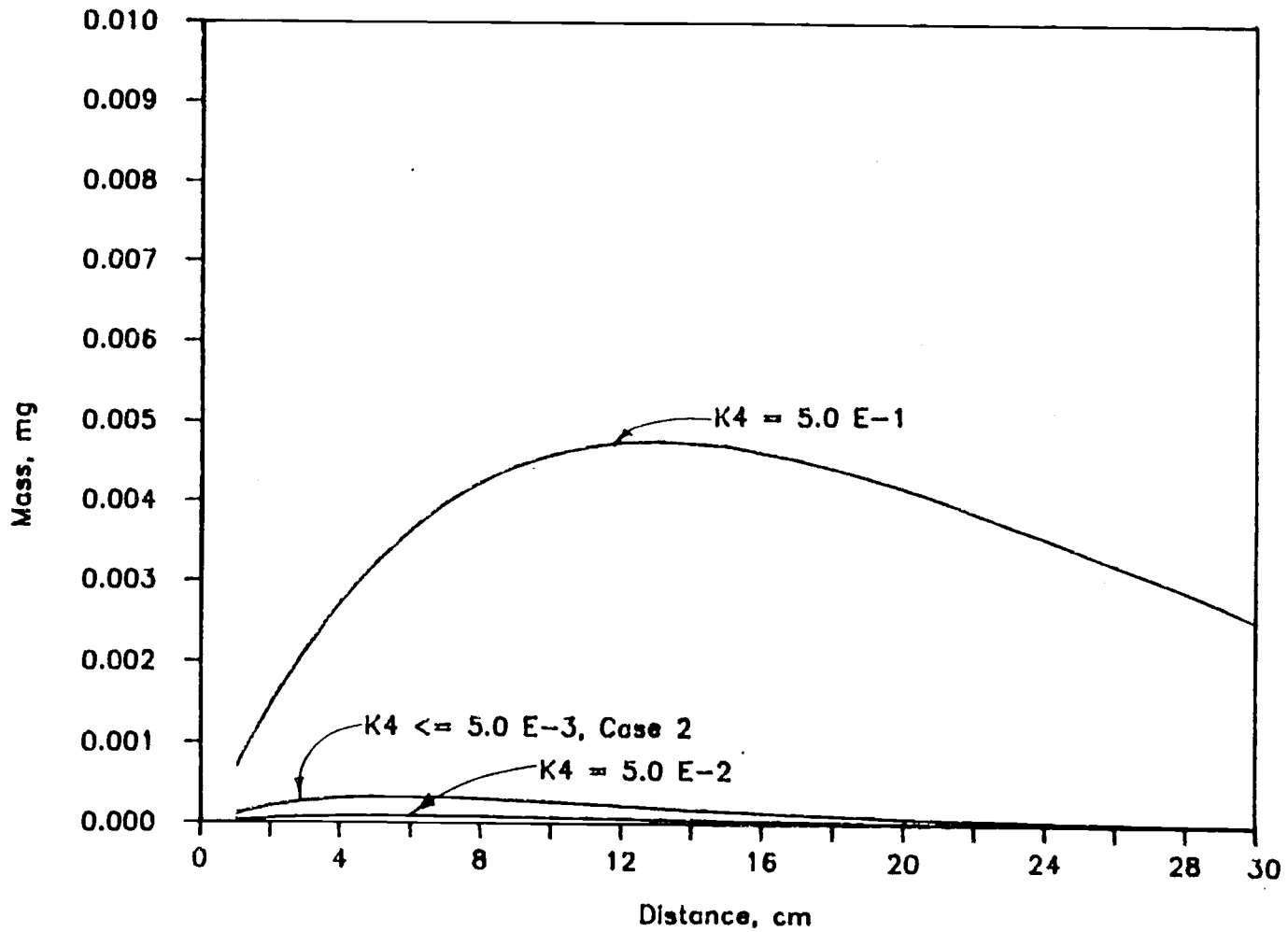


Figure 33. Liquid phase profile at time equals 500 hours varying  $K4$  while maintaining the remaining Case 2 parameters.

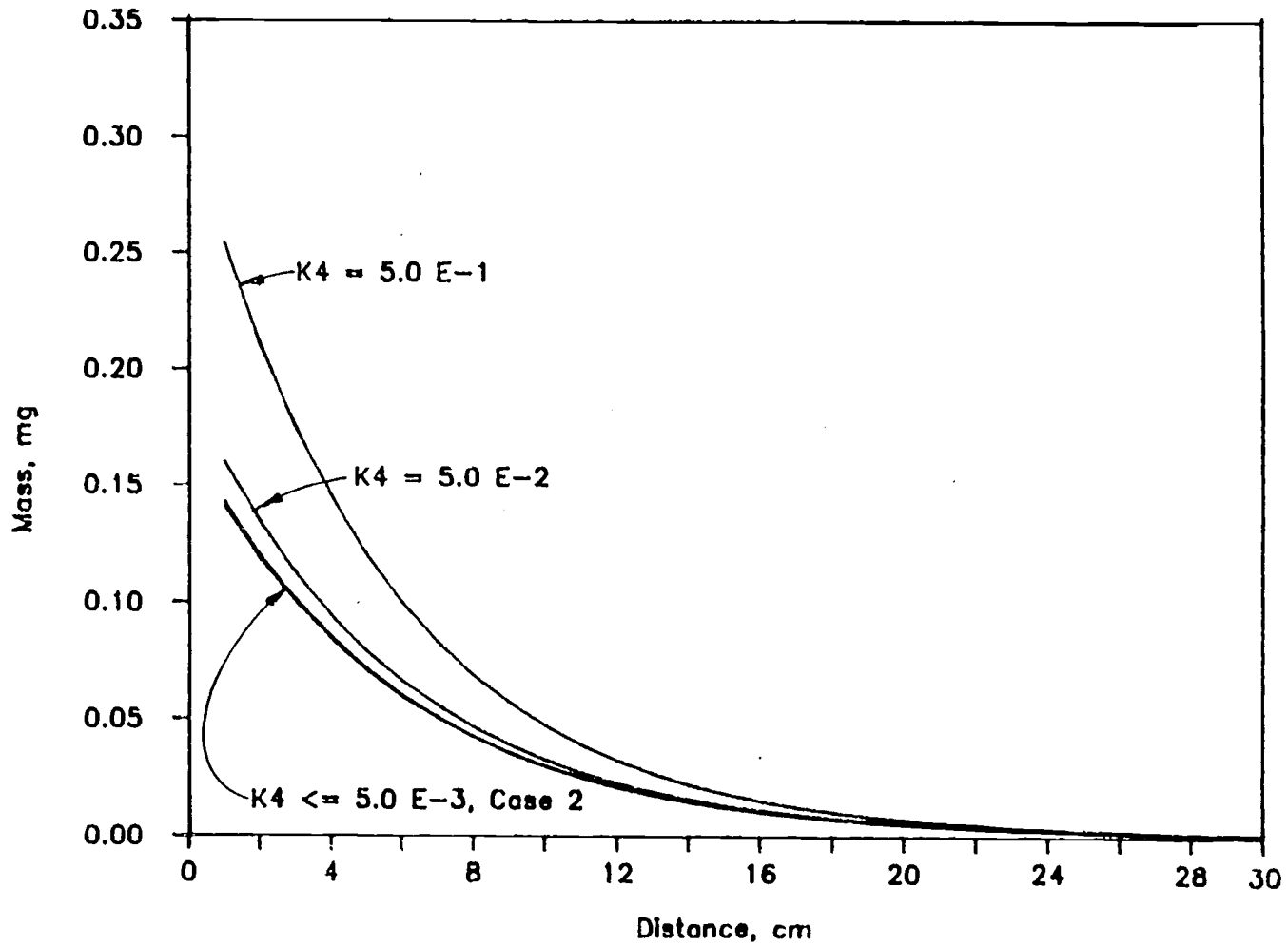


Figure 34. Solid surface phase profile at time equals 50 hours varying  $K4$  while maintaining the remaining Case 2 parameters.

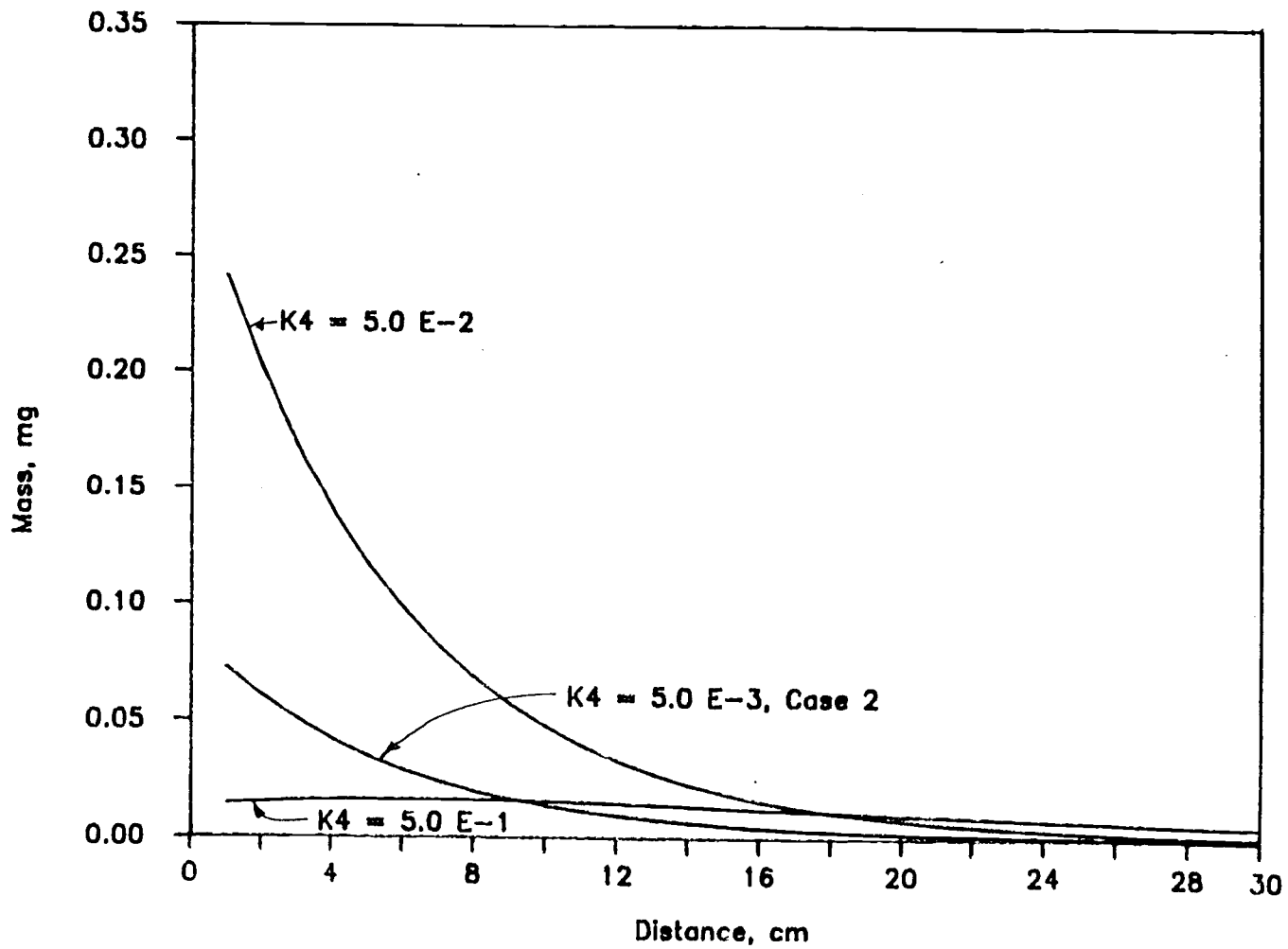


Figure 35. Solid surface phase profile at time equals 500 hours varying K4 while maintaining the remaining Case 2 parameters.

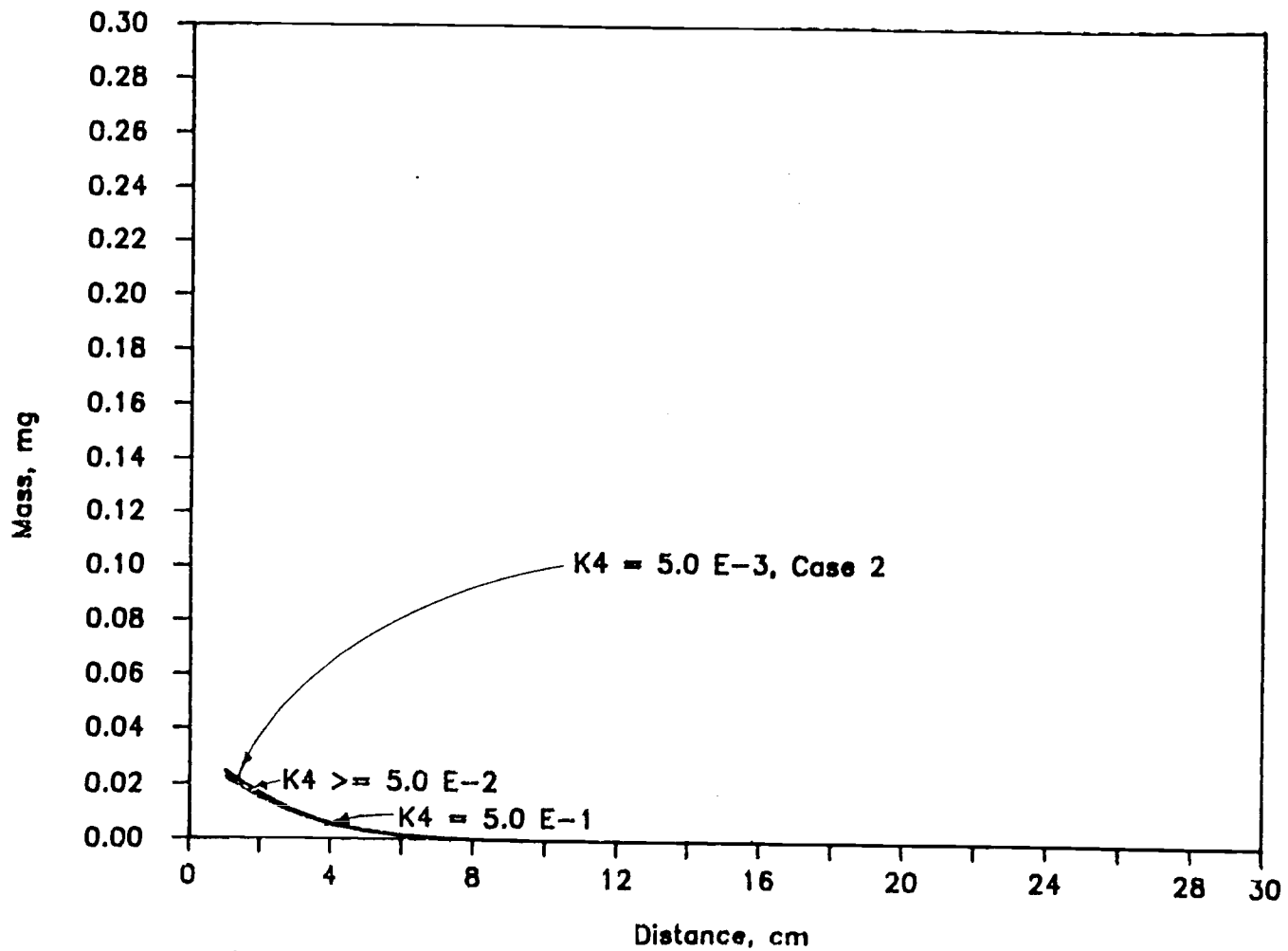


Figure 36. Solid interior phase profile at time equals 5 hours varying K4 while maintaining the remaining Case 2 parameters.

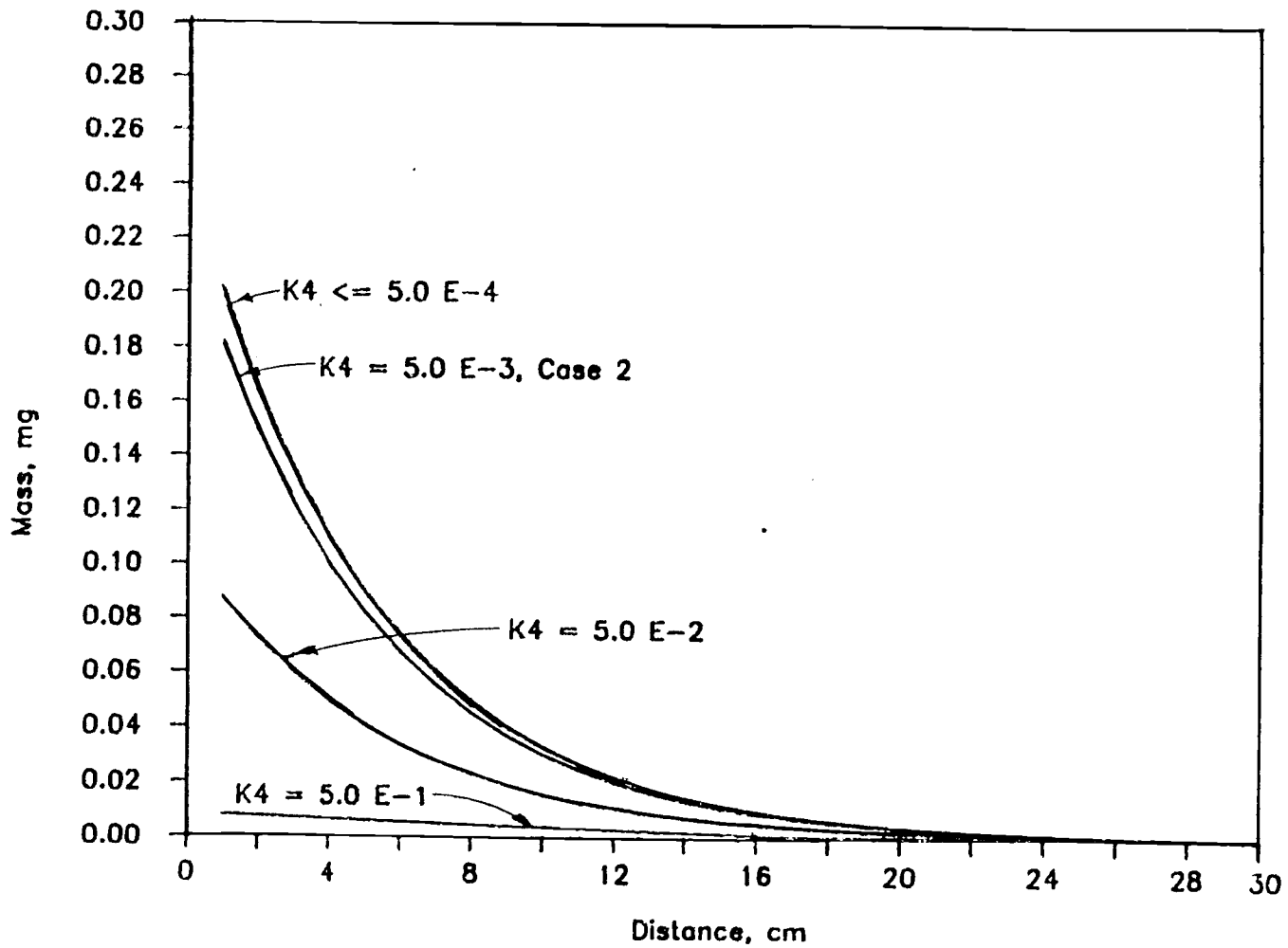


Figure 37. Solid interior phase profile at time equals 50 hours varying  $K4$  while maintaining the remaining Case 2 parameters.

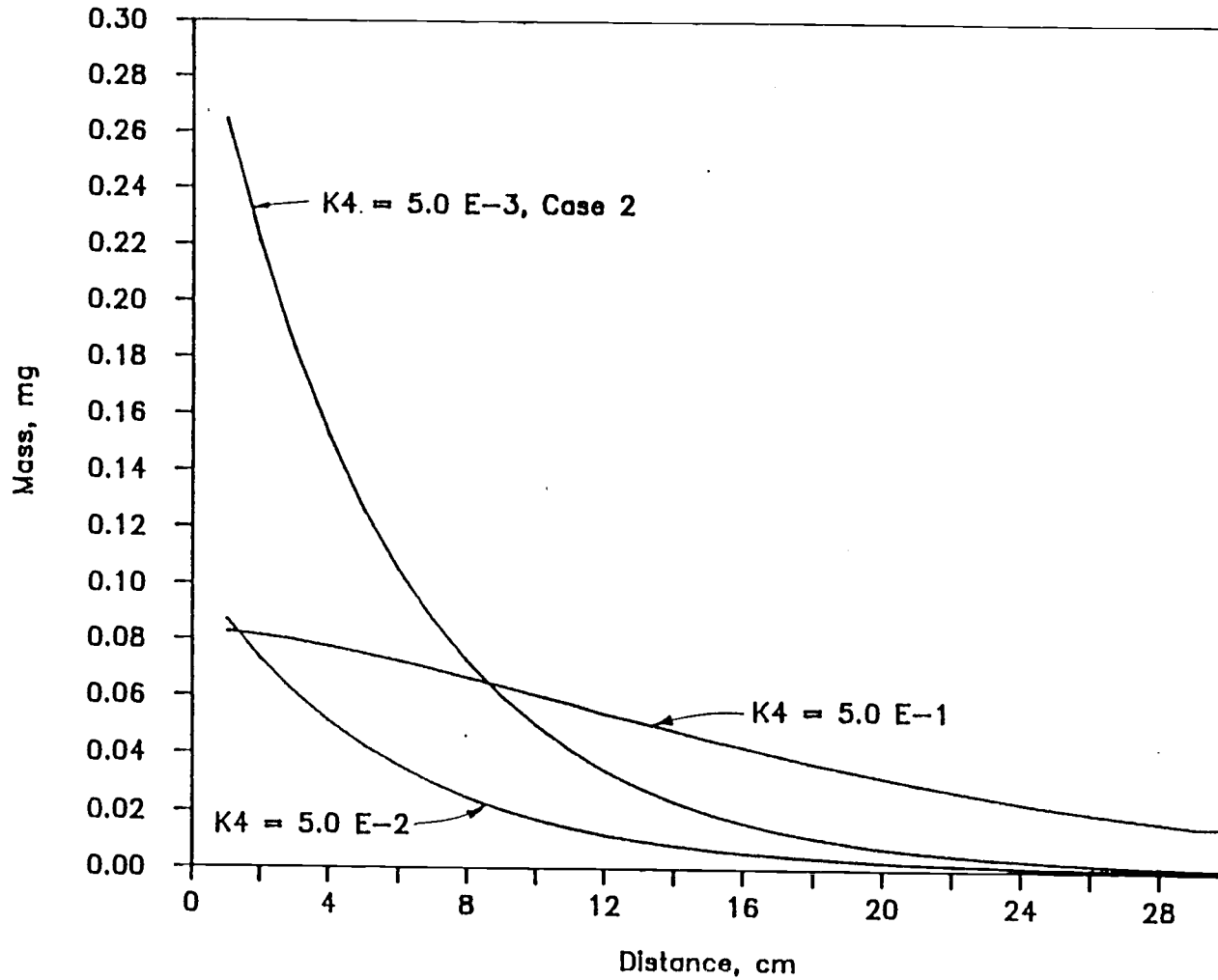


Figure 38. Solid interior phase profile at time equals 500 hours varying  $K4$  while maintaining the remaining Case 2 parameters.

## ANALYSIS OF THE BACTERIAL PHASE

Previous discussions have described processes that affect only non-living sorbate. The sorption and desorption constants and the surface and interior capacities were varied in order to identify the effect of each parameter. In the following sections, the possible effects of the bacterial component of soil systems including sorption and desorption from the bacteria and two mechanisms for metabolism of the pollutant; 1) degradation from the liquid phase fraction and, 2) degradation of the fraction sorbed to the bacterial phase are described. The solids concentration was set at 1% of the total soil mass to represent the organic solid fraction of a typical soil. This represents a realistic organic content for many soils.

## BACTERIAL PHASE SORPTION AND DEGRADATION (K<sub>5</sub>, K<sub>6</sub>, K<sub>b</sub>, AND B<sub>smax</sub>)

Sorption to bacteria was treated as a one box model. Due to a lack of information about bacterial sorption, sorption and desorption constants equal to those chosen for the solid phase processes were used. Although these values may be a low estimate of the actual values for bacteria, they represent an acceptable starting point for the analysis and serve



as a basis for comparison to the effects of sorption to soil solid phases.

Case 3 is the base case for the analyses examining bacterial sorption and desorption (Table 1). The results of increasing the bacterial sorption constant ( $K_5$ ) by one and two orders of magnitude are shown in Figures 39 through 47. Increasing the bacterial sorption rate produced a lag in the liquid phase mass profile. This effect was caused by a relatively large fraction of the liquid phase mass that was resolubilized due to rapid desorption from the bacteria (Figures 39 through 41). The delay in the progression of the profile resulted from the reaction time for the pollutant sorbing to the bacteria, and then desorbing back into the liquid phase. Sorption to the solid surface and interior phases are only slightly less than for Case 2.

Comparing the liquid phase profiles shown in Figures 39 and 40 and the bacterial phase profiles shown in Figures 42 and 43 revealed that the peak liquid phase mass followed the peak bacterial phase sorbed mass. The permeable nature of bacteria tends to support these results; however, the chemical composition of bacterial cells suggests that, once sorbed, the compound would tend to be tightly bound inside the cell. This hypothesis was examined by setting the desorption constant,  $K_6$ , to zero and

setting the adsorption constant,  $K_5$ , to two orders of magnitude larger than in Case 3.

When high bacterial sorption rates and zero desorption from the bacterial phase are considered (Case 4), the peak liquid phase mass was decreased radically compared to low bacterial sorption rates with desorption (Case 3) as shown in Figures 39 and 40. Case 5 includes bacterial degradation. The bacterial phase almost immediately reached saturation (Figure 42) and then slowly begins to decrease as degradation takes place (Figures 43 through 45). After ten hours, the bacteria have reduced the liquid phase mass to a low level (Figure 40). As expected, this process reduced the fraction of pollutant sorbed to the solid phase as shown in Figures 46 and 47. This decrease was due to the reduced availability of pollutant to the solid phase.

Sorption and metabolism by the bacterial phase had a significant effect on the fate of pollutants. Reducing the fraction of the pollutant sorbed to the solid phase may help prevent long term leaching into the ground water by binding pollutant in the bacterial phase. This represents destruction of the contaminant if the compound is subject to degradation in this manner, instead of sorption and eventual resolubilization that occurs when the solute is sorbed to a non-bacterial solid mass.

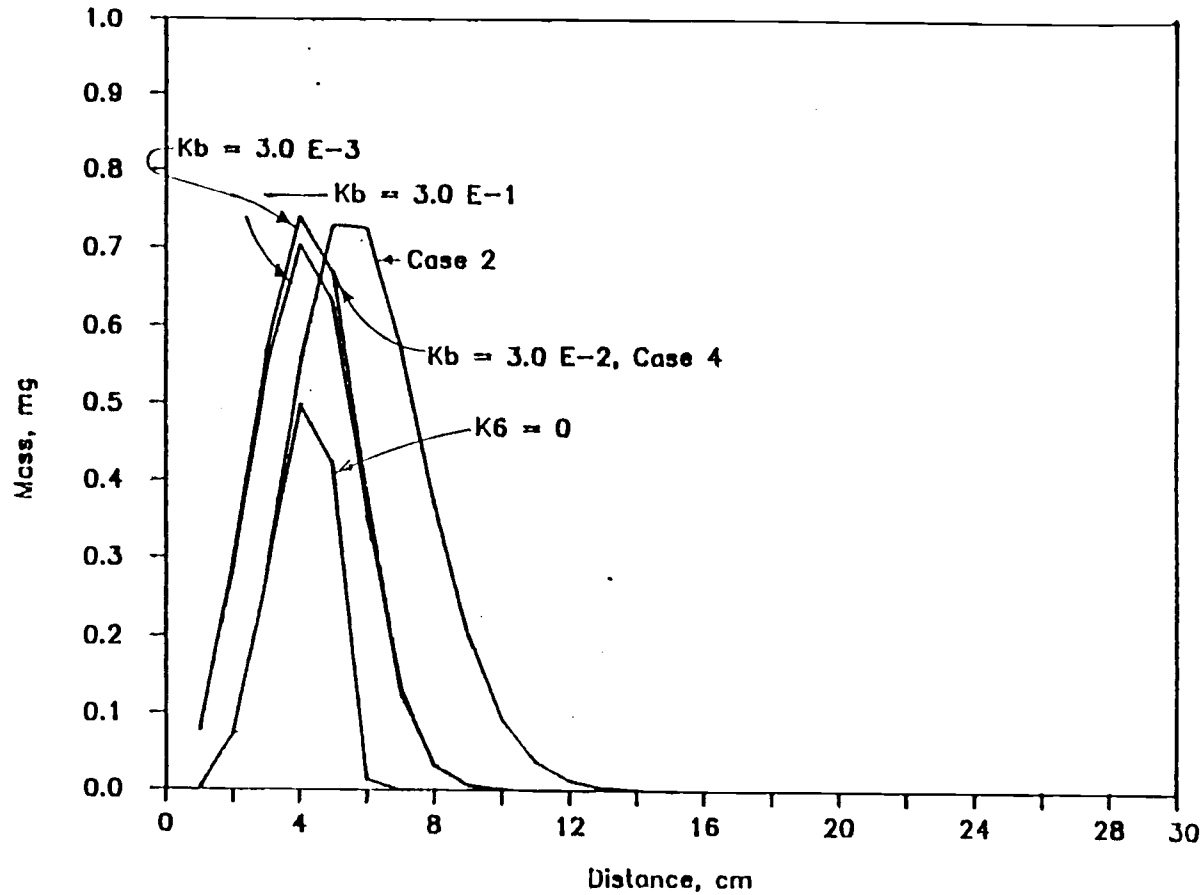


Figure 39. Liquid phase profile at time equals 5 hours for advection, dispersion, sorption to soil solids, sorption to bacterial solids (described by  $K_5$  and  $K_6$ ) and biodegradation (described by  $K_b$ ). The Case 2 curve describes advection, dispersion and sorption to soil solids. The remaining curves reflect changes to a single variable ( $K_b$  or  $K_6$ ) from the parameters described for Case 4.

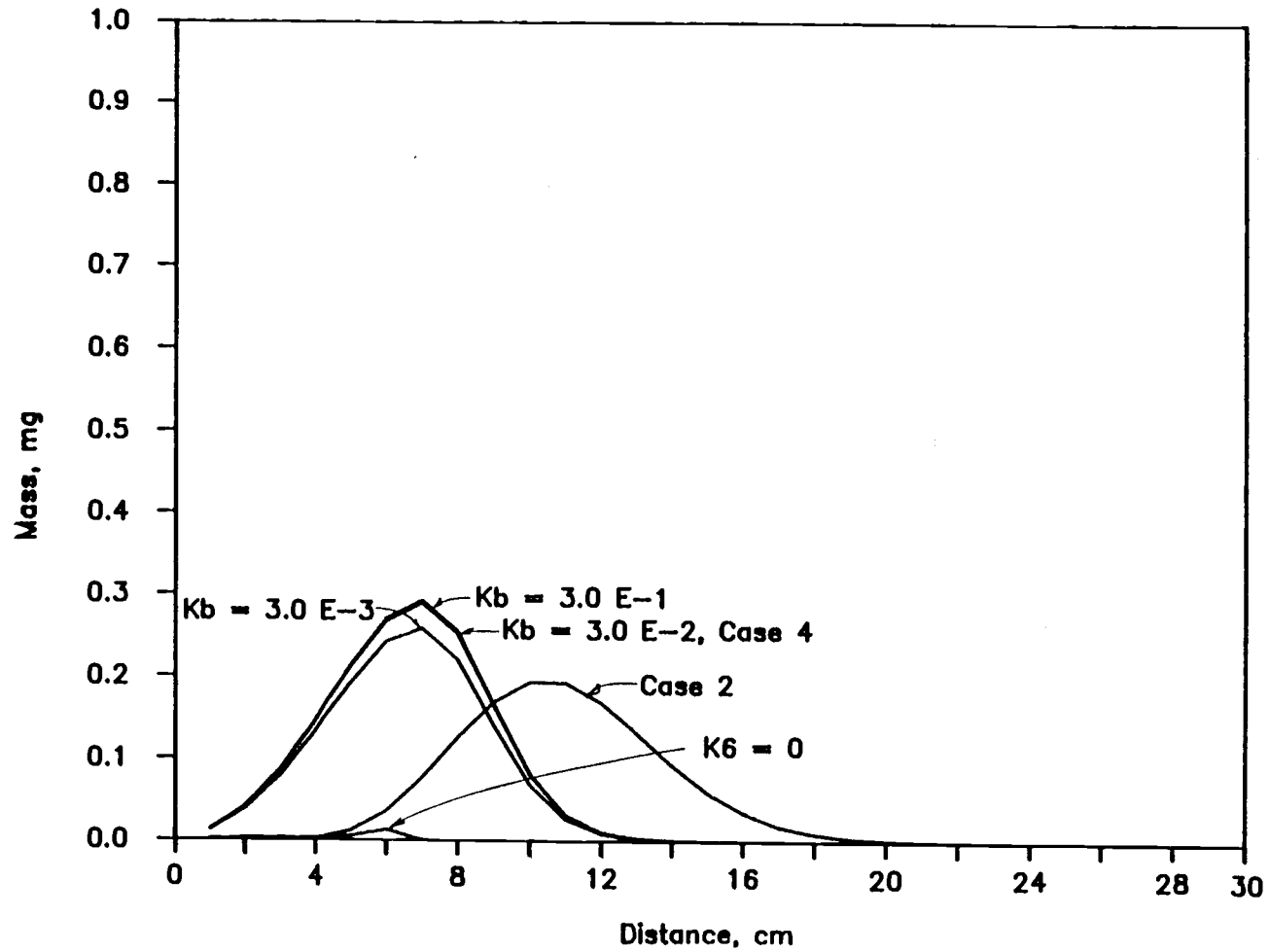


Figure 40. Liquid phase profile at time equals 10 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters.

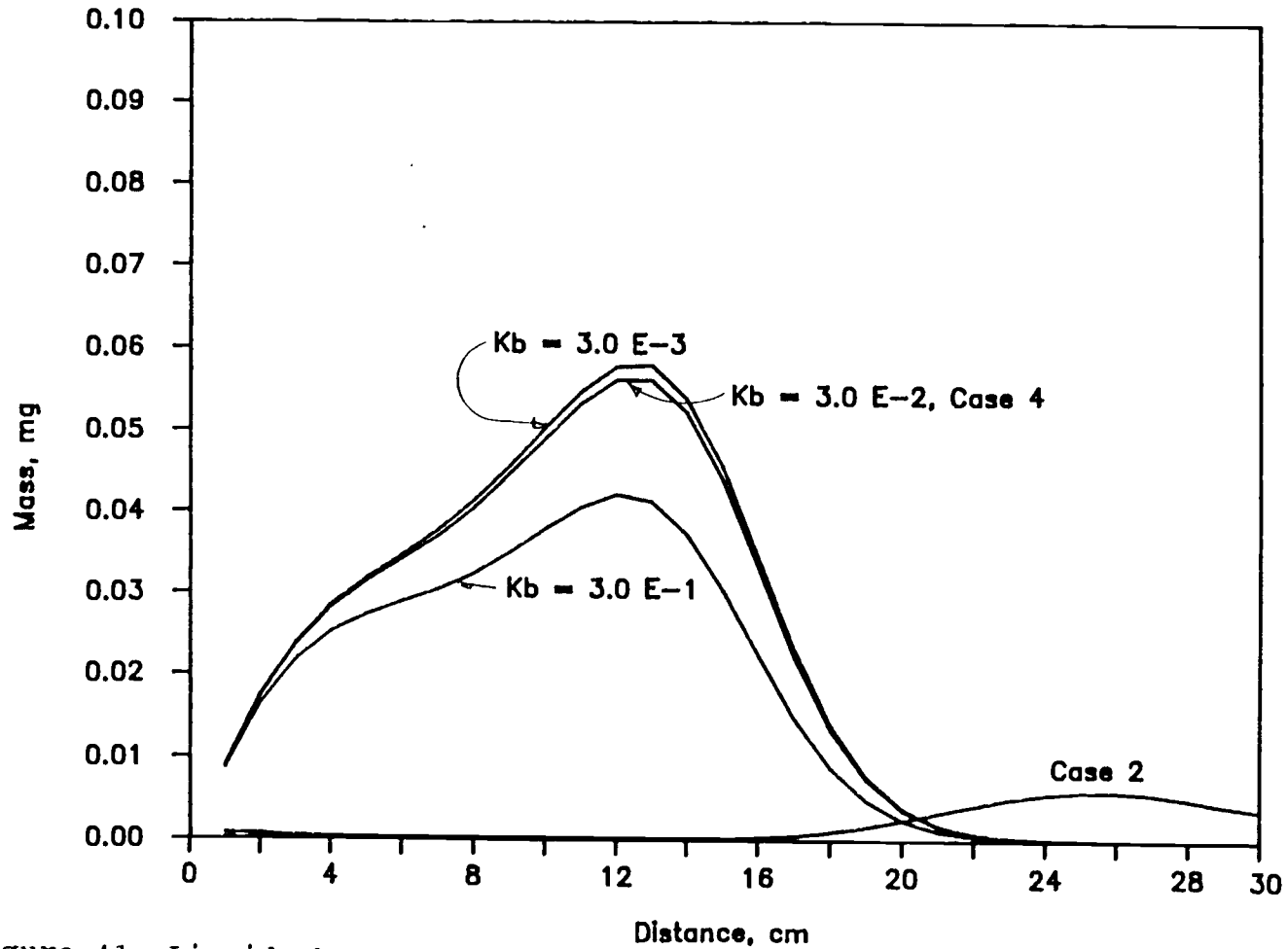


Figure 41. Liquid phase profile at time equals 25 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters.

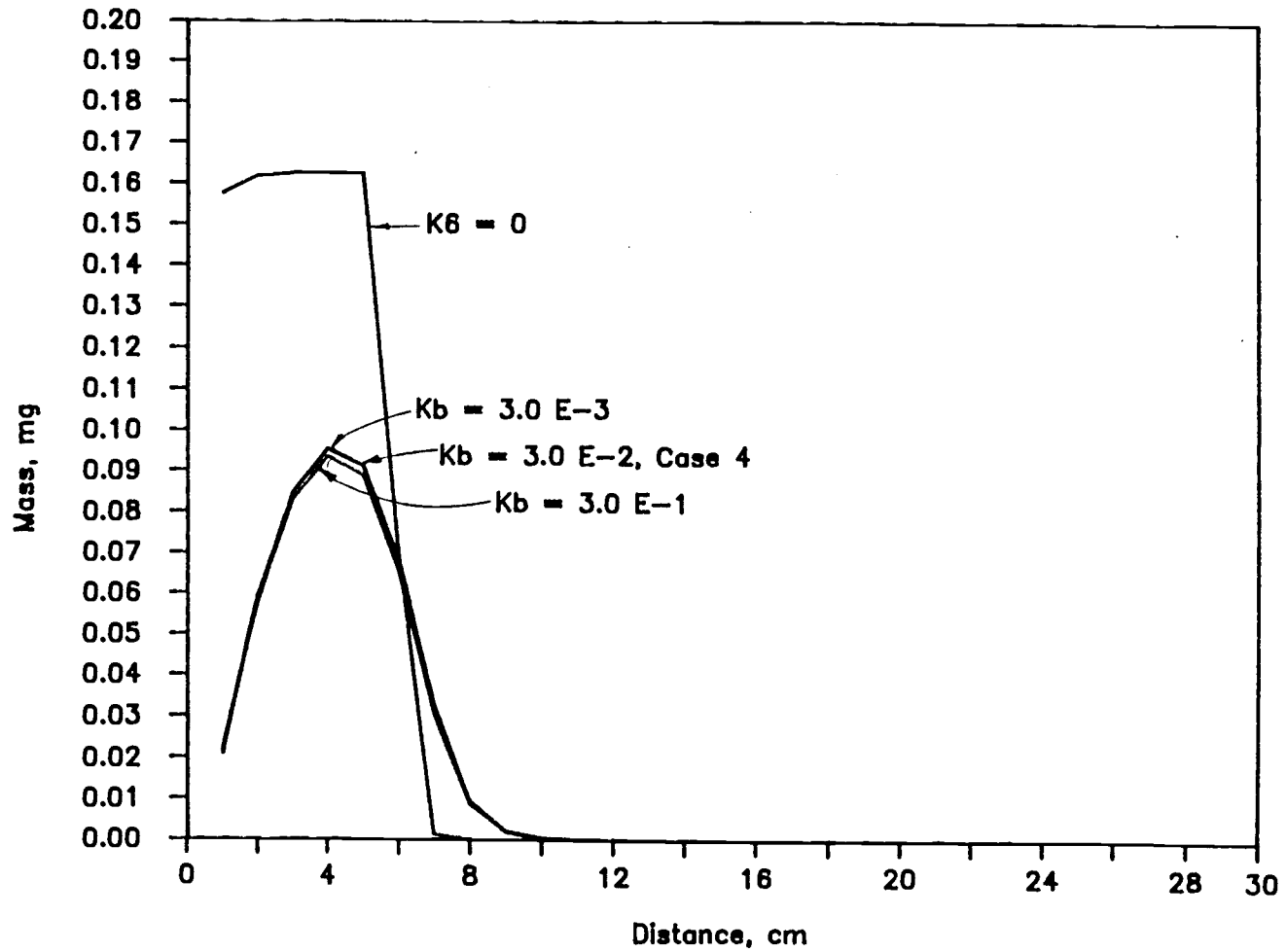


Figure 42. Soil bacterial phase profile at time equals 5 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters.

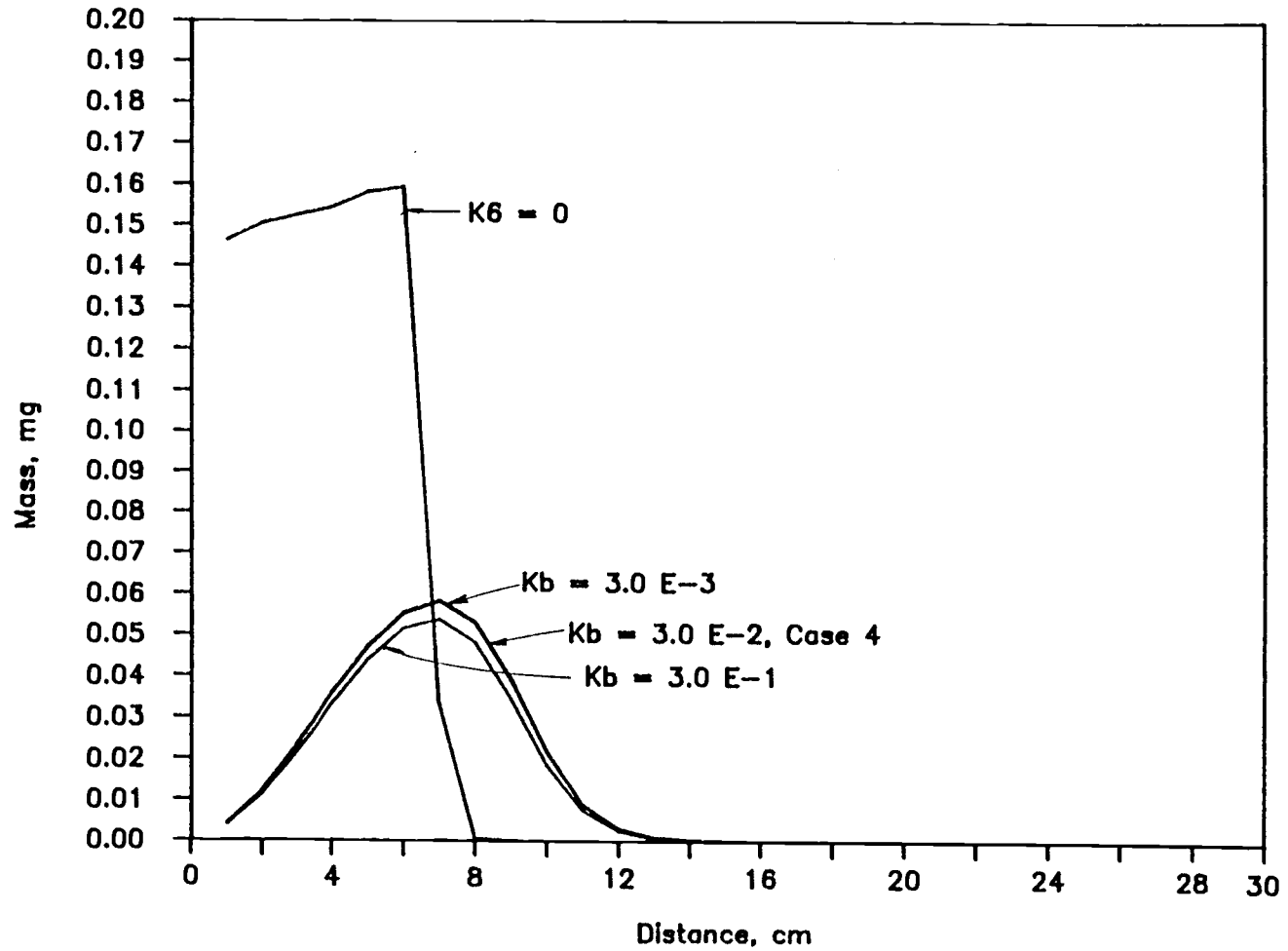


Figure 43. Soil bacterial phase profile at time equals 10 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters.

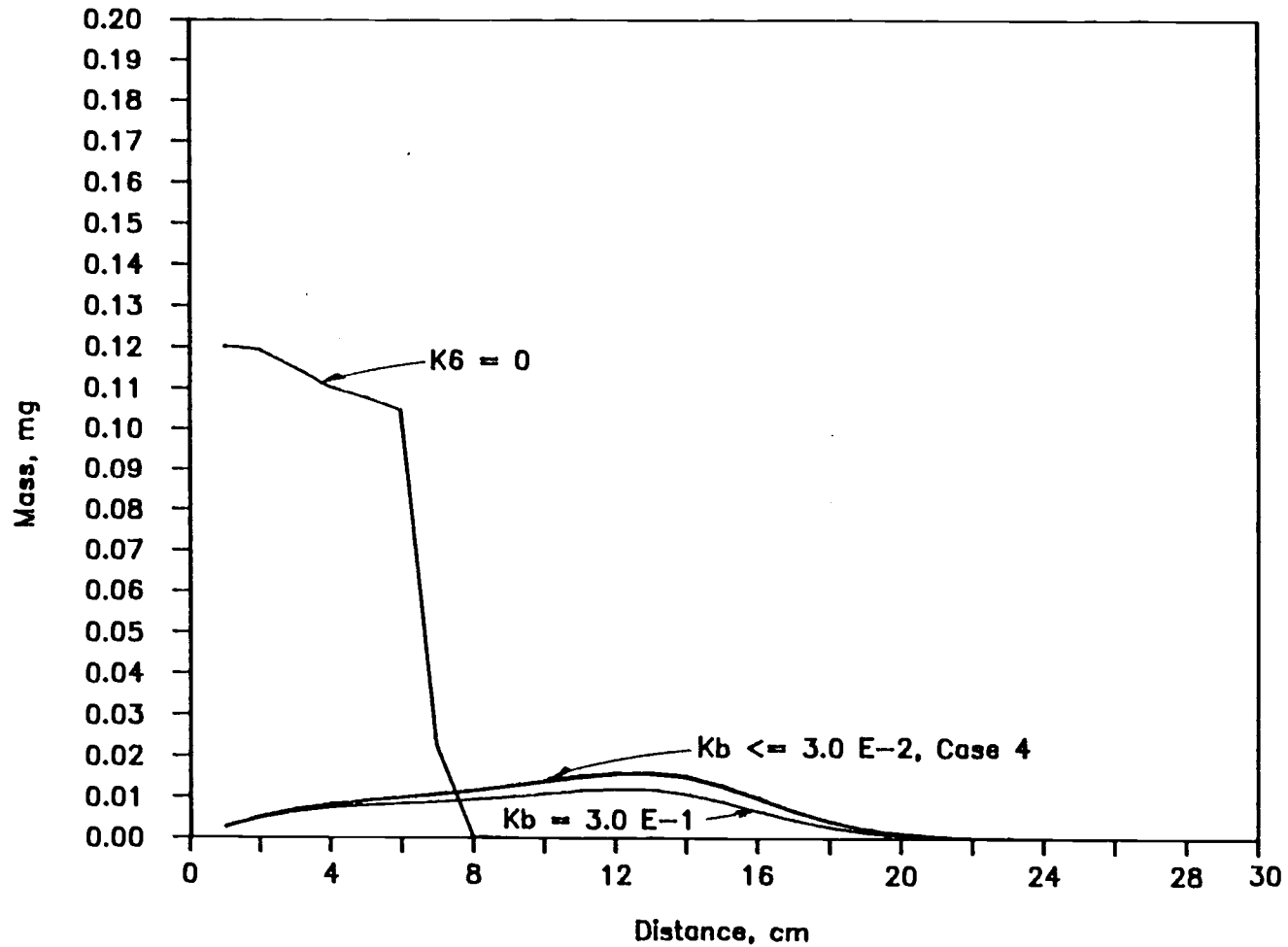


Figure 44. Soil bacterial phase profile at time equals 25 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters.



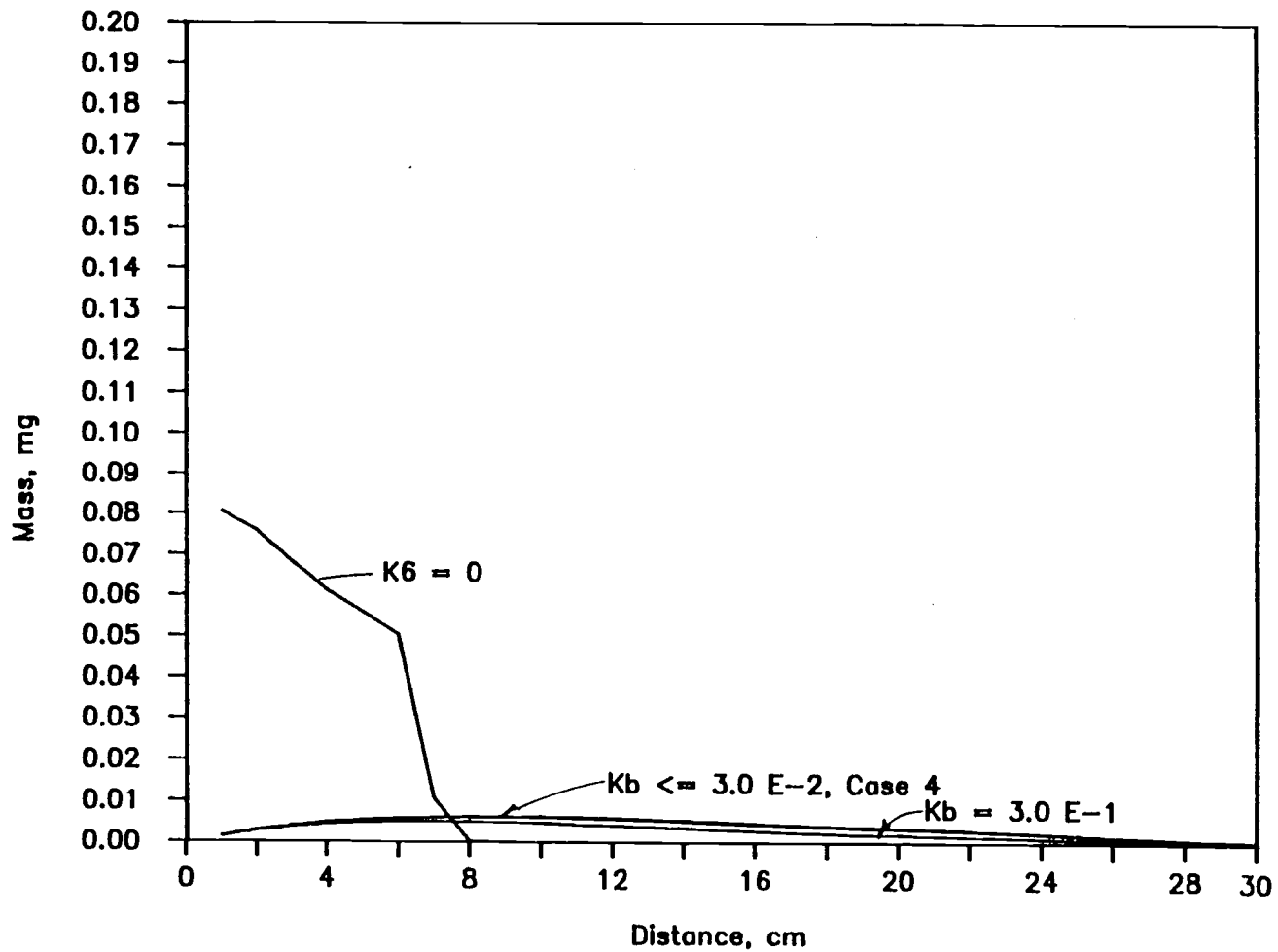


Figure 45. Soil bacterial phase profile at time equals 50 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters.

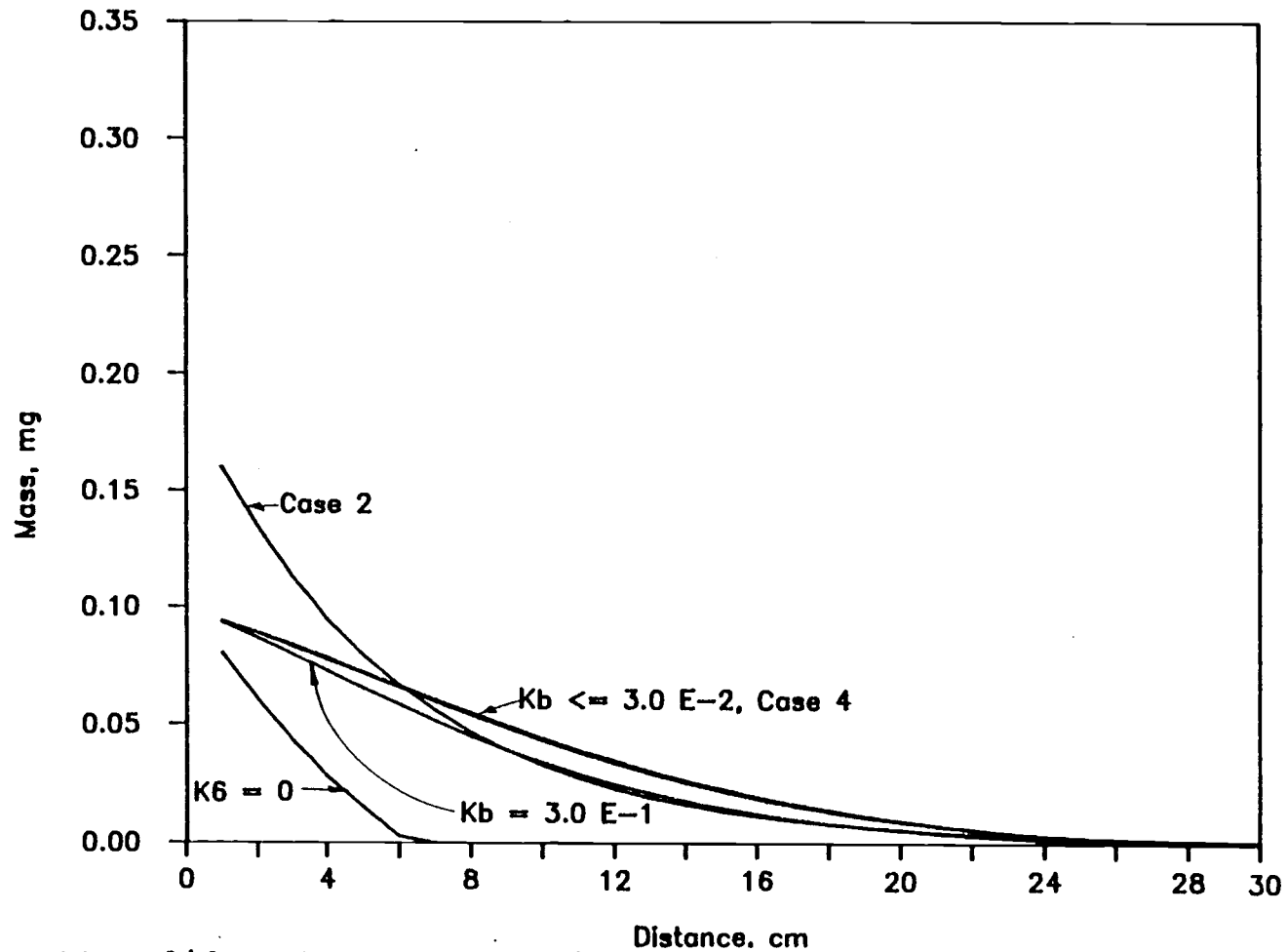


Figure 46. Solid surface phase profile at time equals 50 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters.

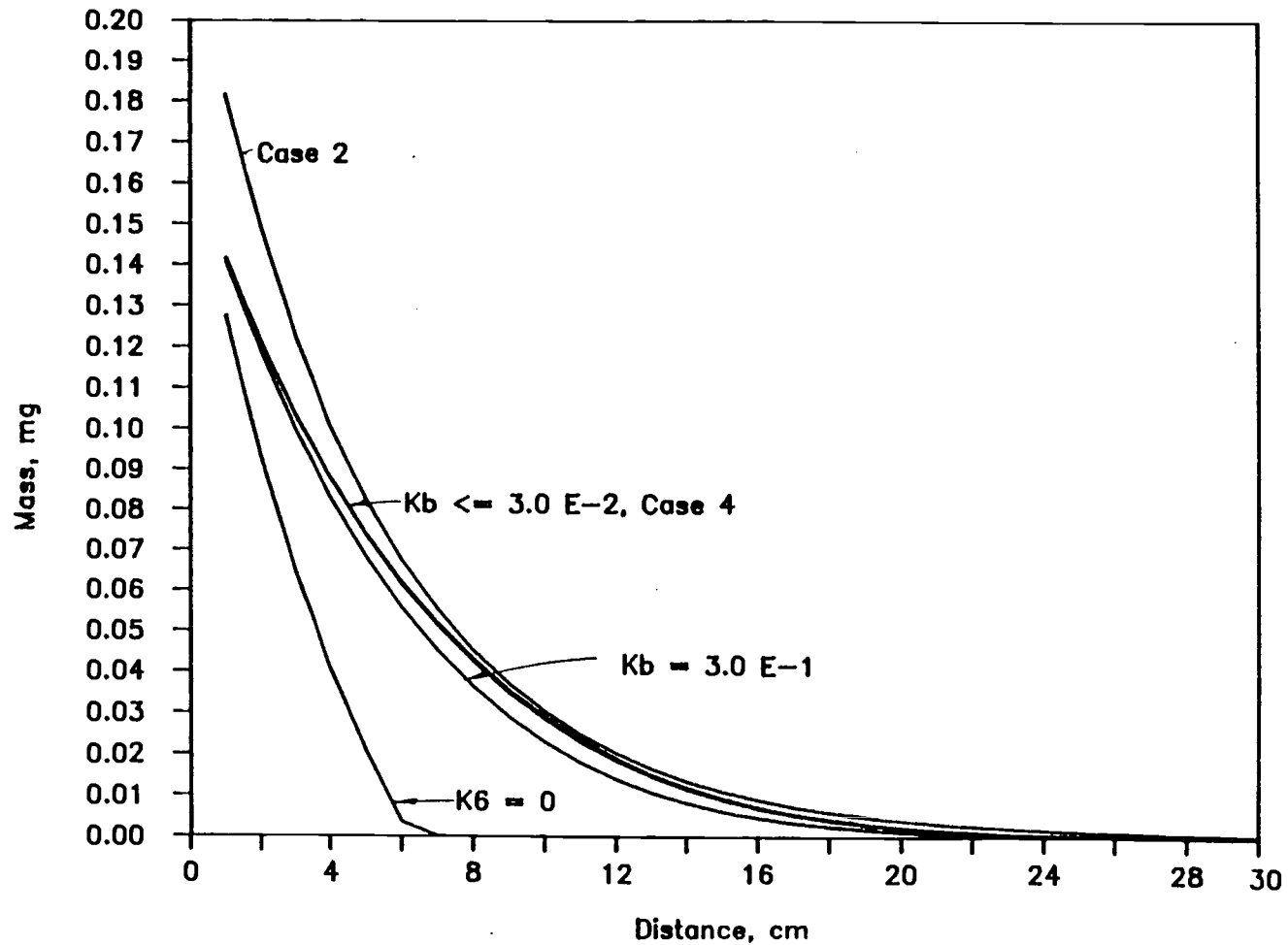


Figure 47. Solid interior phase profile at time equals 50 hours varying  $K_b$  and  $K_6$  while maintaining the remaining Case 4 parameters.

MONOD DEGRADATION FROM THE LIQUID PHASE (Km AND Ks)

A Monod type relation was used to study the effects of liquid phase bacterial degradation constants on the fate and transport of pollutants (Equation 25).

$$R_{su}(n,T) = [K_m (B/p) Cl(n,T)] / [K_s + Cl(n,T)] \quad (25)$$

Degradation of hydrophobic organic pollutants from the liquid phase may occur in two ways: 1) the pollutant may be used as an electron donor or acceptor providing energy to the bacteria for growth or 2) the pollutant may be degraded as a secondary substrate assuming a primary substrate is available to support growth of the bacteria. The pollutant under study was considered a secondary substrate and is assumed to be assumed to be degraded by Monod kinetics and that adequate primary substrates were present to maintain the biomass.

For this analysis, the presence of a primary substrate was assumed and the threshold level of secondary substrate was neglected. The intent was to discover a range of  $K_m$  and  $K_s$  values over which significant biodegradation occurs. The effect of solids concentration,  $S$ , was also studied using values of 2.08 and 0.02 (1% solids) gram solids per cubic centimeter (Case 5 and 6). One percent organic solids

is a reasonable estimate of the organic fraction in many natural soil systems. Base values for  $K_m$  and  $K_s$  are shown in Table 1, Case 5 and 6.

The results of varying  $K_m$  and  $S$  over several orders of magnitude are shown in Figures 48 through 51. Degradation under the assumed base values (Case 5) reduced the liquid phase mass to very low levels at times as early as 10 hours as shown in Figure 49. Very little sorption to the solid phase occurred and the sorption that did occur was in the top several centimeters as shown in Figures 51 and 52. Increasing the maximum substrate utilization rate, ( $K_m$ ), reduced the amount sorbed to the solids to even lower values. Decreasing the degradation constant by one order of magnitude resulted in a significantly higher peak liquid phase mass. At two orders of magnitude decrease, the profile approached the Case 2 having no degradation (Figure 48).

Solids concentration had an interesting effect on the liquid phase profile. For Case 6, a ten fold decrease in the maximum substrate utilization rate,  $K_m$ , increased the peak liquid phase mass slightly compared to Case 5, and began to show a secondary peak in the liquid phase upper soil layers at ten hours (Figure 49). A widening effect was also apparent. This profile may be the result of desorption from a more fully saturated solid fraction. As sorption

sites decreased, desorption became more dominant and low degradation rates allowed the pollutant to pass through the column undegraded.

For a given liquid concentration, increasing the half velocity constant,  $K_s$ , one order of magnitude was nearly identical results as decreasing the maximum substrate utilization rate,  $K_m$ , by the same multiple. Only over a very small range of  $K_s$  and  $K_m$  values where  $K_s$  is near the liquid concentration is this not true. Since each cell in the analysis has an individual liquid concentration, it is difficult to study the effects of  $K_s$  and  $K_m$  relative to each other in this range using a column type analysis. More meaningful results could be obtained using a completely-mixed batch, or continuous-flow, one cell reactor.

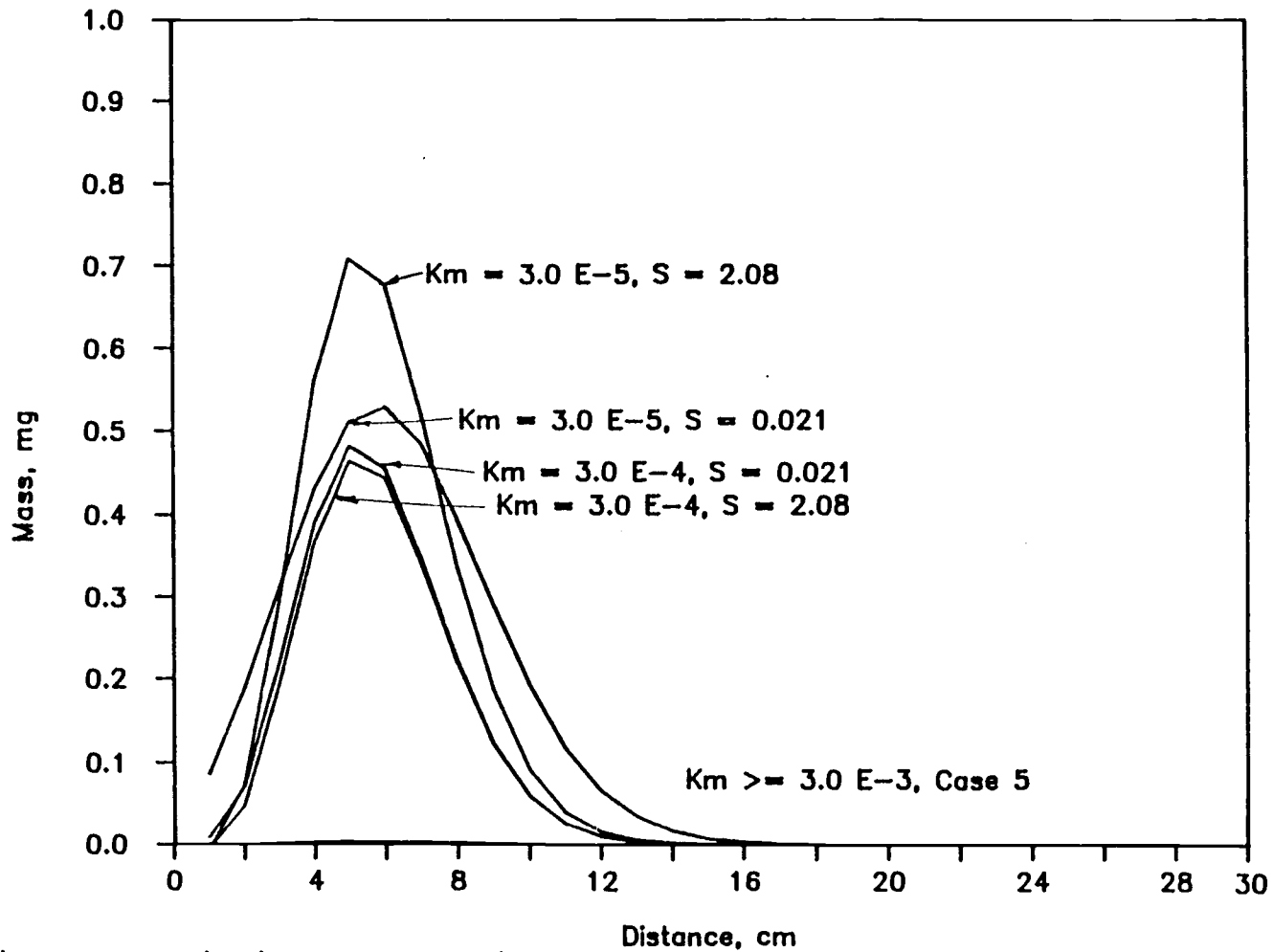


Figure 48. Liquid phase profile at 5 hours varying  $K_m$  and the solids concentration ( $S$ ) while maintaining the remaining Case 5 parameters.

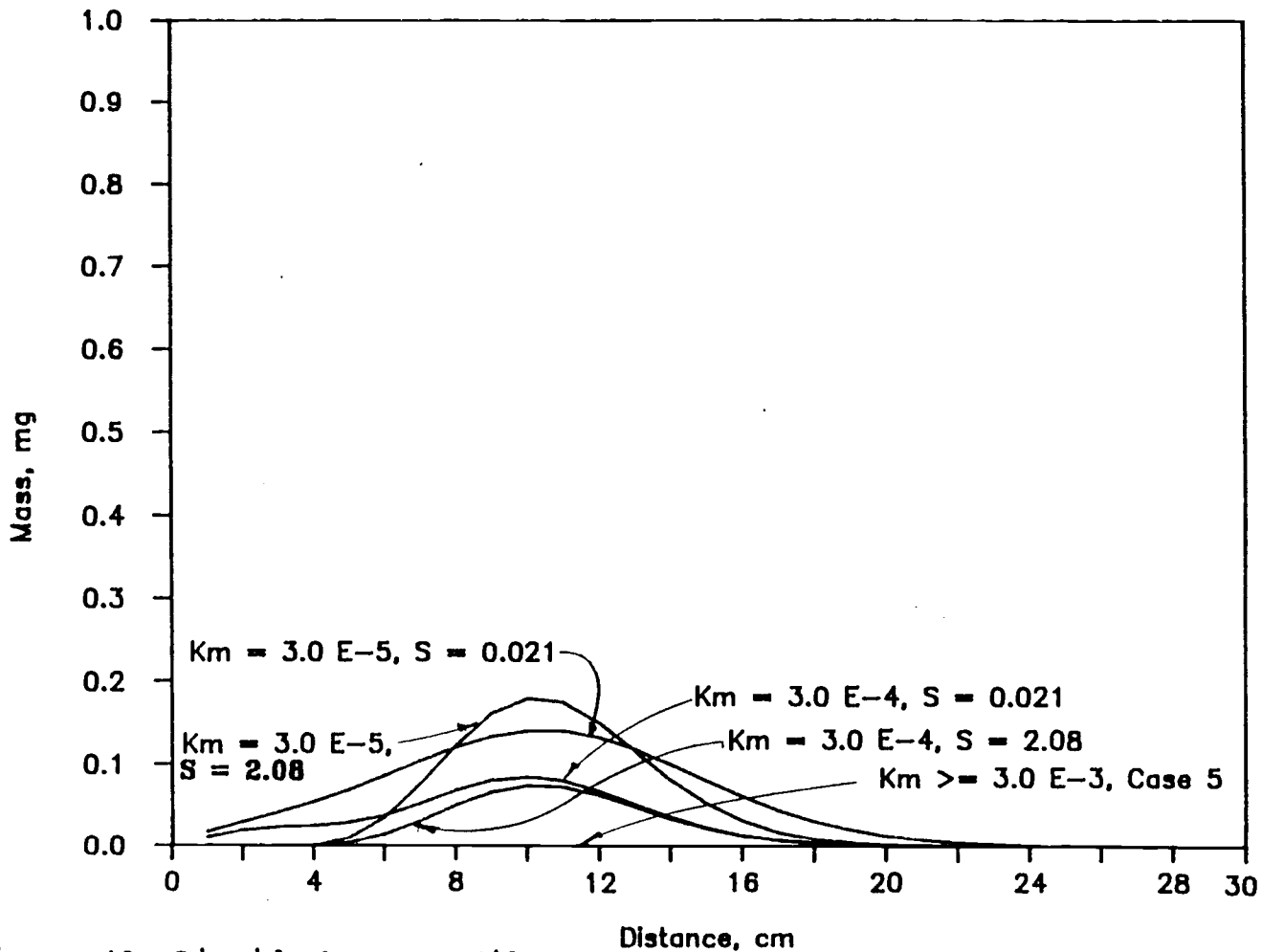


Figure 49. Liquid phase profile at 10 hours varying  $K_m$  and the solids concentration ( $S$ ) while maintaining the remaining Case 5 parameters.



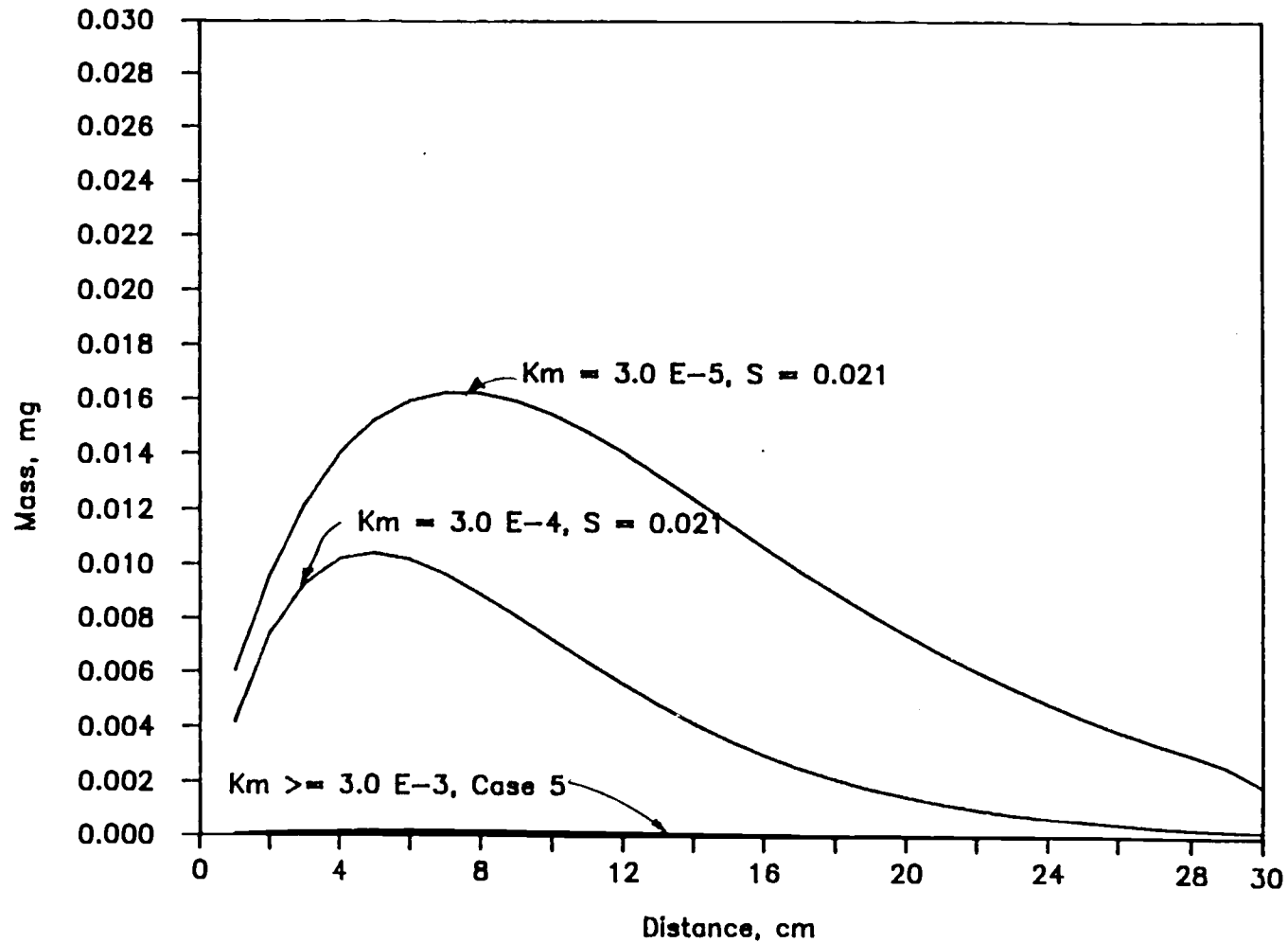


Figure 50. Liquid phase profile at 50 hours varying  $K_m$  and the solids concentration ( $S$ ) while maintaining the remaining Case 5 parameters.

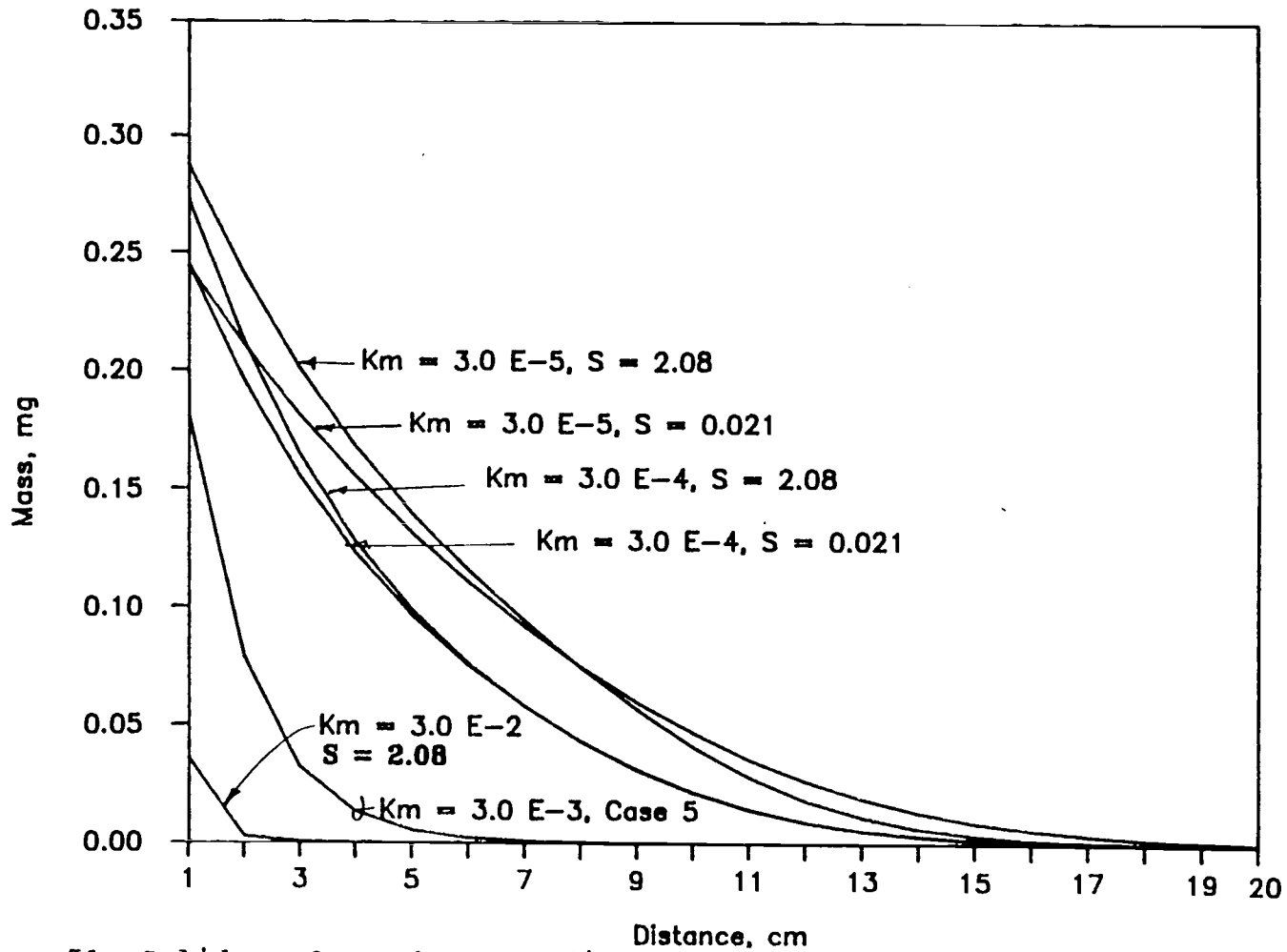


Figure 51. Solid surface phase profile at 10 hours varying  $K_m$  and the solids concentration ( $S$ ) while maintaining the remaining Case 5 parameters.

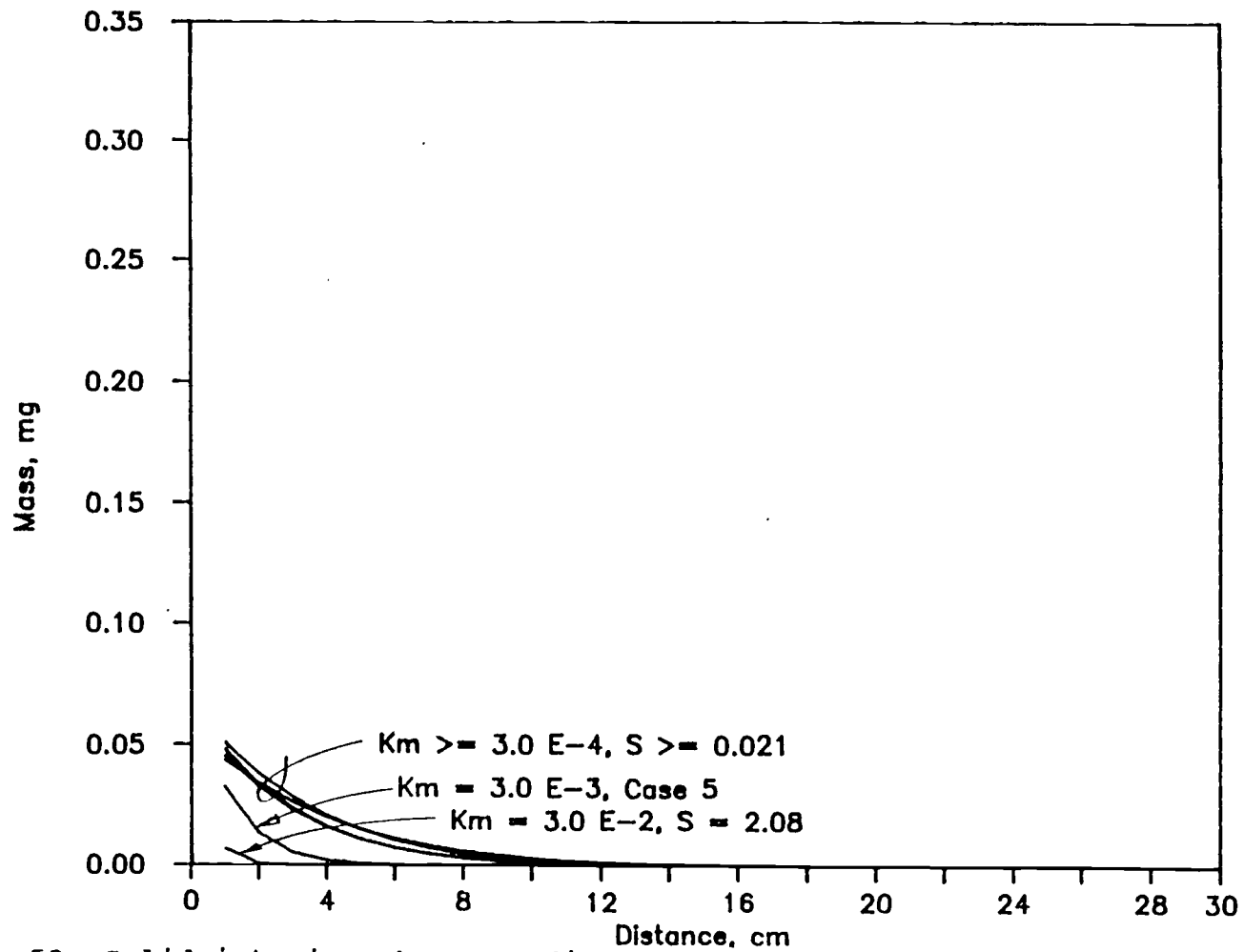


Figure 52. Solid interior phase profile at 10 hours varying  $K_m$  and the solids concentration ( $S$ ) while maintaining the remaining Case 5 parameters.

### SUMMARY

A mathematical model to predict the fate of hydrophobic organic compounds in saturated soil systems was developed. The model considers advective transport with diffusive mixing; sorption to and from the soil solid surface; exchange between the soil particle's surface and the particle's interior; sorption to and from bacteria; and bacterial degradation of the pollutant in the liquid phase and sorbed to the bacteria. Two possible mechanisms for bacterial degradation were analyzed in this study: degradation of the fraction of the pollutant sorbed to the bacterial phase using first order kinetics and degradation directly from the bulk liquid phase using Monod kinetics.

Sensitivity analyses were performed for the sorption rate constants, the soil sorptive capacities, and the constants describing bacterial degradation using the two degradation mechanisms. Solids concentrations representing a completely organic sorbate and a soil with one percent organic solids were also examined to determine the effects of low organic contents typical of many soils. Values for all parameters used in the base cases are presented in Table 1.

## BIODEGRADATION

The environmental fate of pollutants as identified in this model was affected to the greatest extent by the selection of mechanism for bacterial degradation (liquid phase versus bacterial phase degradation) and each mechanism's respective rate constants.

Degradation from the liquid phase (Cases 5 and 6) shows the most effect on the fate of the pollutant. Using estimated values for  $K_m$  and  $K_s$ , the pollutant was so quickly degraded that very little mass was available to sorb to the soil solid phase. The values chosen for  $K_m$  and  $K_s$  shown in Table 1 may vary widely for organic pollutants. However, significant changes in the liquid phase mass did not occur until the maximum substrate utilization rate,  $K_m$ , was decreased by at least one order of magnitude from the base value. The level at which  $K_m$  begins to have a significant effect on fate was in the range of  $10 \text{ E-4}$  moles per gram bacteria per hour or about 0.4 1/day. This indicates that even compounds that are fairly resistant to degradation like chlorinated phenols could be metabolized to some extent. This generalization was highly dependent on the conditions in a soil column including the natural variance of bacterial concentration and population type with depth, the presence of a primary substrate, and many other variable conditions.

Degradation of pollutant from the bacterial phase was also significant given the assumptions that desorption from the bacteria is near zero and the rate of sorption to the bacteria is much greater than the sorption rate to non-living organic solid in the soil. Competition for the available pollutant between bacteria and sorption to soils solids was also an important factor.

While bacterial degradation has a significant effect on the fate of pollutants, there are several areas that are not adequately understood or fully treated in this model. This study, therefore, reveals topics that should be the focus of further research rather than makes specific conclusions about the mechanisms studied herein. Some of these areas of uncertainty include the actual values of the sorption and degradation constants for hydrophobic organic compounds, and the variability of natural soil systems.

#### SORPTION TO SOIL SOLIDS

The importance of sorption parameters can be divided into short, intermediate and long term effects. The surface sorption parameters,  $K_1$  and  $S_{max}$ , are important in the short term environmental fate of pollutants. Small increases or decreases in these parameters control how much of the pollutant can

be immediately sorbed. In a continuous flow system the compound must be sorbed quickly or it passes into the lower soil horizons and eventually into the groundwater. The interior sorption process is dependent on the concentration gradient that exists between the soil surface and soil interior. Without high rates and amounts of short term (surface) sorption taking place, the effects of interior sorptive properties will not manifest themselves.

The interior sorptive properties,  $K_3$  and  $S_{max}$ , have longer term effects on the eventual fate of pollutants. Pollutants that sorb quickly and produce a strong gradient toward the interior phase or sorbates with high interior capacities tend to bind much more pollutant for longer periods of time. This results in longer retention time in the soil column.

The desorption parameters,  $K_2$  and  $K_4$ , are important in the long term fate of pollutants. Small increases in either of these parameters reduced the residence time of the compound in the soil column significantly, while decreases tend to trap compounds in the soil indefinitely.

Priority in future research should be to determine the specific mechanism of degradation used by bacteria to metabolize pollutants in natural soil environments. Information in this area could lend not only to more accurate prediction of the eventual fate

of organic compounds in soil, but also in devising schemes to treat contaminated soil on location, avoiding costly transportation and incineration or storage of soil.

Research is also needed on the long term fates of pollutants (on the order of decades). Information in this area would be useful in predicting the final fate of organic compounds and in prioritizing long term clean up operations of contaminated sites.

Surface sorption rate constants are important for short term prediction of a compound's fate. In addition, these constants are necessary to study the interior sorption rate process. This occurs because the surface phase sorbed mass of pollutant directly controls the degree of sorption occurring in the solid's interior.



Table 2. Relative effect of kinetic sorption and degradation constants on pollutant fate in soil systems.

PARAMETER	SHORT TERM (5 to 25 hours)	INTERMEDIATE TERM (25 to 100 hours)	LONG TERM (>100 hours)
K1	++	+	+
K2	o	+	++
S <sub>smax</sub>	++	+	+
K3	o	++	+
K4	o	+	++
S <sub>i</sub> max	o	++	+
K5	++	+	+
K6	++	+	+
K <sub>b</sub>	+++	++	++
B <sub>smax</sub>	++	+	+
K <sub>m</sub>	+++	++	++
K <sub>s</sub>	+++	++	++

Key to Table:

- o Indicates negligible or no observable effect.
- + Indicates some or minor effects if parameter is changed drastically.
- ++ Indicates that parameter has a significant effect on fate when changed.
- +++ Indicates fate is extremely sensitive to change of this parameter.

## CONCLUSIONS

A mathematical kinetic model was developed to predict the fate of hydrophobic organic compounds in saturated soil systems. The model included parameters for sorption and desorption to soil and bacteria and two possible mechanisms of bacterial biodegradation. Based on sensitivity analysis performed with this model the following conclusions were made.

1. Advection and diffusion of pollutants account for movement and dilution of pollutants flowing through a saturated soil column with a mobile liquid phase.
2. The effect of sorption to soil particles in a saturated aquifer is initially to reduce the liquid phase pollutant mass at any point in the column compared to the advection-dispersion only case and to bind the pollutant in the solid phase for some period of time. The most significant effects of each sorption rate constant and sorptive capacity can be broken down into short, intermediate and long term effects.
  - A. The most important short term effects (5 to 25 hours) are related to the solid surface adsorptive rate constant,  $K_1$ , and the soil surface sorptive capacity,  $S_{smax}$ .
  - B. The most important intermediate term effects (25 to 100 hours) are related to the solid interior adsorptive rate constant,  $K_3$ , and the soil interior sorptive capacity,  $S_{imax}$ .
  - C. The most important long term effects (greater than 100 hours) are related to the soil desorption constants  $K_2$  and  $K_4$ .

3. The effect of degradation of pollutants from the bacterial phase is to decrease the amount of pollutant available for sorption to the solid phase. However, an extremely high adsorptive rate constant ( $K_5$ ) and little or no desorption from the bacterial phase ( $K_6 = 0$ ) must be assumed for the level of biodegradation of pollutant to become a significant sink.
4. The effect of degradation of pollutant from the bulk liquid phase is to reduce the liquid phase pollutant mass to very low levels over fairly short time periods. This assumes a reasonable degradation rate constant ( $K_m$ ) for a chlorinated phenol, the presence of a primary substrate, and neglects any threshold level of pollutant that may be required.

BIBLIOGRAPHY

1. Gschwend. Phillip M., Shian Chee Wu, "Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils," Environ. Sci. and Tech., 20:717-25, 1986.
2. van Genuchten M., R. Cleary, "Movement of Solutes Through Soil: Computer Simulated and Laboratory Results," in Soil Chemistry B, Physicochemical Models, ed. G.H. Bolt, Elsevier, New York, 1979.
3. Vallocchi, Albert J., "Validity of the Local Equilibrium Assumption for Modeling Sorbing Solute Transport Through Homogeneous Soils," Water Res. Research, 21:6:808-20, 1985.
4. Bella, D., Conceptual and Mathematical Models, unpublished.
5. Di Toro, D.M., "Reversible and Resistant Components of PCB Adsorption-Desorption: Adsorbent Concentration Effects," J. Great Lakes Res., 8:2:336-49, 1982.
6. McCarty, P.L., E.J. Bouwer, J.C. Lance, "Trace Organic Behavior in Soil Columns During Rapid Infiltration of Secondary Wastewater," Water Research, 15:151-59, 1981.
7. Gardner, K., "Development of a Method to Accumulate Metabolic Products from Dichloronitrobenzenes Using A Gas-Permeable-Membrane-supported Biofilm," thesis presented to Oregon State University, Corvallis, Or., in 1987 in partial fulfillment of the requirement for the degree of Master of Science.
8. Woods, S.L., "The Fate of Chlorinated, Hydroxylated and Methoxylated Benzenes in Anaerobic Wastewater Treatment," thesis presented to the University of Washington, Seattle, Wa. in 1985 in partial fulfillment of the requirement for the degree of Doctor of Philosophy; submitted for publication.
9. Metcalf and Eddy Inc., Wastewater Engineering: Treatment/Disposal/Reuse, McGraw Hill Inc., ed. G. Tchobanoglous, 1979.

10. Patrier, L., "A Kinetic Approach for the Determination of Sorption Rate Constants Using a Column-Type Reactor," thesis presented to Oregon State University, Corvallis, Or., in 1986 in partial fulfillment of the requirement for the degree of Master of Science.
11. Dolan, M., "The Effect of Organic Sorbent Concentration On Sorption Kinetics," thesis presented to Oregon State University, Corvallis, Or., in 1987 in partial fulfillment of the requirement for the degree of Master of Science.
12. Di Toro, D.M., "A Particle Interaction Model of Reversible Organic Chemical Sorption", unpublished article to appear: Chemosphere, 1985.

APPENDIX

## FORTRAN LISTING OF COLUMN MODEL

```

                                06-02-87
                                11:34:44
                                Microsoft FORTRAN77 U3.13 8/05/83
D Line# 1      7
1      Program Column
2 C      1      2      3      4      5      6      7
3 C23456789*123456789*123456789*123456789*123456789*123456789*123456789*12
4 C
5 .....
6 .....
7 * This program calculates the fate of hydrophobic organic compounds in
8 * a soil column accounting for sorption and desorption to soil and
9 * bacter and metabolism by the bacterial component in the soil.
10 .....
11 .....
12 C
13 .....
14 *      Define real arrays and variables
15 .....
16 C
17      REAL Ss(200,2), Si(200,2), Bs(200,2), Rsu(200)
18      REAL Cl(200,2), Cs(200,2), Ci(200,2), Cb(200,2), CO
19      REAL u, p, A, D, Dp,S, B, dX, X, dI, R, Twrite
20      REAL MW,K1, K2, K3, K4, K5, K6, Kb
21      REAL Ssmax, Simax, Bsmax
22      REAL ks, km
23      REAL EDUAL, UVALUE, RECORD, LOW, HIGH, INCR
24 .....
25 ***** Define Integer Variables
26 .....
27      INTEGER I, J, K, L, II, JJ, KK, N, Wrt, Endsim, Final
28      INTEGER EDREC
29 .....
30 ***** Define CHARACTER variables
31 .....
32      CHARACTER Edit*1, Result*20, Param*20, Par*20
33 .....
34 ***** Open Results and input file.
35 .....
36      WRITE(*,21)'Name of Input file (*.INP)?'
37      READ(*,'(A)') PARAM
38      OPEN(10,FILE=PARAM, STATUS='OLD',ACCESS='DIRECT',RECL=100)
39      WRITE(*,21)'Name of results file (*.RLI)?'
40      READ(*,'(A)') RESULT
41      OPEN(20, FILE=RESULT,STATUS='NEW')
42      WRITE(*,21)'Name of Parameter file (*.PAR)?'
43      READ(*,'(A)') PAR
44      OPEN(21,FILE=PAR, STATUS='NEW')
45 .....
46 *      Load Paramaters from <PARAM>.INP
47 .....
48      CALL INPT (u,p,A,S,B,D,X,MW,K1,K2,K3,K4,K5,K6,Kb,Km,Ks,
49      $          Ssmax,Simax,Bsmax,dX,dI,Twrite,Iend,CO,R,RECORD,
50      $          LOW,HIGH,INCR)
51 .....
52 *      Check Stability Conditions
53 .....
54 102 IF(D*dI/p/dX**2 .GT. 0.5)THEN
55      WRITE(*,21)'Stability condition VIOLATED!'
56      WRITE(*,21)'***** Make Sure D*dI/p/dX^2 <- 1/2 *****'
57      PAUSE

```

```

58     ENDIF
59     IF (u*dT .GT. dx)THEN
60         WRITE(*,21)'Mass transport condition VIOLATED!'
61         WRITE(*,21)'***** Make sure u*dT <- dx *****'
62         PAUSE
63     ENDIF
64     .....
65     *                               Echo Print of Parameters                               *
66     .....
67     WRITE(*,*)
68     WRITE(*,21)          SOIL COLUMN PHYSICAL PROPERTIES'
69     WRITE(*,*)
70     WRITE(*,23)'1. Pore flow velocity,      u = ',u,' cm/hr'
71     WRITE(*,22)'2. Soil column porosity,    p = ',p,'
72     WRITE(*,22)'3. Cross sectional area,    A = ',A,' cm^2'
73     WRITE(*,22)'4. Soil solids content,    S = ',S,' g s./cm^3'
74     WRITE(*,23)'5. Soil bact. count,      B = ',B,' g b./cm^3'
75     WRITE(*,23)'6. Soil dispersion coeff. D = ',D,' cm^2/hr'
76     WRITE(*,22)'7. Length of soil column, X = ',X,' cm'
77     PAUSE
78     WRITE(*,*)
79     WRITE(*,*)
80     WRITE(*,21)'          SORPTION AND METABOLISM RATE CONSTANTS'
81     WRITE(*,*)
82     WRITE(*,23)'8. Molecular Weight      MW = ',MW,' g/mole'
83     WRITE(*,23)'9. Liquid to solid,      K1 = ',K1,' g s./mole sites/hr'
84     WRITE(*,23)'10. Solid to liquid,     K2 = ',K2,' g s./cm^3 l./hr'
85     WRITE(*,23)'11. Solid surf. to int.K3 = ',K3,' g s./mole sites/hr'
86     WRITE(*,23)'12. Solid int. to surf.K4 = ',K4,' l/hr'
87     WRITE(*,23)'13. Liq. to bact.,      K5 = ',K5,' g b./mole sites/hr'
88     WRITE(*,23)'14. Bact. to liq.,      K6 = ',K6,' g b./cm^3 l./hr'
89     WRITE(*,23)'15. Sorbed metab.,      Kb = ',Kb,' l/hr'
90     WRITE(*,23)'16. Monod Km,           Km = ',Km,' mole cmpd./g b./hr'
91     WRITE(*,23)'17. Monod Ks,          Ks = ',Ks,' mole cmpd./ cm^3'
92     PAUSE
93     WRITE(*,*)
94     WRITE(*,21)'          MAXIMUM SORPTION SITE AVAILABILITY'
95     WRITE(*,*)
96     WRITE(*,23)'18. Soil surface,      Ssmax = ',Ssmax,' mole sites/g s.'
97     WRITE(*,23)'19. Soil interior,     Simax = ',Simax,' mole sites/g s.'
98     WRITE(*,23)'20. Bacteria,          Bsmax = ',Bsmax,' mole sites/g b.'
99     WRITE(*,*)
100    WRITE(*,21)'          SIMULATION PARAMETERS'
101    WRITE(*,*)
102    WRITE(*,23)'21. Cell length,         dx = ',dx,' cm'
103    WRITE(*,23)'22. Time increment,      dt = ',dt,' hr'
104    WRITE(*,23)'23. Profile update time each ',Twrite,' hours.'
105    WRITE(*,23)'24. End simulation time at ',Tend,' hours.'
106    WRITE(*,23)'25. Init. liq. conc. in cell 1 = ',CO,'mole/cm^3'
107    WRITE(*,23)'26. Steady state input to cell 1= ',R,' mole/hr.'
108    WRITE(*,*)
109    WRITE(*,24)'27. Sensitivity analysis on param. ',RECORD,'.'
110    WRITE(*,23)'28. Low range = ',LOW,'.'
111    WRITE(*,23)'29. High range = ',HIGH,'.'
112    WRITE(*,23)'30. Step size = ',INCR,'.'
113    WRITE(*,*)
114    .....
115    *                               Edit Routine                               *
116    .....
117    WRITE(*,21)' Do you wish to edit any of these paramaters (Y/N)?'

```



```

118     READ(*, '(A)') EDIT
119 103 IF(EDIT .EQ. 'Y' .OR. EDIT .EQ. 'y') THEN
120     WRITE(*,21)'Enter parameter # and value (#,<value>).'
121     READ(*,*)EDREC,EDUAL
122     WRITE(10,REC=EDREC) EDUAL
123     CLOSE(10)
124     OPEN(10,FILE=PARAM, STATUS = 'OLD',ACCESS='DIRECT',RECL=100)
125     CALL INPT (u,p,A,S,B,D,X,MW,K1,K2,K3,K4,K5,K6,Kb,Km,Ks,
126 $             Smax,Simax,Bsmax,dX,dT,Twrite,Tend,CO,R,RECORD,
127 $             LDW,HIGH,INCR)
128     GOTD 102
129     ELSE
130     WRITE(*,21)'Press "B" to begin simulation or "E" to continue
131     sediting.'
132     READ (*, '(A)') BEGIN
133     IF (BEGIN .EQ. 'E' .OR. BEGIN .EQ. 'e') THEN
134         EDIT = 'Y'
135         GOTD 103
136     ENDIF
137     ENDIF
138 .....
139 *           Copy Input Parameters to Result File           *
140 .....
141     WRITE(21,*)1,u
142     WRITE(21,*)2,p
143     WRITE(21,*)3,A
144     WRITE(21,*)4,S
145     WRITE(21,*)5,B
146     WRITE(21,*)6,D
147     WRITE(21,*)7,X
148     WRITE(21,*)8,MW
149     WRITE(21,*)9,K1
150     WRITE(21,*)10,K2
151     WRITE(21,*)11,K3
152     WRITE(21,*)12,K4
153     WRITE(21,*)13,K5
154     WRITE(21,*)14,K6
155     WRITE(21,*)15,Kb
156     WRITE(21,*)16,Km
157     WRITE(21,*)17,Ks
158     WRITE(21,*)18,Smax
159     WRITE(21,*)19,Simax
160     WRITE(21,*)20,Bsmax
161     WRITE(21,*)21,dX
162     WRITE(21,*)22,dT
163     WRITE(21,*)23,Twrite
164     WRITE(21,*)24,Tend
165     WRITE(21,*)25,CO
166     WRITE(21,*)26,R
167     WRITE(21,*)27,RECORD
168     WRITE(21,*)28,LDW
169     WRITE(21,*)29,HIGH
170     WRITE(21,*)30,INCR
171 .....
172 *           Begin Simulation                               *
173 .....
174     IF(INCR .NE. 0)THEN
175         FINAL = NINT((HIGH - LDW)/INCR) + 1
176         VALUE = LDW
177         WRITE(10,REC=INT(RECORD))VALUE

```

```

178         CLOSE(10)
179         OPEN(10, FILE=PARAM, STATUS = 'OLD', ACCESS='DIRECT', RECL=100)
180         CALL INPT (u,p,A,S,B,D,X,Mw,K1,K2,K3,K4,K5,K6,Kb,Km,Ks,
181         $          Ssmax,Simax,Bsmax,dX,dT,Twrite,Tend,CO,R,RECORD,
182         $          LOW,HIGH,INCR)
183     ELSE
184         FINAL = 1
185     ENDIF
186     DO 1 II = 1, FINAL
1 187         WRITE(*,*) ' Simulation # = ',II
1 188         .....
1 189         *           Counter and Array Initialization           *
1 190         .....
1 191 C ***** Counter for cell 1 to n.
1 192         N = NINT(X/dX)
1 193 C ***** Counter for update of soil phase profile.
1 194         Wrt = NINT(Twrite/dT)
1 195 C ***** Counter for end of one simulation.
1 196         Endsim = NINT(Tend/Twrite)
1 197         WRITE(*,*) ' Endsime = ',Endsim
1 198         WRITE(*,*) ' Simulation # = ',II
1 199 C ***** Initialize all sorption sites in column to initial values.
1 200         DO 202 K = 1, 2
2 201             DO 203 J = 1, N+1
3 202                 Ss(J,k) = Ssmax
3 203                 Si(J,k) = Simax
3 204                 Bs(J,k) = Bsmax
3 205                 Cl(J,k) = 0
3 206                 Cs(J,k) = 0
3 207                 Ci(J,k) = 0
3 208                 Cb(J,k) = 0
3 209                 Rsu(J) = 0
1 210     203     CONTINUE
2 211     202     CONTINUE
1 212         Cl(1,1) = CO
1 213         *
1 214         ***** Write initial profile to result file.
1 215         *
1 216         WRITE(*,*) ' Write to result file.'
1 217         WRITE(20, '(A)')
1 218         WRITE(20, '(G10.3)') UVALUE
1 219         WRITE(20, '(I8)') NINT(KK*dT)
1 220         WRITE(20, '(A)')
1 221         DO 205 I = 1, N
2 222             WRITE(20,25) i, Cl(i,1), Cs(i,1), Ci(i,1), Cb(i,1), Rsu(i)
2 223     205     CONTINUE
1 224         .....
1 225         *           Begin Calculations           *
1 226         .....
1 227         DO 2 KK = 1, ENDSIM
2 228             WRITE(*,*) ' Time = ', KK*dT*WRT
2 229             Dp = u*p/2*(dX - u*dT)
2 230             DO 3 JJ = 1, WRT
3 231                 WRITE(*,*) ' Write # = ', JJ
3 232             DO 4 I = 1, N
4 233             *
4 234             *           Calculate substrate utilization rate Rsu in cell I.
4 235             *
4 236             *            $Rsu(i) = km*B*Cl(i,1)/(Ks + Cl(i,1))/p$ 
4 237             *

```

```

4 238 *      Calculate liquid concentration at I + dT.
4 239 *
4 240 *----- Cell 1
4 241 *      IF(I .EQ. 1)THEN
4 242 *          C1(i,2) = C1(i,1)
4 243 *          $          + R*dT/(A*dX*p)
4 244 *          $          + (D-Dp)*dT/dX**2/p * (C1(i+1,1) - C1(i,1))
4 245 *          $          + dT * (Cs(i,1)*K2 - C1(i,1)*K1*Ss(i,1))
4 246 *          $          + dT * (Cb(i,1)*K6 - C1(i,1)*K5*Bs(i,1))
4 247 *          $          - Rsu(i)*dT
4 248 *----- Cells 2 through N
4 249 *      ELSE
4 250 *          C1(i,2) = C1(i,1)
4 251 *          $          + (D-Dp)*dT/dX**2/p*(C1(i-1,1)+C1(i+1,1)-2*C1(i,1))
4 252 *          $          + dT * (Cs(i,1)*K2 - C1(i,1)*K1*Ss(i,1))
4 253 *          $          + dT * (Cb(i,1)*K6 - C1(i,1)*K5*Bs(i,1))
4 254 *          $          - Rsu(i)*dT
4 255 *      ENDIF
4 256 *
4 257 *      Calculate solid's surface concentration at I + dT.
4 258 *
4 259 *          Cs(i,2) = Cs(i,1)
4 260 *          $          + dT*p/S * (C1(i,1)*K1*Ss(i,1) - Cs(i,1)*K2)
4 261 *          $          + dT * (Ci(i,1)*K4 -Cs(i,1)*K3*Si(i,1))
4 262 *
4 263 *      Calculate solid's interior concentration at I + dT.
4 264 *
4 265 *          Ci(i,2) = Ci(i,1)
4 266 *          $          + dT * (Cs(i,1)*K3*Si(i,1) - Ci(i,1)*K4)
4 267 *
4 268 *      Calculate bacteria's concentration at I + dT.
4 269 *
4 270 *          Cb(i,2) = Cb(i,1)
4 271 *          $          + dT*p/B * (C1(i,1)*K5*Bs(i,1) - Cb(i,1)*K6)
4 272 *          $          - dT * Cb(i,1)*Kb
4 273 *
4 274 *      Calculate remaining solid surface sites available.
4 275 *
4 276 *          Ss(i,2) = Ssmax - Cs(i,2)
4 277 *
4 278 *      Calculate remaining solid interior sites available.
4 279 *
4 280 *          Si(i,2) = Simax - Ci(i,2)
4 281 *
4 282 *      Calculate remaining bacterial sites available.
4 283 *
4 284 *          Bs(i,2) = Bsmax - Cb(i,2)
4 285 *      CONTINUE
3 286 *      Advance time increment one dT by replacing (i,1) with (i,2) *
3 287 *      DO 204 L = 1,N
4 288 *          C1(l,1) = C1(l,2)
4 289 *          Cs(l,1) = Cs(l,2)
4 290 *          Ci(l,1) = Ci(l,2)
4 291 *          Cb(l,1) = Cb(l,2)
4 292 *          Ss(l,1) = Ss(l,2)
4 293 *          Si(l,1) = Si(l,2)
4 294 *          Bs(l,1) = Bs(l,2)
4 295 *      204 CONTINUE
3 296 *----- Advection after all else.
3 297 *      DO 40 I = 1, N

```

```

4 298          IF(I .EQ. 1)THEN
4 299             C1(i,2) = C1(i,1) - u * dT/dX = C1(i,1)
4 300          ELSE
4 301             C1(i,2) = C1(i,1) + u * dT/dX = (C1(i-1,1) - C1(i,1))
4 302          ENDIF
4 303      40  CONTINUE
3 304          DO 41 I = 1, N
4 305             C1(i,1) = C1(i,2)
4 306      41  CONTINUE
3 307  .....
3 308  *                               Write to result file                               *
3 309  .....
3 310      3  CONTINUE
2 311          WRITE(*,*) ' Write Profile to result file.'
2 312          WRITE(20,'(A)')
2 313          WRITE(20,'(G10.3)')UVALUE
2 314          WRITE(20,'(G10.3)') WRT*KK=dT
2 315          WRITE(20,'(A)')
2 316          DO 201 I = 1,N
3 317             WRITE(20,25)I,C1(i,1),Cs(i,1),Ci(i,1),Cb(i,1),Rsu(i)
3 318      201  CONTINUE
2 319      2  CONTINUE
1 320          IF(RECORD .NE. 0)THEN
1 321             VALUE = VALUE + INCR
1 322             WRITE(10,REC=INT(RECORD))VALUE
1 323             CLOSE(10)
1 324             OPEN(10,FILE=PARAM, STATUS = 'OLD',ACCESS='DIRECT',RECL=100)
1 325             CALL INPT (u,p,A,S,B,D,X,MW,K1,K2,K3,K4,K5,K6,Kb,Km,Ks,
1 326             $          Ssmax,Simax,Bsmax,dX,dT,Iwrite,Tend,CO,R,RECORD,
1 327             $          LOW,HIGH,INCR)
1 328          ENDIF
3 329      1  CONTINUE
330 *
331      21  FORMAT(/,1X,A)
332      22  FORMAT(1X,A,F6.2,2X,A)
333      23  FORMAT(1X,A,G10.3,2X,A)
334      24  FORMAT(1X,A,F3.1,A)
335      25  FORMAT(1X,I2,SG10.3)
336      99  END

```

Name	Type	Offset	P	Class
A	REAL	12070		
B	REAL	12078		
BEGIN	REAL	12192		
BS	REAL	3202		
BSMAX	REAL	12138		
CO	REAL	12158		
CB	REAL	10402		
CI	REAL	8802		
CL	REAL	5602		
CS	REAL	7202		
D	REAL	12082		
DP	REAL	12252		
DT	REAL	12146		
DX	REAL	12142		
EDIT	CHAR*1	12182		
I	INTEGER*4	12184		
EDUAL	REAL	12188		
ENDSIM	INTEGER*4	12220		

FINAL	INTEGER*4	12196	
HIGH	REAL	12174	
I	INTEGER*4	12240	
II	INTEGER*4	12204	
INCR	REAL	12178	
INT			INTRINSIC
J	INTEGER*4	12228	
JC	INTEGER*4	12256	
K	INTEGER*4	12224	
K1	REAL	12094	
K2	REAL	12098	
K3	REAL	12102	
K4	REAL	12106	
K5	REAL	12110	
K6	REAL	12114	
KB	REAL	12118	
KK	INTEGER*4	12236	
KM	REAL	12122	
KS	REAL	12126	
L	INTEGER*4	12268	
LDW	REAL	12170	
MW	REAL	12090	
N	INTEGER*4	12212	
NINT			INTRINSIC
P	REAL	12066	
PAR	CHAR*20	12042	
PARAM	CHAR*20	12002	
R	REAL	12162	
RECORD	REAL	12166	
RESULT	CHAR*20	12022	
RSU	REAL	4802	
F	REAL	12074	
S	REAL	1602	
SIMAX	REAL	12134	
SS	REAL	2	
SSMAX	REAL	12130	
TEND	REAL	12154	
TWRITE	REAL	12150	
U	REAL	12062	
VALUE	REAL	12200	
WRT	INTEGER*4	12216	
X	REAL	12086	