AN ABSTRACT OF THE THESIS OF

Fredrick Thomas Lindstrom for the DOCTOR OF PHILOSOPHY
(Name) (Degree)

in MATHEMATICS presented on March 21, 1969
(Major) (Date)

Title: A MATHEMATICAL MODEL SIMULATING MASS TRANSPORT OF CHEMICALS IN SATURATED POROUS MEDIA

Abstract approved: Redacted for privacy
William M. Stone

A mathematical model simulating mass transport of chemicals in saturated porous medium is given in four parts. Included in the development is the physical phenomenon of adsorption of molecules of chemicals on the surrounding walls of the porous medium. The four main areas of study are:

(1) Simple one dimensional diffusion of chemicals into a water saturated porous medium with adsorption and with a zero initial distribution,

(2) One dimensional conduction and diffusion of chemicals in a water saturated porous medium together with adsorption and a zero initial distribution of chemical,

(3) One dimensional mass transport via conduction, diffusion, and adsorption of a non-zero initial distribution of chemical in a water saturated porous medium,

(4) Multi-dimensional mass transport via conduction, diffusion, and adsorption of a non-zero initial distribution of chemical in a water saturated porous medium.

Transport equations are developed for each system considered. Key physical parameters such as the total pore space, effective pore space, hydrodynamic flow velocity, diffusion coefficient, and retentive ability are included. Solutions to the transport equations are derived by the methods of integral transforms and finite differences. Experimental work on the first submodel is included. Theoretical curves for various values of the parameters for the remaining three submodels are given.

A Mathematical Model Simulating Mass Transport of Chemicals in Saturated Porous Media

by

Fredrick Thomas Lindstrom

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

June 1969

APPROVED:

Redacted for privacy

Professor of Mathematics

in charge of major

Redacted for privacy

Chairman of Department of Mathematics

Redacted for privacy

Dean of Graduate School

Date thesis is presented March 21, 1969

Typed by Clover Redfern for Fredrick Thomas Lindstrom

ACKNOWLEDGMENTS

I wish to thank my God for his help in the writing of this paper. "The fear of the Lord is the beginning of knowledge: but fools despise wisdom and instruction." (Prov. 1: 7, National Ed. 1941).

I wish to express my sincere appreciation to Professor . W. Stone for his many suggestions given during the writing of this manuscript. Also, I am deeply indebted to Professor R. Guenther for his most able suggestions and help on both reading and correcting the original draft of this paper.

This research effort was sponsored in part by the U. S. Public Health Service under grant No. ES00040-02.

TABLE OF CONTENTS

Chapter | Page

LIST OF APPENDIX TABLES

LIST OF FIGURES

NOMENCLATURE

$U(x, t)$ = chemical concentration in porous medium voids (μg chemical/gram of solution)

$N(x, t)$ = sorbed chemical concentration (μg chemical/gram of medium)

$M_c(t)$ = total mass in the packed part of the column. (Both free and sorbed phases added together at time t.) (gms)

$U_r(t)$ = concentration of chemical in the well-stirred reservoir at time t. $\frac{gms}{cm^3}$

V_o = volume of reservoir (cm^3)

V_c = volume of packed part of column (cm^3)

M_o = initial mass of chemical in reservoir (gm)

U_o = initial concentration of chemical in reservoir (gm/cm^3)

D_o = diffusion coefficient in non-sorbing medium (open channel voids)

D_{o1} = diffusion coefficient in non-sorbing medium (porous medium voids)

ϵ_o = bulk porosity of medium (percent) (Scheidegger, 1960)

ϵ_d = effective porosity of medium (percent)

ϵ_{min} = minimum effective porosity attainable under reasonably high flow velocity values such as the order of $10 \frac{meters}{day}$ (percent)

α = ratio of chemically active surface area of medium to total surface area

γ = partition coefficient (19) defined as $\gamma = \exp\left[-\Delta G/RT\right]$

ΔG = free energy change of sorbtion (Kilo-cal/mole)

R = gas constant (Kilo-cal/mole-^{o}K)

T = Kelvin temperature (degrees)

L' = length of column packed with porous medium (cm)

L = half-distance between open channels (cm)

Q_o = influx velocity of chemical solution (cm/sec)

λ = coupling coefficient (cm/sec) defined as that coefficient which ties two either related or unrelated systems together

A = plane surface area of packed part of column at $x = 0$ (A assumed uniform down column) (cm^2)

A MATHEMATICAL MODEL SIMULATING MASS TRANSPORT OF CHEMICALS IN SATURATED POROUS MEDIA

I. INTRODUCTION

Importance of Problem

The environment in which man lives is rapidly becoming polluted with a broad spectrum of chemicals. Included in this array of chemicals are the classes known as herbicides, insecticides, and fertilizers (see Appendix I for chemical term definitions). These three classes are rapidly increasing in their importance since man uses great quantities of each of these chemical types every day.

In nature some of these chemicals are concentrated to toxic or lethal concentration levels. The mechanism of concentration is only recently beginning to be understood. Since some of these chemicals may be concentrated to high levels in man's environment and by definition man's environment includes the air he breathes, the water he drinks, and the soil in which he grows his crops, it is of the utmost importance for continued existence of both plants and animals to know how these chemicals move in the environment.

Historical Justification

In recent years several workers have pointed out the seriousness of the problem of chemical concentrations existing in man's environment. A survey carried out by Green, Gunnerson, and Lichtenberg, (1966) has shown that chlorinated hydrocarbons have been present in our national waters since 1958 and that they have done considerable damage to fish populations.

They also emphasize that regular surveys regarding the presence of pesticides (insecticides) are necessary. In a detailed investigation by Butler (1966a, 1966b, 1966c) on the effect of pesticides in estuaries and marine environment it was shown that even the presence of small amounts of pesticides did considerably harm to the production of fish and oysters. Similar results have also been reported by Stickel (1966). Brown and Nishioka (1967) have found considerable amounts of the chemicals DDT, DDD, dieldrin, endrin, heptachlor, 2, 4-D, etc. in the soils, lakes, and rivers of the western United States. The existence of DDT in various crops and soils has also been reported by Seal, Dawsey, and Cavin (1967).

Woodwell (1967) has pointed out that it is possible for chemicals to enter into biological cycles and become distributed in such a way so as to concentrate them to a dangerous level. The existence of pesticides in man is so common that Wasserman and Gon (1967) have shown chemicals to represent a current constituent of the human body fat.

Historical Résumé of Mass Transport of Chemicals in Porous Media

The fate of chemicals in the soil, a type of porous medium, is currently a problem of great interest. The main parameters involved in the process of chemical movement in porous medium are:

(1) the moisture content (water content),

(2) the percolation velocity of the water or chemical solution through the void spaces in the porous medium,

(3) the sorbtive properties of the medium,

(4) the medium partical size distribution (see Appendix A),

(5) the ratio of the chemically active surface area of the particles of the medium to the total surface area of the particles of the medium,

(6) the magnitude of the chemical diffusion coefficient in the medium-water-chemical matrix,

(7) and the biological transportation (i. e., microbiological phenomena).

Much work has been done on the movement, uptake, and degredation of chemicals which have been applied to soils. Examples of this are found in the work of Ashton (1961), Burnside, Feuster, and Wicks (1963), Freed, Vernette, and Montgomery (1962), Harris and Warren (1962), Hartley (1964), Lambert, Porter, and Schieferstein (1965), and Talbert and Fletchall (1965). Most of this work has been of a qualitative nature.

Though very useful by itself, qualitative work sometimes does not give the understanding of the processes involved which can be derived from the development and testing of a quantitative physical model.

Some partial quantitative models have been postulated as shown in the works of Burnside et al. (1963) and Hayward and Trapnell (1964). Most models set forth so far are based on a linear diffusion-type partial differential equation. This type of equation fails to take mass transport via hydrodynamic convection into account and is thus quite limited in its scope. Several detailed analyses of the movement of chemicals in porous medium can be found in the literature. These include the early work on the adsorption of chemicals in chromatography and ion-exchange resins done by Kipling (1965), Lapidus and Amundson (1952), Van Schaik, Kemper, and Olsen (1966), and Vieth and Sladek (1965). For diffusion in proteins and polymers see Chao and Hodscher (1966), Houghton (1963), and Ward and Holly (1966). For mixing in chemical reactors see Bischoff (1966) and Bischoff and Levenspiel (1966a, 1966b). These studies have led to several mathematical models. One early model by Kasten, Lapidus, and Amundson (1952) which has proved very useful in chromatography theory is based on the diffusional plus convective type partial differential equation

$$U_t + VU_x = DU_{xx} - \frac{1}{\epsilon_o} N_t$$

where U is the concentration of chemical flowing in the voids, V is the hydrodynamic flow velocity of the water carrying the chemical, ϵ_o is the fractional void volume of the packed bed or porous medium, and N is the moles of solute adsorbed per unit volume of packed bed. Using the same type of equation, other models have been developed by Houghton (1963) and Chao and Hodscher (1966). However, these models are based on non-linear adsorption, which may be unnecessary for many herbicides applied to the soil in weak concentrations.

Models which more closely represent the conditions of chemical movement in soils (porous medium) may be found in the theory of chromatography (see Littlewood (1962) and Purnell (1962)). Lapidus and Amundson (1952) made a great contribution along the lines of chromatography even though their model assumes a constant surface concentration. Brenner (1962) improved the model postulated by Lapidus by incorporating a realistic boundary condition of fluxing at the surface.

In this paper we shall state three distinct models:

(1) a diffusion type model for both finite and semi-infinite length packed beds (porous medium);

(2) diffusional plus convective mass transport type model for the semi-infinite packed bed;

(3) diffusional, convective, and linear accumulative loss term type model for the semi-infinite packed bed.

Figures and equations for each model will be given together with sufficient justification. The first model and part of the second one have been published in connection with work currently being conducted at Oregon State University. For definitions of the various chemical and soil terms used throughout the paper refer to Appendix A. Note also the special nomenclature section which defines all the terms, parameters, quantities, etc. used in the paper.

II. SIMPLE DIFFUSIONAL MODEL

Introduction

In this chapter we shall develop a one-dimensional mass transport model based upon diffusion only. Appropriate boundary and initial conditions will be given for two cases:

(1) finite length packed bed of porous medium;

(2) semi-infinite length packed bed.

Mass Transport Model

Consider an experimental arrangement as shown in Figure 1. A column of large diameter of homogeneous porous medium (possibly soil) is maintained in intimate contact with a reservoir containing a well-mixed chemical solution. The initial concentration of chemical in the reservoir is U_o and the initial mass is M_o. It is assumed that the concentration gradient developed along the boundary $x = 0$ tends to distribute the chemical into the water saturated porous medium according to the partial differential equation given by Lindstrom et al. (1968).

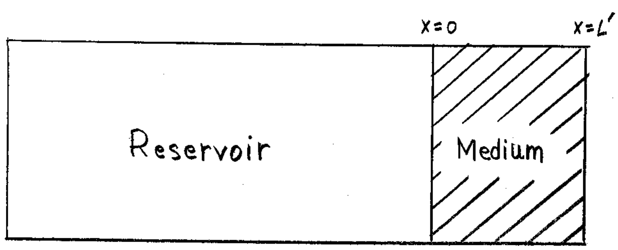

Figure 1. Sketch of first experimental model.

(2. 1) $$U_t = D_o U_{xx} - \frac{1}{\epsilon_o} N_t \, .$$

Assuming that the chemical is sorbed (see Appendix A) quickly once it is brought by diffusion into the force field of the active sorbing sites on the porous medium particles, and assuming a partition of chemical between free and adsorbed phases of the form

(2. 2) $$N(x, t) = \alpha\gamma U(x, t),$$

we obtain upon substitution of (2. 2) into (2. 1) and with subsequent re-arrangement

(2. 3) $$(1+\frac{\alpha\gamma}{\epsilon_o})U_t = D_o U_{xx} \, .$$

Define

(2. 4) $$D = \frac{D_o}{1+\frac{\alpha\gamma}{\epsilon_o}}$$

as the reduced diffusion coefficient. By substituting (2. 4) into (2. 3) the diffusion equation (2. 1) is reduced to the standard form given by Churchill (1944).

(2. 5) $$DU_{xx} = U_t \, .$$

In light of (2. 5) it is easily seen that when measuring diffusion coefficients in a sorbing porous medium, one is actually measuring D, as given by (2. 4) which incorporates the chemical and physical properties of the porous medium α, γ, and ϵ_o.

Two different sets of boundary conditions will be considered. For the first case the packed column is considered to be of finite length, which imposes a lower boundary condition of no mass transport across the plane $x = L'$. In the second case the length of the column is considered to tend to infinity (i. e., semi-infinite case). In both cases the solution theory employed is that of Laplace transforms.

Case 1: Packed Column of Finite Length

Assume that at time $t = 0$ the initial concentration in the porous medium is zero, for example,

$$U(x, +0) = 0, \quad 0 < x \leq L'. \tag{2. 6}$$

It is furthermore assumed that for all time $t \geqq 0$ the lower boundary condition

$$U_x(L', t) = 0 \tag{2. 7}$$

holds. Assume that the surface boundary condition

$$U(0, t) = U_r(t) \tag{2. 8}$$

is valid $0 \leq t < \infty$. We must now determine $U_r(t)$. According to the principle of conservation of mass

$$M_o = U_r(0)V_o = U_r(t)V_o + M_c(t). \tag{2.9}$$

Solving for $U_r(t)$ we find

$$U_r(t) = U_r(0) - \frac{M_c(t)}{V_o}. \tag{2.10}$$

Since the mass of chemical which has been transported into the porous medium via diffusion is divided into that which is free and that which is sorbed, the total mass in the medium is given as

$$M_c(t) = A\epsilon_o(1+\alpha'\gamma)\int_o^{L'} U(x,t)dx \tag{2.11}$$

where

$$\alpha' = \frac{\alpha(1-\epsilon_o)}{\epsilon_o}.$$

By substituting (2.11) into (2.10), the concentration in the reservoir $U_r(t)$ is found to be

$$U_r(t) = U_r(0) - \frac{A\epsilon_o(1+\alpha'\gamma)}{V_o}\int_0^{L'} U(x,t)dx. \tag{2.12}$$

<u>Solution Technique.</u> Recall that the definition of the one sided Laplace transform of a function $f(t)$, $f(t)$ bounded and measurable on $[0,\infty)$, is given as

(2.13) $$f(s) = \int_0^{\infty} e^{-st} f(t)dt.$$

The definition of the inverse transform is given as (McLachlan, 1963)

(2.14) $$f(t) = \frac{1}{2\pi i} \int_{Br_1} e^{st} f(s)ds,$$

where Br_1 is the Bromwich right line contour. Assuming that U is twice continuously differentiable with respect to x, and once with respect to t, we find upon applying Laplace transforms to both sides of (2.5), (2.6), (2.7), and (2.12) the following set of transformed equations:

(2.15) (i) $$D \frac{d^2u}{dx^2} = su - u(x, +0),$$

(ii) $$u(x, +0) = 0,$$

(iii) $$u_x(L', s) = 0,$$

(iv) $$u(0, s) = \frac{U_r(0)}{s} - \frac{A\epsilon_o}{V_o}(1+a'\gamma)\int_0^{L'} u(x, s)ds.$$

The solution to (2.15i) subject to (2.15ii, iii, and iv) is given by the equation

(2.16)
$$u(x, s) = \frac{L'^2}{D} U_r(0) \frac{\cosh\sqrt{\frac{s}{D}}(L'-x)}{s\frac{L'^2}{D}\cosh\sqrt{\frac{s}{D}}L' + BL'\sqrt{\frac{s}{D}}\sinh\sqrt{\frac{s}{D}}L'},$$

where

$$B = \frac{A\epsilon_o L'}{V_o}(1+a'\gamma) = \epsilon_o \frac{V_c}{V_o}(1+a'\gamma).$$

The set of zeros of the denominator in (2.16) is given by

$$i\beta_n = L'\sqrt{\frac{s_n}{D}},$$

where the set $\{\beta_n\}$ is the set of zeros of the equation

(2.17)
$$\beta \cos \beta + B \sin \beta = 0, \quad B \geqq 0.$$

Tables of values of β_n for various values of B may be found in Carslaw and Jaeger (1959).

The residue at $s = 0$ is easily found to be

$$R_o = \lim_{s \to 0} s\frac{L'^2}{D} U_r(0) \frac{e^{st}\cosh\sqrt{\frac{s}{D}}(L'-x)}{s\frac{L'^2}{D}\cosh\sqrt{\frac{s}{D}}L' + BL'\sqrt{\frac{s}{D}}\sinh\sqrt{\frac{s}{D}}L'}.$$

Passing to the limit yields

(2.18)
$$R_o = \frac{U_r(0)}{(2\pi i)(1+B)}$$

The residue at

$$s_n = -\frac{\beta_n^2 D}{L'^2}$$

is

$$R_n = \lim_{s \to \frac{-\beta_n^2 D}{L'^2}} \left\{ \frac{\left(s+\frac{\beta_n^2 D}{L'^2}\right) e^{st} \cosh \sqrt{\frac{s}{D}}\,(L'-x)}{\frac{sL'^2}{D} \cosh \sqrt{\frac{s}{D}}\, L' + BL'\sqrt{\frac{s}{D}} \sinh \sqrt{\frac{s}{D}}\, L'} \right\} .$$

This limit is

$$(2.19) \qquad R_n = \frac{2BU_r(0) e^{-\beta_n^2 \frac{Dt}{L'^2}} \cos \beta_n (1-\frac{x}{L'})}{(2\pi i)[\beta_n^2 + B(1+B)] \cos \beta_n} .$$

We thus have from the residue theorem

$$(2.20) \qquad U(x,t) = U_r(0) \left\{ \frac{1}{1+B} + 2B \sum_{n=1}^{\infty} \frac{\cos \beta_n (1-\frac{x}{L'}) e^{\frac{-\beta_n^2 Dt}{L'^2}}}{\cos \beta_n (\beta_n^2 + B(1+B))} \right\} .$$

This representation of $U(x,t)$ is of the Fourier series type with the set of orthogonal functions $\{\cos \beta_n (1-\frac{x}{L'})\}$ forming the basis for the Hilbert space of L^2 functions defined on $[0, L']$. Observe that we can also write

$$(2.21) \qquad U(x,t) = U_r(0) \left\{ \frac{1}{1+B} - 2 \sum_{n=1}^{\infty} \frac{\beta_n \cos \beta_n (1-\frac{x}{L'}) e^{\frac{-\beta_n^2 Dt}{L^2}}}{[\beta_n^2 + B(B+1)] (\sin \beta_n)} \right\} .$$

This is accomplished by using Equation (2. 17) which defines the set of β_n. We now show that (2. 20) satisfies the original partial differential equation (2. 5) in the strip

$$Q = \{(x, t) | \; 0 < x < L', \; 0 < t < \infty\},$$

that is $U(x, t) \in C^{2,1}[Q]$. The formal second partial derivative of U with respect to x is given as

$$U_{xx} = \frac{-2BU_r(0)}{L'^2} \sum_{n=1}^{\infty} \frac{\beta_n^2 \cos \beta_n (1 - \frac{x}{L'}) e^{\frac{-\beta_n^2 Dt}{L'^2}}}{\cos \beta_n (\beta_n^2 + B(1+B))}$$

and the first formal partial derivative of U with respect to t is given as

$$U_t = \frac{-2BDU_r(0)}{L'^2} \sum_{n=1}^{\infty} \frac{\beta_n^2 \cos \beta_n (1 - \frac{x}{L'}) e^{\frac{-\beta_n^2 Dt}{L'^2}}}{\cos \beta_n (\beta_n^2 + B(1+B))} .$$

Thus, we see that formally at least

$$DU_{xx} = U_t, \quad \text{all} \quad x, t \in Q.$$

That the term wise differentiation is valid follows from the uniform convergence of the resulting series. We show the uniform convergence by showing that a marjorant exists.

By observing a table of values of equation (2. 17) (see Carslaw and Jaeger (1959)) for various values of $B \geqq 0$, we quickly see that the set of zeros β_n has the following property,

$$\frac{1}{\beta_n^2} \leqq \frac{1}{[(2n-1)\frac{\pi}{2}]^2}, \quad n = 1, 2, 3, \ldots .$$

Also, it is evident that

$$\frac{1}{\beta_n^2+B(1+B)} \leqq \frac{1}{\beta_n^2}, \quad \text{and} \quad \epsilon_o, V_o, V_o, \alpha'\gamma > 0; \; n = 1, 2, 3, \ldots$$

As $\max |\cos \beta_n(1-\frac{x}{L'})| \leqq 1, \quad 0 \leqq x \leqq L'$, we have the following chain of inequalities

$$\frac{D}{U_r(0)} \frac{\partial^2 U}{\partial x^2} = \frac{1}{U_r(0)} \frac{\partial U}{\partial t} = \frac{2BD}{L'^2} \sum_{n=1}^{\infty} \frac{\beta_n^2 \cos \beta_n (1-\frac{x}{L'}) \, e^{\frac{-\beta_n^2 DT}{L'^2}}}{\cos \beta_n (\beta_n^2 + B(1+B))}$$

$$\leqq \frac{2BD}{L'^2} \sum_{n=1}^{\infty} \psi_{,} \, e^{\frac{-\beta_n^2 Dt}{L'^2}}$$

$$\leqq \frac{2BD}{L'^2} \psi \int_0^{\infty} e^{-(2x-1)^2 \frac{\pi^2 Dt}{4L'^2}} dx$$

$$= \frac{B}{L'} \sqrt{\frac{D}{\pi t}} \, \psi \, \{1+ \operatorname{erf} (\frac{\pi}{2L'} \sqrt{Dt})\}, \quad t > 0,$$

where

$$\psi = \max_{1 \le n < \infty} \left|\frac{1}{\cos \beta_n}\right|$$

and

$$\operatorname{erf} W = \frac{2}{\sqrt{\pi}} \int_0^W e^{-V^2} dV .$$

Thus, we have found a majorant and the interchange of differentiation and summation is justified.

By computing the formal derivative of $U(x, t)$ with respect to x we find

$$U_x = \frac{2BU_r(0)}{L'} \sum_{n=1}^{\infty} \frac{\beta_n \sin \beta_n (1 - \frac{x}{L'}) e^{\frac{-\beta_n^2 Dt}{L'^2}}}{\cos \beta_n (\beta_n^2 + B(1+B))} ,$$

which can be shown to be a uniformly convergent series representation in Q by the same type of analysis as was carried out for U_{xx} and U_t. In particular for the line $\{(L', t) | \ 0 < t < \infty\}$ we find

$$U_x(L', t) = 0.$$

This is in agreement with boundary condition (2. 7).

We now will proceed to check the solution by substituting the series representation into (2. 12) and noting the short and long time values of $U_r(t)$. Substituting $U(x, t)$ from (2. 21) into (2. 12) obtains

(2.22)
$$U_r(t) = U_r(0) - U_r(0)\frac{B}{L'}\int_0^{L'}\left\{\frac{1}{1+B} - 2\sum_{n=1}^{\infty}\frac{\beta_n \cos\beta_n(1-\frac{x}{L'})e^{\frac{-\beta_n^2 Dt}{L'^2}}}{[\beta_n^2+B(B+1)\,(\sin\beta_n)]}\right\} dx.$$

Carrying out the integration formally yields

(2.23)
$$U_r(t) = U_r(0) - \frac{BU_r(0)}{L'}\left\{\frac{L'}{1+B} - 2L'\sum_{n=1}^{\infty}\frac{e^{\frac{-\beta_n^2 Dt}{L'^2}}}{[\beta_n^2+B(B+1)]}\right\}.$$

Using the results of Appendix F, namely

$$\frac{1}{1+B} = \lim_{t\to 0} 2\sum_{n=1}^{\infty}\frac{e^{\frac{-\beta_n^2 Dt}{L'^2}}}{(\beta_n^2+B(B+1))},$$

we have that,

(2.24)
$$\lim_{t\to 0} U_r(t) = U_r(0) - \frac{BU_r(0)}{L'}\left\{\frac{L'}{1+B} - \frac{L'}{1+B}\right\} = U_r(0).$$

Also, from (2.23) we find

(2.25)
$$\lim_{t\to\infty} U_r(t) = \frac{U_r(0)}{1+B}.$$

Result (2. 25) can also be obtained directly from the steady state solution of (2. 5) subject to the bottom boundary condition and conservation of mass.

<u>Asymptotic Formula for $U(x, t)$.</u> For small values of time, it would be advantageous to have a formula which is rapidly convergent to compute $U(x, t)$ with. Observe that Equation (2. 20), while affording an exact solution to the original partial differential equation (2. 5), is slow in its convergence for small values of time. Let us replace Equation (2. 16) which is written as

$$U(x, s) = \frac{L'^2}{D} U_r(0) \frac{\cosh \sqrt{\frac{s}{D}}(L'-x)}{\frac{sL'^2}{D} \cosh \sqrt{\frac{s}{D}} L' + B \cdot L' \sqrt{\frac{s}{D}} \sinh \sqrt{\frac{s}{D}} L'} ,$$

by the expression

$$U_1(x, s) = U_r(0) \frac{\exp\left[-x\sqrt{\frac{s}{D}}\right]}{\sqrt{s}\left(\sqrt{s} + B\frac{\sqrt{D}}{L'}\right)} . \tag{2. 26}$$

The inverse of the transform in (2. 26) is found in the tables (Erdelyi <u>et al.</u>, 1964) to be

$$U_1(x, t) = U_r(0) \cdot \exp\left[B\frac{x}{L'}\right] \exp\left[B^2\frac{Dt}{L'^2}\right] \operatorname{erfc}\left(\frac{x+2\frac{BDt}{L}}{2\sqrt{Dt}} \right) , \tag{2. 27}$$

where

$$\operatorname{erfc} W = \frac{2}{\sqrt{\pi}} \int_{W}^{\infty} e^{-p^2} dp \; .$$

This asymptotic formula is rapidly convergent towards zero for small values of time t with $x > 0$. It will be of interest to note that we will see an equation like (2. 27) again in the case of chemical flow into a semi-infinite porous medium.

Since, $U_1(x, t)$ defined by Equation (2. 27) becomes a better and better approximation to $U(x, t)$ defined by (2. 20) as t tends smaller and smaller, we have by the asymptotic nature of (2. 27)

$$|U_1(x, t) - U(x, t)| < \epsilon , \quad \epsilon > 0$$

for

$$0 \leq |t| \leq \delta(\epsilon), \quad 0 < x \leq L' \; .$$

Thus,

$$\lim_{t \to 0+} U_1(x, t) = U(x, 0+)$$

This limit is computed immediately with the aid of (2. 27).

$$\lim_{t \to 0+} U_1(x, t) = 0,$$

which agrees with the initial condition (2. 6).

Case 2: Packed Column of Semi-Infinite Length

Referring to Figure 1 again let $L' \to \infty$. Then, the lower boundary condition becomes

$$\lim_{L' \to \infty} U_x(L', t) = 0 \tag{2.28}$$

and the upper boundary condition is given as

$$U(0, t) = U_r(t) = U_r(0) - \frac{A\epsilon_o(1+\alpha'\gamma)}{V_o} \int_0^\infty U(x, t)dx. \tag{2.29}$$

Again assuming (2.5) to be valid and the same initial condition as before, i.e.

$$U(x, +0) = 0,$$

we find the transformed system of equations given as:

(2.30) (i) $D\dfrac{d^2u}{dx^2} = su - U(x, +0),$

(ii) $U(x, +0) = 0,$

(iii) $\lim\limits_{L' \to \infty} u_x(L', s) = 0,$

(iv) $u(0, s) = \dfrac{U_r(0)}{s} - \dfrac{A\epsilon_o}{V_o}(1+\alpha'\gamma)\displaystyle\int_0^\infty u(x, s)dx.$

The solution of (2.30i) subject to (2.30ii, iii, iv) is given as

$$(2.31) \qquad u(x, s) = \frac{U_r(0) \exp\left[-x\sqrt{\frac{s}{D}}\right]}{\sqrt{s}\,(\sqrt{s} + B_1\sqrt{D})},$$

where

$$B_1 = \epsilon_o \frac{A}{V_o} (1+\alpha'\gamma) .$$

The inverse transform of (2. 31) is found in the tables (Erdelyi et al., 1964) to be,

$$(2.32) \qquad U(x, t) = U_r(0) \exp[B_1 x] \exp[B_1^2 Dt] \operatorname{erfc}\left\{\frac{x+2B_1 Dt}{2\sqrt{Dt}}\right\},$$

with erfc W being defined in (2. 27).

When V_o is large, or for small value of t (i. e., whenever $B_1\sqrt{Dt} \ll 1$) Equation (2. 32) reduced to

$$(2.33) \qquad U(x, t) = U_r(0) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right).$$

Hence, one is justified in using (2. 33) instead of (2. 32) whenever t is small. Note the similarity between (2. 27) and (2. 32).

This theory has been applied by Lindstrom et al. (1968) to calculate diffusion coefficients for the chemical 2, 4-D (2, 4-dichlorophenoxy acetic acid) in different soils (examples of porous medium). For figures and tables of data recovered from experiments performed refer to Appendix B.

III. MASS TRANSPORT VIA DIFFUSION AND CONVECTION

Introduction

In this chapter we will develop a one dimensional mass transport model based upon diffusion and hydrodynamic convection of mass. Again, as in Chapter II, we state the appropriate boundary and initial conditions. Only the semi-infinite case will be given here.

Mass Transport Model

Consider an experimental setup as is shown in Figure 2.

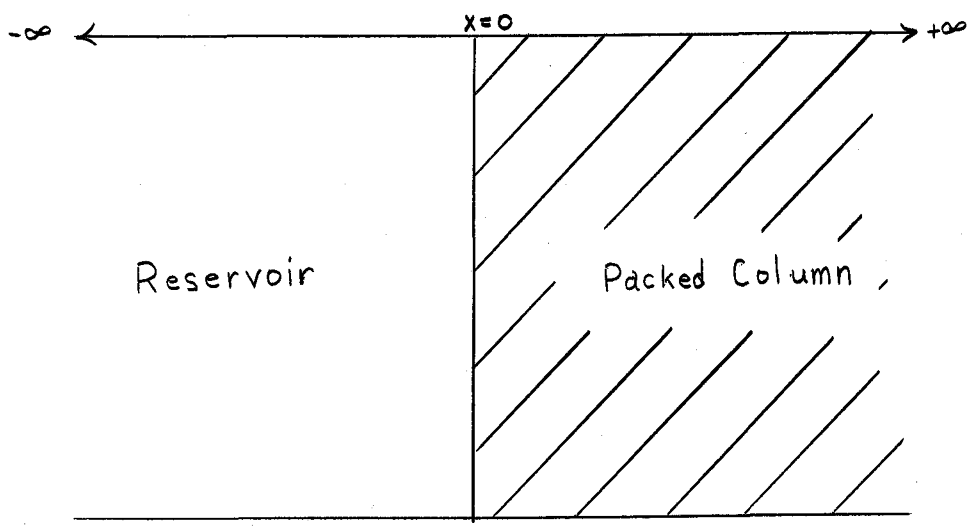

Figure 2. Sketch of semi-infinite medium for second model.

As we have a mass transport problem in which there exist concentration gradients, we shall base our derivation on 1) Fick's Law, 2) conservation of matter, and 3) an adsorption equation. For the last stated assumption we will use the same form of partitioning between adsorbed and free chemical as was stated in Chapter II,

(3.1) $$N(x, t) = \alpha\gamma U(x, t).$$

Now by considering the flux of chemical J across an imaginary boundary of a plane sheet of packed porous bed at depth x, we have the vector expression (one dimensional) for the flux

(3.2) $$J = -D_o(U)U_x + V_o(x, t) \cdot U(x, t),$$

where $D_o(U)$ is the diffusivity of the chemical in the void spaces of the packed bed. $V_o(x, t)$ is the average water velocity in the interparticle voids. Note, all the mass transport is assumed to be uniform along the plane $x = a$ (a constant). Gradients exist normal to this plane only. Proceeding to a depth $x + \Delta x$, we find the same type of expression. The net gain of flux is given as

$$J_{x+\Delta x} - J_x = -D_o(U)\frac{\partial U}{\partial x}\bigg|_{x+\Delta x} + D_o(U)\frac{\partial U}{\partial x}\bigg|_x + V_oU\Big|_{x+\Delta x} - V_oU\Big|_x,$$

or

(3.3) $$\frac{\partial J}{\partial x} = \lim_{\Delta x \to 0} \frac{\Delta J_x}{\Delta x} = -(D_o(U)U_x)_x + (V_oU)_x .$$

Now by the law of conservation of matter for one dimensional flow

(3.4) $$U_t = -J_x .$$

Hence, we find upon substitution that

$$(3.5) \qquad U_t = (D_o(U)U_x)_x - (V_oU)_x \,.$$

To this equation we must add the appropriate loss of mass term to take into account adsorption of mass by the surrounding porous medium. Partial differentiation of (3.1) and subsequent multiplication of N_t by $\frac{\alpha\gamma}{\epsilon_d}$ yields

$$U_t = (D_o(U)U_x)_x - (V_oU)_x - \frac{\alpha\gamma}{\epsilon_d}U_t,$$

or upon combining like terms

$$(3.6) \qquad U_t = (D(U)U_x)_x - (VU)_x \,,$$

where

$$(3.7) \qquad \text{(i)} \qquad D(U) = \frac{D_o(U)}{1+\frac{\alpha\gamma}{\epsilon_d}}$$

and

$$\text{(ii)} \qquad V(x,t) = \frac{V_o(x,t)}{1+\frac{\alpha\gamma}{\epsilon_d}} \,.$$

For the remainder of this chapter, it is assumed that $D_o(U)$ is constant in U, i.e.,

$$D_o(U) = D_o, \qquad \text{(a constant)}.$$

Furthermore, for steady saturated plane flow in porous medium

$$V_x = V_t = 0.$$

Thus, (3. 6) is written as

$$U_t = DU_{xx} - VU_x , \tag{3.8}$$

which is the equation we are interested in solving subject to the following initial and boundary conditions:

(3. 9) (i) $U(x, +0) = 0,$

(ii) $-DU_x(0, t) = (h+V)(U_o - U(0, t)),$

(iii) $\lim_{x \to \infty} U_x = 0,$

where h is a constant parameter in space and time but is probably dependent upon temperature and surface forces acting in the porous medium.

We have chosen this set of initial and boundary conditions to simulate a chemical flow in porous medium which is initially at zero chemical concentration, is a mass conserving system, and the chemical moves into the porous medium under the combined driving forces of

(i) hydrodynamic convection (V)

(ii) molecular diffusion gradients (h).

We note here that the input flux of solution Q_o (see Appendix A) $(\frac{cm}{sec})$ is related to the effective porosity and the solution velocity (average velocity assumed here) in the porous medium voids by the simple relation

$$(3.10) \qquad V_o = \frac{Q_o}{\epsilon_d} .$$

A relation between the effective porosity ϵ_d and the bulk porosity ϵ_o has been postulated by Lindstrom and Boersma (work yet to be published) on the grounds of some recent experiments conducted at O. S. U., Department of Soils by Professor Boersma. The empirical equation is

$$(3.11) \qquad \epsilon_d = (\epsilon_o - \epsilon_{min}) \exp[-\theta V_o] + \epsilon_{min}$$

where θ is a constant parameter characterizing the soil. θ is temperature dependent, though as yet sufficient experimentation has not been done to attempt to deduce the form of this dependence. ϵ_{min} is defined as the minimum effective porosity attainable. $\epsilon_{min} > 0$ always; but, it may be small in numerical value.

Solution Technique

As (3. 8) and (3. 9) form a set of linear partial differential equations in space and time and since the coefficients are continuous (constant) on the space-time cylinder $\overline{Q}$, where

$$\overline{Q} = \{(x, t) \mid 0 \leq x < \infty, \; 0 \leq t < \infty\},$$

we assume that U is twice continuously differentiable with respect to x and once continuously differentiable with respect to t in Q, where

$$Q = \{(x, t) \mid 0 < x < \infty, \; 0 < t < \infty\}.$$

Also, it is assumed that U is Laplace transformable in Q. Hence, in applying Laplace transforms to (3. 8) and (3. 9) we obtain the following system:

(3. 12) (i) $$D\frac{d^2u}{dx^2} - V\frac{du}{dx} = su,$$

(ii) $$-Du_x(0, s) = (h+V)\left(\frac{U_o}{s} - u(0, s)\right),$$

(iii) $$\lim_{x \to \infty} u_x = 0.$$

Since $U(x, 0+) = 0$, we have the solution to (3. 12 i) subject to (3. 12 ii, iii) given as

(3. 13) $$u(x, s) = \left(\frac{h+V}{\sqrt{D}}\right) \frac{U_o \exp\left[\frac{xV}{2D} - x\sqrt{\frac{s}{D} + \frac{V^2}{4D^2}}\right]}{s\left[\frac{h+V/2}{\sqrt{D}} + \sqrt{D}\sqrt{\frac{s}{D} + \frac{V^2}{4D^2}}\right]}.$$

Applying the Mellin inversion theorem (McLachlan, 1963) to (3. 13) yields

$$U(x,t) = \frac{h+V}{\sqrt{D}}\, U_o \frac{e^{\frac{xV}{2D}}}{2\pi i} \int_{Br_1} \frac{e^{st} e^{-x\sqrt{\frac{s}{D} + \frac{V^2}{4D^2}}}\, ds}{s\left(\frac{h+\frac{V}{2}}{\sqrt{D}} + \sqrt{s + \frac{V^2}{4D}}\right)} \tag{3.14}$$

where Br_1 is the Bromwich right line contour. Let $p = s + \frac{V^2}{4D}$, $dp = ds$, then (3.14) reduces to the following complex integral

$$U(x,t) = \left(\frac{h+V}{\sqrt{D}}\right) U_o \frac{e^{\frac{xV}{2D} - \frac{V^2 t}{4D}}}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x\sqrt{\frac{p}{D}}}\, dp}{\left(p - \frac{V^2}{4D}\right)\left(\sqrt{p} + \frac{h+\frac{V}{2}}{\sqrt{D}}\right)} . \tag{3.15}$$

This integral has not been found in readily accessible tables, books, nor journals; therefore, we propose to evaluate it and thus form an extension to the tables of integral transforms.

We begin this analysis by observing that the integral expression (3.15) can be rewritten in the form

$$U(x,t) = \left(\frac{h+V}{\sqrt{D}}\right) U_o \frac{e^{\frac{xV}{2D} - \frac{V^2 t}{4D}}}{2\pi i}$$

$$\times \int_{Br_1} \frac{e^{pt}}{\sqrt{p}\left(p - \frac{V^2}{4D}\right)} \left\{ 1 - \frac{\frac{h+\frac{V}{2}}{\sqrt{D}}}{\sqrt{p} + \frac{h+\frac{V}{2}}{\sqrt{D}}} \right\} e^{-x\sqrt{\frac{p}{D}}}\, dp$$

or

(3.16)

$$U(x,t) = \left(\frac{h+V}{\sqrt{D}}\right)U_o \frac{e^{\frac{xV}{2D} - \frac{V^2 t}{4D}}}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x\sqrt{\frac{p}{D}}}\, dp}{\sqrt{p}\,(p - \frac{V^2}{4D})}$$

$$- \frac{(h+V)}{\sqrt{D}} \frac{(h+\frac{V}{2})}{\sqrt{D}} U_o \frac{e^{\frac{xV}{2D} - \frac{V^2 t}{4D}}}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x\sqrt{\frac{p}{D}}}\, dp}{\sqrt{p}\,(p - \frac{V^2}{4D})(\sqrt{p} + \frac{h+\frac{V}{2}}{\sqrt{D}})} .$$

Now we observe that (3.16) can formally be written as

(3.17)

$$U(x,t) = \left(\frac{h+V}{\sqrt{D}}\right)U_o\, e^{\frac{xV}{2D} - \frac{V^2 t}{4D}} \left(-\frac{1}{\sqrt{D}}\right) \int^x \frac{1}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x'\sqrt{\frac{p}{D}}}\, dx'}{p - \frac{V^2}{4D}}$$

$$+ \left(\frac{h+V}{\sqrt{D}}\right)\left(\frac{h+\frac{V}{2}}{\sqrt{D}}\right) U_o \frac{e^{\frac{xV}{2D} - \frac{V^2 t}{4D}}}{\sqrt{D}} \int^x \frac{1}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x'\sqrt{\frac{p}{D}}}\, dp}{(p - \frac{V^2}{4D})(\sqrt{p} + \frac{h+\frac{V}{2}}{\sqrt{D}})} dx'$$

where $\int^x$ symbolizes an anti-derivative. Since

$$\frac{\sqrt{D}}{U_o(h+V)} e^{-\frac{xV}{2D} + \frac{V^2 t}{4D}} U(x,t) = \frac{1}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x\sqrt{\frac{p}{D}}}\, dp}{(p - \frac{V^2}{4D})(\sqrt{p} + \frac{h+\frac{V}{2}}{\sqrt{D}})}$$

we substitute this definition into the second integral expression in

(3.17) to find

(3.18)
$$U(x,t) = -\left(\frac{h+V}{D}\right)U_o e^{\frac{xV}{2D}-\frac{V^2t}{4D}}\int^x \frac{1}{2\pi i}\int_{Br_1}\frac{e^{pt}e^{-x'\sqrt{\frac{p}{D}}}dp}{p-\frac{V^2}{4D}}\,dx'$$

$$+\left(\frac{h+\frac{V}{2}}{D}\right)e^{\frac{xV}{2D}}\int^x e^{-\frac{x'V}{2D}}U(x',t)dx' .$$

We find from the tables (Erdelyi et al., 1964) that

$$\frac{1}{2\pi i}\int_{Br_1}\frac{e^{pt}e^{-x\sqrt{\frac{p}{D}}}}{p-\frac{V^2}{4D}}dp = \frac{1}{2}e^{\frac{V^2t}{2D}}\left\{e^{\frac{xV}{2D}}\operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)+e^{-\frac{xV}{2D}}\operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right)\right\}.$$

Thus, substituting this result into (3.18) obtains

(3.19)
$$U(x,t) = -\left(\frac{h+V}{2D}\right)U_o e^{\frac{xV}{2D}}\int^x\left\{e^{\frac{x'V}{2D}}\operatorname{erfc}\left(\frac{x'+Vt}{2\sqrt{Dt}}\right)+e^{-\frac{x'V}{2D}}\operatorname{erfc}\left(\frac{x'-Vt}{2\sqrt{Dt}}\right)\right\}dx'$$

$$+\left(\frac{h+\frac{V}{2}}{D}\right)e^{\frac{xV}{2D}}\int^x e^{-\frac{x'V}{2D}}U(x',t)dx' .$$

Integration by parts once in the first integral expression yields

(3.20)
$$U(x,t) = -\left(\frac{h+V}{2D}\right)U_o e^{\frac{xV}{2D}}\left\{\frac{2D}{V}e^{\frac{xV}{2D}}\operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)+\frac{2D}{V}\frac{1}{\sqrt{\pi Dt}}\int^x e^{+\frac{x'V}{2D}}e^{-\frac{(x'+Vt)^2}{4Dt}}dx'\right.$$

$$\left.-\frac{2D}{V}e^{-\frac{xV}{2D}}\operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right)-\frac{2D}{V}\frac{1}{\sqrt{\pi Dt}}\int^x e^{-\frac{x'V}{2D}}e^{-\frac{(x'-Vt)^2}{4Dt}}dx'\right\}+$$

$$+ \left(\frac{h+\frac{V}{2}}{D}\right) e^{\frac{xV}{2D}} \int^{x} e^{-\frac{x'V}{2D}} U(x', t) dx' .$$

Observe that the two inside integrals are equal and opposite in algebraic sign; hence, we find

(3.21)

$$U(x, t) = -\left(\frac{h+V}{V}\right) U_o \left\{ e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) - \operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) \right\}$$

$$+ \left(\frac{h+\frac{V}{2}}{D}\right) e^{\frac{xV}{2D}} \int^{x} e^{-\frac{x'V}{2D}} U(x', t) dx' .$$

Let us multiply through both sides of (3.21) by $e^{-\frac{xV}{2D}}$. Doing this obtains

(3.22)

$$e^{-\frac{xV}{2D}} U(x, t) = e^{-\frac{xV}{2D}} \left(1+\frac{h}{V}\right) U_o \left\{ \operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) - e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) \right\}$$

$$+ \left(\frac{h+\frac{V}{2}}{D}\right) \int^{x} e^{-\frac{x'V}{2D}} U(x', t) dx' .$$

Differentiating (3.22) once with respect to x yields

(3.23)

$$U_x(x, t) - \left(\frac{h+V}{D}\right) U = -\frac{U_o V}{2h} \left(1+\frac{h}{V}\right) \left\{ \operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) + e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) \right\} .$$

Define

$$f(x, t) = \operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) + e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)$$

and rewrite (3.23) to read

$$(3.24) \qquad U_x - \left(\frac{h+V}{D}\right)U = -\frac{U_oV}{2D}\left(1+\frac{h}{V}\right)f(x,t).$$

Applying Laplace transforms with respect to x to both sides of (3.24) we have

$$pu(p,t) - U(0,t) - \left(\frac{h+V}{D}\right)u(p,t) = -\frac{U_oV}{2D}\left(1+\frac{h}{V}\right)f(p,t).$$

Solving for $u(p,t)$ obtains

$$(3.25) \qquad u(p,t) = \frac{U(0,t)}{p-\frac{h+V}{D}} - \frac{U_oV}{2D}\,\frac{\left(1+\frac{h}{V}\right)f(p,t)}{p-\frac{h+V}{D}}$$

Inversion of (3.25) yields

(3.26)

$$U(x,t) = U(0,t)e^{\frac{x}{D}(h+V)} - \frac{U_oV}{2D}\left(1+\frac{h}{V}\right)\int_0^x e^{(x-p)\left(\frac{h+V}{D}\right)} f(p,t)dp.$$

Substituting into (3.26) the definition of f, we have

(3.27)

$$U(x,t) = U(0,t)e^{\frac{x}{D}(h+V)} - \frac{U_oV}{2D}\left(1+\frac{h}{V}\right)e^{\frac{x}{D}(h+V)}\int_0^x e^{-\frac{p}{D}(h+V)}\operatorname{erfc}\left(\frac{p-Vt}{2\sqrt{Dt}}\right)dp$$

$$- \frac{U_oV}{2D}\left(1+\frac{h}{V}\right)e^{\frac{x}{D}(h+V)}\int_0^x e^{-\frac{p}{D}(h+V)}\, e^{\frac{pV}{D}}\operatorname{erfc}\left(\frac{p+Vt}{2\sqrt{Dt}}\right)dp.$$

or

(3. 28)

$$U(x,t) = U(0,t)e^{\frac{x}{D}(h+V)} - \frac{U_o V}{2D}(1+\frac{h}{V})e^{\frac{x}{D}(h+V)} \int_0^x e^{-\frac{p}{D}(h+V)} \operatorname{erfc}\left(\frac{p-Vt}{2\sqrt{Dt}}\right)dp$$

$$- \frac{U_o V}{2D}(1+\frac{h}{V})e^{\frac{x}{D}(h+V)} \int_0^x e^{-p\frac{h}{D}} \operatorname{erfc}\left(\frac{p+Vt}{2\sqrt{Dt}}\right)dp.$$

Continuing with the analysis, we now integrate by parts the integral expressions found in (3. 28). The first integral expression yields

$$(3.29) \quad \int_0^x e^{-\frac{p}{D}(h+V)} \operatorname{erfc}\left(\frac{p-Vt}{2\sqrt{Dt}}\right)dp = -\left(\frac{D}{h+V}\right)e^{-\frac{p}{D}(h+V)} \operatorname{erfc}\left(\frac{p-Vt}{2\sqrt{Dt}}\right)\Big|_0^x$$

$$- \frac{D}{(h+V)\sqrt{\pi Dt}} \int_0^x e^{-\frac{p}{D}(h+V)} e^{-\frac{(p-Vt)^2}{4Dt}} dp.$$

By completing the square in the argument of the exponential in the last integral we obtain the expression

(3. 30)

$$\int_0^x e^{-\frac{p}{D}(h+V)} \operatorname{erfc}\left(\frac{p-Vt}{2\sqrt{Dt}}\right)dp$$

$$= -\left(\frac{D}{h+V}\right)e^{-\frac{x}{D}(h+V)} \operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) + \left(\frac{2D}{h+V}\right) - \frac{D}{h+V}\operatorname{erfc}\frac{V}{2}\sqrt{\frac{t}{D}}$$

$$- \left(\frac{D}{h+V}\right)e^{\frac{hVt+h^2t}{D}} \operatorname{erfc}\left[(h+\frac{V}{2})\sqrt{\frac{t}{D}}\right] - \operatorname{erfc}\left[\frac{x+2(h+\frac{V}{2})t}{2\sqrt{Dt}}\right] .$$

The second integral expression is found, with the help of the last integral in (3. 29), to be

(3. 31)

$$\int_0^x e^{-p\frac{h}{D}} \operatorname{erfc}\left(\frac{p+Vt}{2\sqrt{Dt}}\right) dp$$

$$= -\frac{D}{h} e^{-x\frac{h}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) + \frac{D}{h} \operatorname{erfc}\left(\frac{V}{2}\sqrt{\frac{t}{D}}\right)$$

$$-\frac{D}{h} e^{\frac{hVt+h^2t}{D}} \operatorname{erfc}\left[(h+\frac{V}{2})\sqrt{\frac{t}{D}}\right] - \operatorname{erfc}\left[\frac{x+2(h+\frac{V}{2})t}{2\sqrt{Dt}}\right] \quad .$$

Combining both parts now gives

(3. 32)

$$U(x,t) = U(0,t)e^{\frac{x}{D}(h+V)} - U_o e^{\frac{x}{D}(h+V)} + \frac{U_o}{2} \operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right)$$

$$+ \frac{U_o}{2h}(V+h)e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) - \frac{U_o V}{2h} e^{\frac{x}{D}(h+V)} \operatorname{erfc}\left(\frac{V}{2}\sqrt{\frac{t}{D}}\right)$$

$$+ U_o\left(1+\frac{V}{2h}\right)e^{\frac{x}{D}(h+V)+\frac{hVt}{D}+\frac{h^2t}{D}} \left\{\operatorname{erfc}\left[(h+\frac{V}{2})\sqrt{\frac{t}{D}}\right] - \operatorname{erfc}\left[\frac{x+2(h+\frac{V}{2})t}{2\sqrt{Dt}}\right]\right\}.$$

Now we must evaluate $U(0,t)$. To do this we consider the real integral representation of $U(x,t)$ and pass to the limit i. e.: $x \to 0$ to find $U(0,t)$ which is then substituted into (3. 32). Let us now proceed to find the real integral representation for $U(x,t)$. Recall that

$$\text{(3.15)} \qquad U(x,t) = \left(\frac{h+V}{\sqrt{D}}\right)U_o \frac{e^{\frac{xV}{2D} - \frac{V^2t}{4D}}}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x\sqrt{\frac{p}{D}}} \, dp}{\left(p - \frac{V^2}{4D}\right)\left(\sqrt{p} + \frac{h+\frac{V}{2}}{\sqrt{D}}\right)} .$$

We deform Br_1 into Br_2 for the condition on the denominator at the branch point $p = 0$ is satisfied. Note that in (3.15) we have a first order pole at $p = \frac{V^2}{4D}$ and a branch point at the origin. Hence, we have $U(x, t)$ given as the sum of 7 integrals.

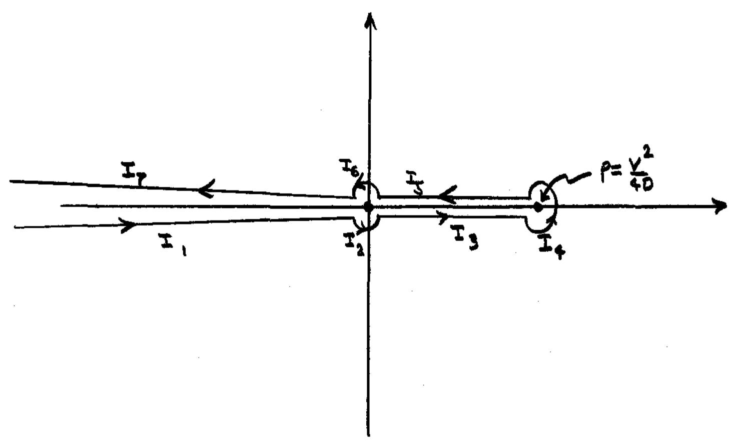

Figure 3. Bromwich two contour in the complex plane.

Define

$$I_1 = \lim_{\substack{\epsilon \to 0 \\ \rho_o \to 0}} \frac{1}{2\pi i} \int_{\infty}^{\rho_o} \frac{e^{yte^{-i(\pi-\epsilon)}} e^{-x\sqrt{\frac{x}{D}}\, e^{-i\left(\frac{\pi-\epsilon}{2}\right)}} e^{i(\pi-\epsilon)} dy}{\left(ye^{-i(\pi-\epsilon)} - \frac{V^2}{4D}\right)\left(\sqrt{y}e^{-i\left(\frac{\pi-\epsilon}{2}\right)} + \frac{h+\frac{V}{2}}{\sqrt{D}}\right)} ,$$

$$I_2 = \lim_{\substack{\delta\to 0\\ \rho_o\to 0}} \frac{1}{2\pi i}\int_{(\pi+\delta)}^{2\pi-\delta} \frac{e^{t\rho_o e^{i\theta}}\, e^{-x\sqrt{\frac{\rho_o}{D}}\, e^{i\frac{\theta}{2}}}\, i\rho_o e^{i\theta} d\theta}{(\rho_o e^{i\theta} - \frac{V^2}{4D})(\sqrt{\rho_o}\, e^{i\frac{\theta}{2}} + \frac{h+\frac{V}{2}}{\sqrt{D}})},$$

$$I_3 = \lim_{\substack{\epsilon\to 0\\ \rho_o\to 0\\ \rho_1\to 0}} \frac{1}{2\pi i}\int_{\rho_o}^{\frac{V^2}{4D}-\rho_1} \frac{e^{yte^{i(2\pi-\epsilon)}}\, e^{-x\sqrt{\frac{y}{D}}\, e^{\frac{i(2\pi-\epsilon)}{2}}}\, e^{i(2\pi-\epsilon)} dy}{(ye^{i(2\pi-\epsilon)} - \frac{V^2}{4D})(\sqrt{y}\, e^{\frac{i(2\pi-\epsilon)}{2}} + \frac{h+\frac{V}{2}}{\sqrt{D}})},$$

$$I_4 = \lim_{\substack{\epsilon\to 0\\ \rho_1\to 0}} \frac{1}{2\pi i}\int_{-(\pi-\epsilon)}^{\pi-\epsilon} \frac{e^{t(\rho_1 e^{i\theta} + \frac{V^2}{2D})}\, e^{-x\sqrt{\frac{\rho_1}{D} e^{i\theta} + \frac{V^2}{4D^2}}}\, i\rho_1 e^{i\theta} d\theta}{(\rho_1 e^{i\theta})(\sqrt{\rho_1 e^{i\theta} + \frac{V^2}{4D}} + \frac{h+\frac{V}{2}}{\sqrt{D}})},$$

$$I_5 = \lim_{\substack{\epsilon\to 0\\ \rho_o\to 0\\ \rho_1\to 0}} \frac{1}{2\pi i}\int_{\frac{V^2}{4D}-\rho_1}^{\rho_0} \frac{e^{yte^{-i(2\pi-\epsilon)}}\, e^{-x\sqrt{\frac{y}{D}}\, e^{-\frac{i(2\pi-\epsilon)}{2}}}\, e^{-i(2\pi-\epsilon)} dy}{(ye^{-i(2\pi-\epsilon)} - \frac{V^2}{4D})(\sqrt{y}\, e^{\frac{-i(2\pi-\epsilon)}{2}} + \frac{h+\frac{V}{2}}{\sqrt{D}})},$$

$$I_6 = \lim_{\substack{\delta\to 0\\ \rho_o\to 0}} \frac{1}{2\pi i}\int_{\delta}^{\pi-\delta} \frac{e^{t\rho_o e^{i\theta}}\, e^{-x\sqrt{\frac{\rho_o}{D}}\, e^{i\frac{\theta}{2}}}\, i\rho_o e^{i\theta} d\theta}{(\rho_o e^{i\theta} - \frac{V^2}{4D})(\sqrt{\rho_o}\, e^{i\frac{\theta}{2}} + \frac{h+\frac{V}{2}}{\sqrt{D}})},$$

$$I_7 = \lim_{\substack{\epsilon \to 0 \\ \rho_o \to 0}} \frac{1}{2\pi i} \int_{\rho_o}^{\infty} \frac{e^{yte^{i(\pi-\epsilon)}} e^{-x\sqrt{\frac{y}{D}}e^{i(\frac{\pi-\epsilon}{2})}} e^{i(\pi-\epsilon)}dy}{(ye^{i(\pi-\epsilon)} - \frac{V^2}{4D})(\sqrt{y}\, e^{i(\frac{\pi-\epsilon}{2})} + \frac{h+\frac{V}{2}}{\sqrt{D}})} .$$

Observe that in the limit $\rho_o \to 0$ both I_2 and I_6 vanish. Also note that as $\epsilon \to 0$, $I_3 + I_5 = 0$ for the integrand of (3.15) is analytic along these contours and the algebraic sign of I_5 is opposite that of I_3; hence, they add to zero. I_4 does not vanish but contributes

$$I_4 = e^{\frac{V^2 t}{4D} - \frac{xV}{2D}} \left(\frac{\sqrt{D}}{h+V}\right).$$

Finally, we have the sum $I_1 + I_7$ which yields the real integral

$$I_1 + I_7 = -\frac{1}{\pi}\int_0^{\infty} \frac{e^{-yt}}{(y+\frac{V^2}{4D})(y+\frac{(h+\frac{V}{2})^2}{D})} \left\{\sqrt{y}\cos\left(x\sqrt{\frac{y}{D}}\right) + \frac{h+\frac{V}{2}}{\sqrt{D}}\sin\left(x\sqrt{\frac{y}{D}}\right)\right\}dy.$$

Thus, it is easily seen by adding $I_4 + I_1 + I_7$ together and multiplying by the appropriate functions that the real integral expression for $U(x, t)$ is given as

$$(3.33)\qquad U(x,t) = U_o - \left(\frac{h+V}{\sqrt{D}}\right)U_o \, \frac{e^{\frac{xV}{2D} - \frac{V^2t}{4D}}}{\pi} \int_0^\infty \frac{e^{-yt}}{\left(y+\frac{V^2}{4D}\right)\left(y+\frac{(h+\frac{V}{2})^2}{D}\right)}$$

$$\times \left\{ \sqrt{y}\cos\left(x\sqrt{\frac{y}{D}}\right) + \frac{h+\frac{V}{2}}{\sqrt{D}} \sin\left(x\sqrt{\frac{y}{D}}\right) \right\} dy \, .$$

Let $x \rightarrow 0$ and we have

$$(3.34)\qquad U(0,t) = U_o - \frac{h+V}{\sqrt{D}} \, \frac{U_o}{\pi} \, e^{-\frac{V^2t}{4D}} \int_0^\infty \frac{e^{-yt}\sqrt{y}\,dy}{\left(y+\frac{V^2}{4D}\right)\left(y+\frac{(h+\frac{V}{2})^2}{D}\right)} \, .$$

We decompose the integrand of (3. 34) by partial fractions to find a more convenient form for $U(0, t)$

$$(3.35)\qquad U(0,t) = U_o - \frac{\sqrt{D}}{h} \, \frac{U_o}{\pi} \, e^{-\frac{V^2t}{4D}} \int_0^\infty \frac{e^{-yt}\sqrt{y}\,dy}{y+\frac{V^2}{4D}}$$

$$+ \frac{\sqrt{D}}{h} \, \frac{U_o}{\pi} \, e^{-\frac{V^2t}{4D}} \int_0^\infty \frac{e^{-yt}\sqrt{y}\,dy}{y+\frac{(h+\frac{V}{2})^2}{D}} \, .$$

Again using the tables of Laplace transforms (Erdelyi _et al._, 1964) we have

$$(3.36)\qquad \int_0^\infty \frac{e^{-yt}\sqrt{y}\,dy}{y+a} \, dy = \sqrt{\frac{\pi}{t}} - \pi\sqrt{a}\, e^{at} \operatorname{erfc}\left(\sqrt{at}\right) .$$

Substituting this definition into (3. 35) we obtain after some algebra

$$(3.37) \qquad U(0,t) = U_o + \frac{U_o V}{2h} \operatorname{erfc}\left(\frac{V}{2}\sqrt{\frac{t}{D}}\right)$$

$$= U_o\left(1+\frac{V}{2h}\right)e^{\frac{Vht}{D}+\frac{h^2 t}{D}} \operatorname{erfc}\left[\left(h+\frac{V}{2}\right)\sqrt{\frac{t}{D}}\right].$$

This is the result we have been seeking, for now we substitute this result into (3. 32) and after some algebra we arrive at

(3. 38)

$$U(x,t) = \frac{U_o}{2}\left\{\operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) + e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)\right\} + \frac{U_o V}{2h} e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)$$

$$- U_o\left(1+\frac{V}{2h}\right)e^{\frac{x}{D}(h+V)+\frac{hVt}{D}+\frac{h^2 t}{D}} \operatorname{erfc}\left[\frac{x+2\left(h+\frac{V}{2}\right)t}{2\sqrt{Dt}}\right].$$

It is a laborious but straight forward computation to check that (3.28) does in fact satisfy the original partial differential equation in Q. Also it can be shown that for $x \neq 0$, $U(x,t) \to U(x,0) = 0$ as $t \to 0$. Lastly the two boundary conditions can be checked by formal differentiation of (3. 38), for $t > 0$, letting $x \to 0$ and substituting the results into (3. 9 ii) to obtain equality. Hence, the claim is made that (3. 38) is a solution to (3. 8) subject to the conditions in (3. 9). We now discuss two limiting cases of (3. 38): (1) no hydrodynamic flux, $V = 0$, and (2) large hydrodynamic flux, $V \gg h$.

Limiting Cases

Case 1: Let $V \to 0$ in (3. 38), $h \neq 0$.

The limit as $V \to 0$ in (3. 38) yields .

$$(3.39) \qquad U(x,t) = U_o\left\{\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - e^{\frac{xh}{D}+\frac{h^2t}{D}}\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}+h\sqrt{\frac{t}{D}}\right)\right\}.$$

This limit gives exactly the expression one would find for the diffusion of a material under the Neumann (or radiative transport) boundary condition at the plane $x = 0$ of a semi-infinite slab of porous medium originally at zero concentration of diffusant. That this type of system should arise is evident when we consider that Equation (3. 8) reduces to

$$DU_{xx} = U_t, \quad \text{all} \quad x, t \text{ in } Q,$$

and the boundary condition (3. 9 ii) reduces to

$$-DU_x(0,t) = h(U_o - U(0,t)), \qquad 0 < t < \infty.$$

The other conditions remain unchanged. Also, we see that as $V \to 0$ in Equation (3. 15) we have

$$U(x,t) = \lim_{V \to 0} \left(\frac{h+V}{\sqrt{D}}\right) U_o \frac{e^{\frac{xV}{2D} - \frac{V^2 t}{4D}}}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x\sqrt{\frac{p}{D}}} dp}{\left(p - \frac{V^2}{4D}\right)\left(\sqrt{p} + \frac{h + \frac{V}{2}}{\sqrt{D}}\right)}$$

$$= \frac{h}{\sqrt{D}} U_o \frac{1}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x\sqrt{\frac{p}{D}}} dp}{p\left(\sqrt{p} + \frac{h}{\sqrt{D}}\right)} .$$

This complex integral is found in the tables (Erdely et al., 1964) as

$$U(x,t) = U_o \left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - e^{\frac{h^2 t}{D} + \frac{hx}{D}} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + h\sqrt{\frac{t}{D}}\right) \right\} .$$

Case 2: Let $h \to 0$ in (3.38), $V \neq 0$

Note! This case corresponds to allowing large hydrodynamic flux into the porous medium so that any molecular diffusion into the medium is negligible by comparison. We find

(3.40)

$$U(x,t) = \frac{U_o}{2} \operatorname{erfc}\left(\frac{x - Vt}{2\sqrt{Dt}}\right) - \frac{U_o}{2} e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)$$

$$- \lim_{h \to 0} \frac{U_o V}{2h} e^{\frac{xV}{D}} \left\{ e^{\frac{hx}{D} + \frac{hVt}{D} + \frac{h^2 t}{D}} \operatorname{erfc}\left(\frac{x + (2h+V)t}{2\sqrt{Dt}}\right) - \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) \right\} .$$

To compute this limit we expand the exponential to obtain

$$U(x,t) = \frac{U_o}{2}\left\{ \operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) - e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) \right\}$$

$$- \lim_{h\to 0} \frac{U_o V}{2h} e^{\frac{xV}{D}} \left\{ (1+h(\frac{x+Vt}{D}) + O(h^2)) \operatorname{erfc}\left(\frac{x+(2h+V)t}{2\sqrt{Dt}}\right) \right.$$

$$\left. - \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) \right\}.$$

Note that the term

$$- \lim_{h\to 0} \frac{\operatorname{erfc}\left(\frac{x+(2h+V)t}{2\sqrt{Dt}}\right) - \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)}{2h}$$

is the definition of

$$- \frac{\partial}{\partial V}\left(\operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)\right).$$

Thus, we finally obtain

$$U(x,t) = \frac{U_o}{2}\left\{ \operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) + 2V\sqrt{\frac{t}{\pi D}}\, e^{-\frac{(x-Vt)^2}{4Dt}} \right. \tag{3.41}$$

$$\left. - \frac{V}{D}\left(x+Vt+\frac{D}{V}\right) e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right) \right\}.$$

as the limiting solution to (3.8) subject to (2.9) with $h \to 0$. Equation (3.41) was arrived at earlier by Lindstrom _et al._, (1967) in conjunction with the work done on setting up a model to predict chemical movement in saturated soil under a hydrodynamic driving force.

For several theoretical plots of Equation (3.41) ($V \gg h$ in 3.38) subject to various values of the parameters, refer to Appendix C.

IV. ONE DIMENSIONAL MODEL FOR MASS TRANSPORT: NON-ZERO INITIAL DISTRIBUTION

Introduction

As previously discussed in Chapter III, we shall base the discussion in this chapter upon Equation (3. 8); however, we now assume a non-zero initial distribution and a no chemical flux boundary condition at the surface $x = 0$. Refer to Figure 2 for a schematic diagram of the physical system.

Mass Transport Model

Assuming that Equation (3. 8) holds in the voids of the porous medium let us change our model now to the case of a non-zero initial distrubition and the top boundary condition to no chemical flow. This type of system is commonly called "leaching" as found in the agricultural and mining engineering literature and "dispersion" or "convection" in the chemical engineering literature.

The chemical mass in the voids moves according to the equation

(3. 8) $$DU_{xx} - VU_x = U_t$$

and is subject to the initial condition

(4. 1) $$U(x, 0) = U_o f(x), \quad U_o \text{ constant.}$$

$f(x)$ is assumed integrable in the strip $\overline{Q}$, where

$$\overline{Q} = \{(x, t) | \; 0 \leq x < \infty, \quad 0 \leq t < \infty\}.$$

The top boundary condition is assumed to be

$$-DU_x(0, t) + V(U(0, t) = 0 \tag{4. 2}$$

for all time $t > 0$ (note! we assume h negligible compared to V). Since the boundary condition at the top surface, as given by (4. 2), is a no chemical mass flow condition and the mass in the column at any time $t > 0$ must remain constant, we have that

$$\lim_{x \to \infty} U_x(x, t) = 0 \tag{4. 3}$$

is equivalent to

$$M_c(0) = \lim_{L' \to \infty} A\epsilon_d(1+\alpha'\gamma) \int_0^{L'} U(x, t)dx \tag{4. 4}$$

We shall show this by construction.

Assume as before that $U(x, t)$ is twice continuously differentiable with respect to x and once with respect to t. Applying Laplace transforms to (3. 8) first with respect to t and then with respect to x we find (3. 8) transforms into

(4. 5)

$$Dp^2u(p, s) - Dpu(0, s) - Du_x(0, s) - Vpu(p, s) + Vu(0, s) = su(p, s) - U_of(p).$$

Transforming (4. 2) and substituting the results into (4. 5) we find upon simplification

$$(4.6) \qquad u(p, s) = \frac{pu(0, s)}{(p-\frac{V}{2D})^2 - (\frac{s}{D}+\frac{V^2}{4D^2})} - \frac{1}{D}\,\frac{U_of(p)}{(p-\frac{V}{2D})^2 - (\frac{s}{D}+\frac{V^2}{4D^2})}\,.$$

Define

$$(4.7) \qquad A = -\frac{V}{2D} \quad \text{and} \quad B = (\frac{s}{D}+\frac{V^2}{4D^2})^{1/2},$$

then upon substitution of (4. 7) into (4. 6) and with subsequent inversion being found in the tables (Erdelyi et al., 1964) we have

$$(4.8) \qquad u(x, s) = \frac{u(0, s)}{2B}\, e^{-Ax}\{(B-A)e^{Bx} + (B+A)e^{-BA}\}$$

$$- \frac{1}{2BD}\int_0^x f(\tau)e^{-A(x-\tau)}\{e^{B(x-\tau)} - e^{-B(x-\tau)}\}d\tau.$$

Applying our equivalent condition we ask for the mass to be conserved; hence, require that $\lim_{x\to\infty} u_x = 0$. This condition is satisfied if

$$(4.9) \qquad u(0, s) = \frac{1}{D(B-A)}\int_0^\infty f(\tau)e^{(A-B)\tau}d\tau.$$

Substitution of (4. 9) into (4. 8) and reducing (4. 8) to a more tractable form gives

$$(4.10)\quad u(x, s) = \frac{1}{2DB}\int_0^x f(\tau)e^{-(B+A)(x-\tau)}d\tau + \frac{1}{2DB}\int_x^\infty f(\tau)e^{(B-A)(x-\tau)}d\tau$$

$$+ \frac{B+A}{2DB(B-A)}\int_0^\infty f(\tau)e^{-A(x-\tau)}\, e^{-B(x+\tau)}d\tau .$$

Resubstitution of the definitions of A and B into (4. 10) permits one to use the tables again. We have, upon inversion with respect to time

$$(4.11)\quad U(x,t) = \frac{U_o}{2\sqrt{\pi Dt}}\int_0^\infty f(\tau)e^{\frac{V}{2D}(x-\tau)}\, e^{-\frac{V^2t}{4D}}\left\{ e^{-\frac{(x+\tau)^2}{4Dt}} + e^{-\frac{(x-\tau)^2}{4Dt}}\right\} d\tau$$

$$-\frac{VU_o}{2D}\int_0^\infty f(\tau)e^{\frac{xV}{D}} \operatorname{erfc}\left(\frac{x+\tau+Vt}{2\sqrt{Dt}}\right) d\tau .$$

This equation is a solution to (3. 8). It can be shown that (4. 11) also satisfies the initial condition (4. 1) and the two boundary conditions (4. 2) and (4. 3) respectively.

Justification of Equivalent Conditions

In obtaining (4. 11) we used a very convenient form of the conservation equation. Now we will proceed to justify using this equation.

Beginning with Equation (4. 8), we have upon substitution of this equation into the transformed conservation of mass equation

$$\frac{M_o}{s} = A\epsilon_d(1+a'\gamma)\int_0^{L'} u(x, s)dx$$

the following equation

(4. 12)

$$\frac{M_o}{s} = A\epsilon_d(1+a'\gamma)\frac{u(0, s)}{2B}(B-A)\int_0^{L'} e^{-(A-B)x}\,dx$$

$$+ A\epsilon_d(1+a'\gamma)\frac{u(0, s)}{2B}(B+A)\int_0^{L'} e^{-(A+B)x}\,dx$$

$$- A\epsilon_d(1+a'\gamma)\frac{U_o}{2DB}\int_0^{L'}\int_0^{x} f(\tau)\{e^{-(A-B)(x-\tau)} - e^{-(A+B)(x-\tau)}\}d\tau dx.$$

Carrying out the indicated integration in the first part of (4. 12) and with subsequent reduction of terms obtains

(4. 13)

$$\frac{M_o}{s} = A\epsilon_d(1+a'\gamma)u(0, s)\; e^{(B-A)L'} - e^{-(B+A)L'}$$

$$- \frac{A\epsilon_d(1+a'\gamma)}{2DB}U_o\int_0^{L'}\int_0^{x} f(\tau)\{e^{(B-A)(x-\tau)} - e^{-(B+A)(x-\tau)}\}d\tau dx.$$

Consider the iterated integral in (4. 13). As $f(x)$ is integrable, $0 \leq x < \infty$, we find upon inversion of the order of integration

$$\int_0^{L'}\int_0^{x} f(\tau)e^{(B-A)(x-\tau)}d\tau dx = \int_0^{L'} f(\tau)\ \{e^{-(B-A)\tau}\int_\tau^{L'} e^{(B-A)x}dx\}d\tau,$$

or with further integration and subsequent reduction

$$(4.14)\qquad \frac{M_o}{s} = \frac{A\epsilon_d(1+a'\gamma)}{2B}\Big\{u(0,s)(e^{(B-A)L'} - e^{-(B+A)L'})$$

$$-\frac{U_o}{D(B-A)}\int_0^{L'} f(\tau)(e^{(B-A)(L'-x)}-1)d\tau$$

$$=\frac{U_o}{D(B+A)}\int_0^{L'} f(\tau)(e^{(B+A)(\tau-L')}-1)d\tau\Big\}.$$

Solving for $u(0, s)$ in (4.14) obtains

(4.15)

$$u(0,s) = \frac{\dfrac{M_o}{s}+\dfrac{U_oA\epsilon_d(1+a'\gamma)}{2DB}\left\{\displaystyle\int_0^{L'} f(\tau)\ \frac{(e^{(B-A)(L'-\tau)}-1)}{B-A}+\frac{(e^{(B+A)(\tau-L')}-1)}{B+A}\ d\tau\right\}}{\dfrac{A\epsilon_d(1+a'\gamma)}{2B}\ \{e^{(B-A)L'} - e^{-(B+A)L'}\}}.$$

Multiplying both numerator and denominator in (4.15) by $e^{-(B-A)L'}$ and reducing gives

(4.16)

$$u(0,s) = \Big\{\frac{2BM_o e^{-(B-A)L'}}{sA\epsilon_d(1+a'\gamma)}+\frac{e^{-(B-A)L'}}{D(B-A)}\int_0^{L'} f(\tau)(e^{(B-A)(L'-\tau)}-1)d\tau$$

$$+\frac{e^{-(B-A)L'}}{D(B+A)}\int_0^{L'} f(\tau)(e^{(B+A)(\tau-L')}-1)d\tau\Big\}\Big/(1-e^{-2L'B}).$$

As B is positive for $0 \leq t < \infty$, $|B| > |A|$, and $\int_0^\infty f(\tau)d\tau < \infty$, we have as $L' \to \infty$

$$\lim_{L' \to \infty} u(0, s) = \frac{1}{D(B-A)} \int_0^\infty f(\tau) e^{-(B-A)\tau} d\tau$$

which is identical to Equation (4.9).

This theory is currently being tested in the laboratory. For plots of Equation (4.11) for various values of the parameters and three different initial distributions refer to Appendix D.

V. ONE-TWO MIXED DIMENSIONAL MASS TRANSPORT: NON-ZERO INITIAL DISTRIBUTION

Introduction

A model system for mass transport of chemicals in saturated porous medium will be considered by assuming a two component system. The first component to be considered is that of mass transport in the porous medium dead spaces (see Appendix A). The second component will be that of mass transport in the more or less open channels direction of the porous medium (see Appendix A). A non-zero initial distribution will be used and as in Chapter IV a no-flux of chemical boundary condition at $x = 0$ is assumed. Also, conservation of mass will be assumed throughout. The resulting partial differential equation of interest will be solved by using the well-known Crank-Nicholson Finite Difference Method (Douglas and Jones, 1962).

Mass Transport Model

Consider the physical model shown in Figure 4. Chemical mass can be transported in two directions:

(i) $U = U(x, t)$ as the open channel chemical concentration

(ii) $\overline{U} = \overline{U}(x, y, t)$ as the chemical concentration in the inter-particle (dead spaces) voids of the porous medium.

Let the physical phenomena of mass transport in the porous medium be represented by the following system of equations:

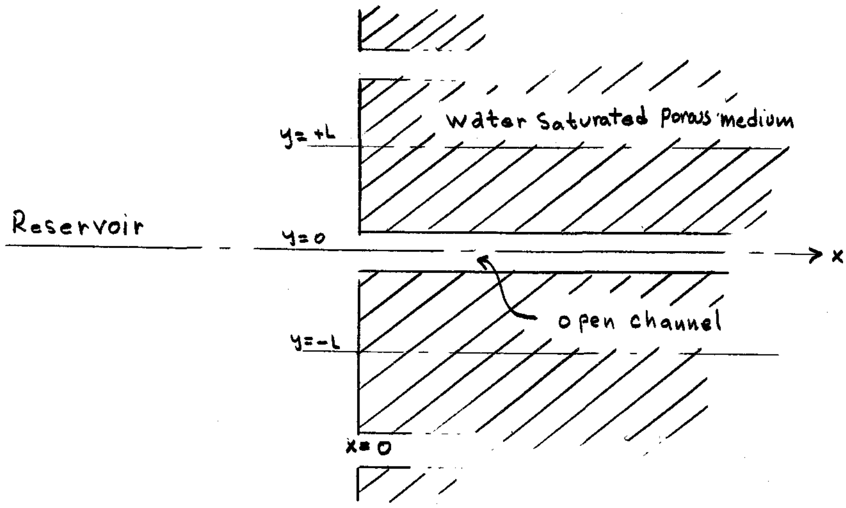

Figure 4. Sketch of semi-infinite medium for third model.

(i) open channels;

(5.1) (a) $D_o U_{xx} - V_o U_x = (1+\frac{a\gamma}{\epsilon_d})U_t + \lambda \overline{U}_y(0, t),$

$$0 < x < \infty, \quad 0 < t < \infty, \quad 0 < y < L$$

(5.2) (b) $-D_o U_x(0, t) + V_o U(0, t) = 0,$ (no flux at $x = 0$)

(5.3) (c) $\lim_{x \to \infty} U_x(x, t) = 0,$ (conservation of mass),

(5.4) (d) $U(x, +0) = U_o f(x),$ f integrable$[0, \infty),$

where the parameter λ, defined as a coupling coefficient, couples the open channel flow system to the dead space transport system below,

(ii) dead space transport system;

(5.5) (a) $$D_{o1}(\overline{U}_{xx}+\overline{U}_{yy}) = (1+\frac{\alpha\gamma}{\epsilon_o})\overline{U}_t ,$$

$$0 < x < \infty, \quad 0 < y < L, \quad 0 < t < \infty$$

(5.6) (b) $$\overline{U}_y(x, L, t) = 0, \quad \overline{U}_x(0, y, t) = 0,$$

(5.7) (c) $$D_{o1}\overline{U}_y(x, 0, t) = \beta\ (U(x, t)-\overline{U}(x, 0, t),$$

where β is defined as the mass transfer coefficient (see Nomenclature),

(5.8) (d) $$\overline{U}(x, y, 0) = U(x, 0) = U_o f(x).$$

For the remainder of this paper the approximation is made that diffusion in the x direction in the dead spaces can be neglected in comparison with mass transport in the x direction in the open channels. Equation (5.5) then reduced to

(5.5') $$D_{o1}\overline{U}_{yy} = (1+\frac{\alpha\gamma}{\epsilon_o})\overline{U}_t$$

and the boundary condition, $\overline{U}_x(0, y, t) = 0$, is dropped. Define

$$D_1 = \frac{D_{o1}}{1+\frac{\alpha\gamma}{\epsilon_o}} .$$

Now we are ready to begin the analysis of the system.

Solution Technique: y Dimension

Assuming that both U and $\overline{U}$ are Laplace transformable with respect to time, we transform Equations (5.5'), (5.6), (5.7), and (5.8). The resulting system is given as

(5.9) (i) $$D_1 \frac{d^2\overline{u}}{dy^2} = s\overline{u} - \overline{u}(x, y, 0),$$

$$0 < x < \infty, \quad 0 < y < L, \quad 0 < s < \infty.$$

(ii) $$\overline{u}_y(x, L, s) = 0,$$

(iii) $$-D_1\overline{u}_y(x, 0, s) = \beta(u(x, s) - \overline{u}(x, 0, s)),$$

(iv) $$\overline{u}(x, y, 0) = U(x, 0) = U_o f(x).$$

The solution to (5.9 i) subject to the other three conditions is

(5.10) $$\overline{u} = -\frac{\beta U_o f(x) \cosh\sqrt{\frac{s}{D_1}}(L-y)}{s[\sqrt{D_1 s}\ \sin h(\sqrt{\frac{s}{D_1}}\,L) + \beta \cosh(\sqrt{\frac{s}{D_1}}\,L)]} + \frac{U_o f(x)}{s}$$

$$+ \frac{\beta u(x, s) \cosh\sqrt{\frac{s}{D_1}}\,(L-y)}{\sqrt{sD_1}\ \sinh(\sqrt{\frac{s}{D_1}}\,L) + \beta \cosh(\sqrt{\frac{s}{D_1}}\,L)}.$$

Notice that the zeros of the denominator occur at $s = 0$, and

$$\sqrt{D_1 s_n}\ \sinh(\sqrt{\frac{s_n}{D_1}}\,L) + \beta \cosh(\sqrt{\frac{s_n}{D_1}}\,L) = 0.$$

Define

$$i\gamma_n = \sqrt{\frac{s_n}{D_1}}\, L, \qquad n = 1, 2, 3, , , . \tag{5.11}$$

Using the residue theorem and (5.11) we find

(5.12)

$$\overline{U}(x, y, t) = 2B^2 U_o f(x) \sum_{n=1}^{\infty} \frac{\cos[\gamma_n(1-\frac{y}{L})]\exp[-\frac{\gamma_n^2 D_1 t}{L^2}]}{\gamma_n \sin\gamma_n(\gamma_n^2 + B(B+1)}$$

$$+ 2B^2 \frac{D_1}{L^2} \sum_{n=1}^{\infty} \frac{\gamma_n \cos[\gamma_n(1-\frac{y}{L})] \int_0^t U(x,\tau)\exp[-\frac{\gamma_n^2 D_1}{L^2}(t-\tau)]d\tau}{\sin\gamma_n(\gamma_n^2 + B(B+1)}$$

where γ_n is the n-th zero of the trancendental equation

$$\gamma_n \tan\gamma_n = B,$$

and where

$$B = \frac{\beta L}{D_1} .$$

Equation (5.12) solves Equation (5.5') subject to the modified boundary condition $\overline{u}_y(x, L, t) = 0$ and the mass transport type boundary condition (5.7).

Returning now to the equation of more interest to us i. e., Equation (5.1), we make the following definitions. Define

$$D = \frac{D_o}{1+\frac{\alpha\gamma}{\epsilon_d}}, \qquad V = \frac{V_o}{1+\frac{\alpha\gamma}{\epsilon_d}}$$

and

$$\bar{\lambda} = \frac{\lambda}{1+\frac{\alpha\gamma}{\epsilon_d}} .$$

Substituting (5. 12) into (5. 1) yields

(5. 13)

$$DU_{xx} - VU_x = U_t + \frac{2B^2U_o\bar{\lambda}f(x)}{L}\sum_{n=1}^{\infty}\frac{\exp[-\frac{\gamma_n^2D_1t}{L^2}]}{\gamma_n^2+B(B+1)}$$

$$+ \frac{2B^2D_1\bar{\lambda}}{L^3}\sum_{n=1}^{\infty}\frac{\gamma_n^2\int_0^t U(x,\tau)\exp[-\gamma_n^2\frac{D_1}{L^2}(t-\tau)]d\tau}{\gamma_n^2+B(B+1)} .$$

We now discuss the solution of this linear integro-differential equation for mass transport subject to initial condition (5. 4) and boundary conditions (5. 2) and (5. 3), respectively.

To begin, let us formally integrate once by parts the indicated expression in (5. 13). We find

(5.14)

$$DU_{xx} - VU_x = U_t + \frac{2B^2\bar{\lambda}}{L} U(x,t) \sum_{n=1}^{\infty} \frac{1}{\gamma_n^2 + B(B+1)}$$

$$- \frac{2B^2\bar{\lambda}}{L} \sum_{n=1}^{\infty} \frac{\int_0^t \frac{\partial U}{\partial \tau} \exp\left[-\frac{\gamma_n^2 D_1}{L^2}(t-\tau)\right] d\tau}{\gamma_n^2 + B(B+1)} .$$

Observe that the coefficient of $U(x,t)$ in (5.14) is bounded. We show this in Appendix G. In particular from (G.7) we have

$$\frac{1}{2B} = \sum_{n=1}^{\infty} \frac{1}{\gamma_n^2 + B(B+1)}, \qquad B > 0,$$

for this particular set of zeros γ_n. Thus, we can replace (5.14) by the equation

(5.15)

$$DU_{xx} - VU_x = U_t + \frac{B\bar{\lambda}}{L} U(x,t)$$

$$- \frac{2B^2\bar{\lambda}}{L} \sum_{n=1}^{\infty} \frac{\int_0^t U_\tau \exp\left[-\frac{\gamma_n^2 D_1}{L^2}(t-\tau)\right] d\tau}{\gamma_n^2 + B(B+1)} .$$

Define

$$(5.16) \qquad g(t, \tau) = \sum_{n=1}^{\infty} \frac{\exp\left[-\gamma_n^2 \frac{D_1}{L^2}(t-\tau)\right]}{\gamma_n^2 + B(B+1)} .$$

and observe that

$$(5.17) \qquad \max_{0 \leq \tau \leq t} |g(t, \tau)| \leqq \frac{1}{2B} .$$

Hence, the solution of Equation (5.15) is bounded by the solution to an equation of the form

$$(5.18) \qquad DU_{xx} - VU_x - C_1 U - U_t = f(x).$$

where D, V, C_1, are constants defined in the strip $R_1 \times [0, T)$, R_1 is Euclidean 1-space. $f(x)$ is defined and Hölder continuous, on the same strip. U is $C^{2,1}(0, T)$ i.e., U is twice continuously differentiable with respect to x and once continuously differentiable with respect to t on the interior of the space-time domain defined by the topological product $R_1 \times (0, T)$. That a solution to (5.18) exists in the afore mentioned space has been shown by Guenther (1967) and a uniqueness theorem has been given by several workers, one of which is Hopf (1950). Guenther mentions more who have shown uniqueness.

Now that we know a solution to our problem exists and that it is unique we now move on to the problem of actually solving Equation (5.15).

Solution Technique: x Dimension

The method of finding a solution to Equation (5.14) is that of Finite Differences. That is, we replace the partial differential Equation (5.14) by a Finite difference equation and proceed to solve the difference equation under suitable hypothesis on the domain and $U(x, t)$ defined on said domain. Following the notation of Douglas and Jones (1962), define in the (x, t) plane

$$R = \{(x,t) \mid 0 < x < L, \ 0 < t \leq T\}$$

$$B_o = \{(x,0) \mid 0 \leq x \leq L\}$$

$$B_1 = \{(0,t) \mid 0 < t \leq T\}$$

$$B_2 = \{(L',t) \mid 0 < t \leq T\}$$

$$B = B_o \cup B_1 \cup B_2.$$

We denote the closure of R by $\overline{R}$.

Let us now replace the continuous domain by a discrete one (lattice work). Let N and M be positive integers. Let

$$h = \frac{L'}{N}, \quad k = \frac{T}{M}$$

$$\overline{R}_{hk} = \{(ih, nk) \mid i = 0, 1, 2, \ldots, N;\; n = 0, 1, 2, \ldots, M\}$$

$$B^{a}_{hk} = B_{a} \cap \overline{R}_{hk}, \quad a = 0, 1, 2$$

$$B_{hk} = B^{o}_{hk} \cup B^{1}_{hk} \cup B^{2}_{hk}$$

$$\sigma_{m} = \{(ih, hk) \mid i = 1, 2, 3, \ldots, N-1\}$$

$$\sigma^{o}_{m} = \sigma_{m} \cup \{(L', hk)\},$$

and the reason for introducing L' will be explained later. Note that for any function U defined on R_{hk} on $\overline{R}_{hk}$ we set

$$U_{i,n} = U(ih, nk).$$

Let us now introduce a Crank-Nicholson difference analog for (5. 14)

(5. 19)
$$\frac{\Delta_x^2}{2}(U_{i,n+1} + U_{i,n})$$

$$= F\left\{ih, (n+\tfrac{1}{2})k, \frac{U_{i,n+1}+U_{i,n}}{2}, \delta_x \frac{(U_{i,n+1}+U_{i,n})}{2}, \Delta_{\overline{t}} U_{i,n+1},\right.$$

$$\left. k\left(\frac{1}{2} g((n-\frac{1}{2})k, \Delta_{\overline{t}} U_{i,1} + \sum_{m=2}^{n} g(n+\frac{1}{2}-m)\Delta_{\overline{t}} U_{i,m}\right)\right\}, (ih, (n+1)k) \in R_{hk}$$

$$U = U_{i,n}, \; (ih, nk) \in B_{hk}$$

where

$$\Delta_x^2 U_{i,n} = \frac{1}{h^2}\{U_{i+1,n} - 2U_{i,n} + U_{i-1,n}\}$$

$$\delta_x U_{i,n} = \frac{1}{2h}\{U_{i+1,n} - U_{i-1,n}\}$$

$$\Delta_{t^-} U_{i,n} = \frac{1}{k}\{U_{i,n} - U_{i,n-1}\}$$

and g is the kernel in the integrand of (5. 14). Define the following norms on $\overline{R}_{hk}$

(i) $$\|U\|_o^n = \{h \sum_{\sigma_n^o} U^2\}^{1/2},$$

(ii) $$\|U\|_1^h = \{(\|U\|_o^h)^2 + (\|\Delta_{x^-} U\|_o^h)^2\}^{1/2},$$

where

$$\Delta_{x^-} U_{i,n} = \frac{1}{h}(U_{i,n} - U_{i-1,n}).$$

By using a Taylor series representation for U it can be shown that, provided $U \epsilon C^{4,2}$, $U(x, t)$ satisfies the difference equation locally to within the error of $kO(h^2+k^2)$. By defining the error to be z i. e.,

$$z = U - \mho, \quad (ih, nk) \epsilon \overline{R}_{hk}$$

where $\mho$ is the solution to the difference equation (5. 19), Douglas and Jones (1962) show that not only is the local error $kO(h^2+k^2)$, but that using the above definitions of the norms in $\overline{R}_{hk}$ the global error i. e., the error at any net point (ih, nk), $i = 0, 1, 2 \ldots N$, $n = 0, 1, 2, \ldots, M$, is of the form

$$O(h^2+k^2).$$

The difference equation we then wish to solve is written as

(5.20)
$$\frac{D}{2h^2}\{U_{i+1,\,n+1}-2U_{i,\,n+1}+U_{i-1,\,n+1}+U_{i+1,\,n}-2U_{i,\,n}+U_{i-1,\,n}\}$$

$$-\frac{V}{4h}\{U_{i+1,\,n+1}-U_{i-1,\,n+1}+U_{i+1,\,n}-U_{i-1,\,n}\}$$

$$=\frac{1}{k}(U_{i,\,n+1}+U_{i,\,n})+\frac{B\bar{\lambda}}{2L}(U_{i,\,n+1}+U_{i,\,n})+\mathcal{F}((n+\tfrac{1}{2})k,\ \Delta_t-U_{i,\,n+1}),$$

where

$$\mathcal{F}((n+\tfrac{1}{2})k,\ \Delta_t-U_{i,\,n+1})$$

$$=-\frac{2B^2\bar{\lambda}}{L}\sum_{\ell=1}^{\infty}\frac{k\{\frac{1}{2}(\Delta_t-U_{i,1})\exp[-\frac{\gamma_\ell^2 D_1}{L^2}(n+\frac{1}{2})k+\sum_{m=1}^{n}(\Delta_t-U_{i,m})\exp[-\frac{\gamma_\ell^2 D_1}{L^2}(n+\frac{1}{2}-m)]\}}{\gamma_\ell^2+B(B+1)}$$

The no flux of chemical boundary condition at the surface $x = 0$ is replaced by the three point formula

(5.21)
$$U_{o,\,n+1}=\frac{(4U_{1,\,n+1}-U_{2,\,n+1})\,D}{2hV+3D}$$

The error introduced here is still $O(h^2)$. The initial condition is given as

(5.22)
$$U_{i,\,o}=U_o f_i,\qquad i=0,1,2,\ldots,N$$

Observe that $L' \to \infty$ for the semi-infinite porous medium case; however, it is possible to choose a sequence of $L'(n)$ i.e., $\{L'(n)\}$, $n = 0, 1, 2, \ldots$ such that $L'(n)$ increases at each time step n to maintain the accuracy $O(h^2+k^2)$. Thus, we have a moving false lower boundary which approximates the semi-infinite medium case. We define

$$U_{L'(n), n} = 0 \tag{5.23}$$

Our problem is well-posed in the sense of Lax (Richtmyer and Morton, 1967) and possesses a unique solution which is stable. Define:

(5.24)

(i) $$A = \frac{Dk}{2h^2} + \frac{Vk}{4h},$$

(ii) $$B = -\left(1 + \frac{kB\bar{\lambda}}{2L} + \frac{Dk}{h^2}\right),$$

(iii) $$C = \frac{Dk}{2h^2} - \frac{Vk}{4h}.$$

Rewriting (5.20), we have the system of equations

$$AU_{i-1, n+1} + BU_{i, n+1} + CU_{i+1, n+1} = d_i^n, \quad i = 1, 2, 3, , , N. \tag{5.25}$$

where

$$d_i^n = -AU_{i-1, n}$$

$$+ \left(B + \frac{2Dk}{h^2} + \frac{B\bar{\lambda}k}{L}\right)U_{i,n} - CU_{i+1,n} + k\mathcal{F}\left(\left(n+\frac{1}{2}\right)k, \Delta_t - U_{i,n+1}\right).$$

The resulting system is tri-diagaonal; hence, the Gaussian elimination scheme is used because of its ease in programming and it is the most efficient method presently known.

Observe that the infinite sum indicated in the definition of $\mathcal{F}((n+\frac{1}{2})k, \Delta_t - U_{i, n+1})$ cannot be carried out on the computer. However, a reasonable approximation to the sum can be made. That is, it is possible to truncate the series and preserve $O(h^2+k^2)$. The number of terms kept depends upon the parameters β, L, D_1, and in particular the set of zeros defined by equation

$$\gamma_\ell \tan \gamma_\ell = B. \quad \ell = 1, 2, , , .$$

For a solution to (5.25), subject to the stated boundary conditions, calculated by arbitrarily choosing values for the parameters, refer to Appendix E.

VI. CONCLUSION

The models heretofore mentioned have proved themselves to be valuable in the preliminary investigation of mass transport of chemicals in soils (a type of porous media). Future work based upon analysis of this type is currently being planeed in the Department of Agricultural Chemistry at Oregon State University. It is hoped that future analysis will include mass transport in unsaturated porous media. There the equations of Darcy, Stokes, and others (Scheidegger, 1960) will have to be brought into play in conjuction with the mass transport of chemical equations.

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APPENDICES

APPENDIX A

Definitions of special soil terms: (Scheidegger, 1960)

Porous Medium;

A solid containing holes or voids, either connected or non-connected, dispersed within it in either a regular or random manner.

Bulk Porosity;

The ratio of the total pore volume to the total volume of the sample (percent).

Effective Porosity;

The ratio of the total volume of the inter connecting pore spaces to the total volume of the sample (percent).

Dead Space Voids;

Those pores which apparently do not transmit solutions through them. They may contain solution but do not allow it to pass through them.

Open Channels;

Those pores which are interconnected in such a way so as to offer little resistance to a flowing fluid.

Input Flux of Solution;

Defined to be the volume of solution per unit time crossing a unit area $(\frac{cm}{sec})$.

Definitions of special chemical terms: (Hartley, 1964)

Herbicides and Pesticides;

The broad class of chemical compounts used in agriculture to control the growth of undesirable plant and insect life.

Fertilizers;

The class of chemical compounds used in agriculture to promote or enhance high quality crop production.

DDT;

1, 1, 1-trichloro-2, 2-bis (p-chlorophenyl)ethane.

DDD;

1, 1-dichloro-2, 2-bis (p-chlorophenyl)ethane.

Dieldrine;

1, 2, 3, 4, 10, 10-hexachloro 6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-1, 4-endro-exo-5, 8-dimethanonapthalene.

Heptachlor;

1,4, 5,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene.

2, 4-D;

2, 4-dichlorophenoxy acetic acid.

Adsorption of Chemicals;

That observable phenomenon where by molecules of one substance are held on the surface of a second substance. The holding forces may be physical, electrical, or a combination of both.

APPENDIX B

Laboratory experiments were conducted based upon a water saturated soil column in contact with a large volume reservoir of chemical solution. The diffusion time was three days and the condition stated in conjunction with Equation (2. 27) was fulfilled. Thus, Equation (2. 27) was used to estimate the value of D (the reduced diffusion coefficient).

Since the reservoir was large and the diffusion time was short, a 10 cm. packed column approximated the semi-infinite media very well. For, the maximum depth of measurable penetration was less than 2 cm. Repeating the above diffusion experiment only letting the transport process proceed to equilibrium we were able to use (2. 21) to arrive at estimates on the retentive ability term. The above experiment was carried out on nine different Oregon soils which represent several types of porous media.

Figure B-1 shows the sample curve obtained by experiment for Jory soil and the chemical 2, 4-D.

Figure B-2 shows the plot of the retentive ability versus percent organic matter found in the soil. Points one and seven are the two standard soils so chosen for their similar major soil component similarities except percent organic matter.

Table B-1 shows the physical and chemical properties of the

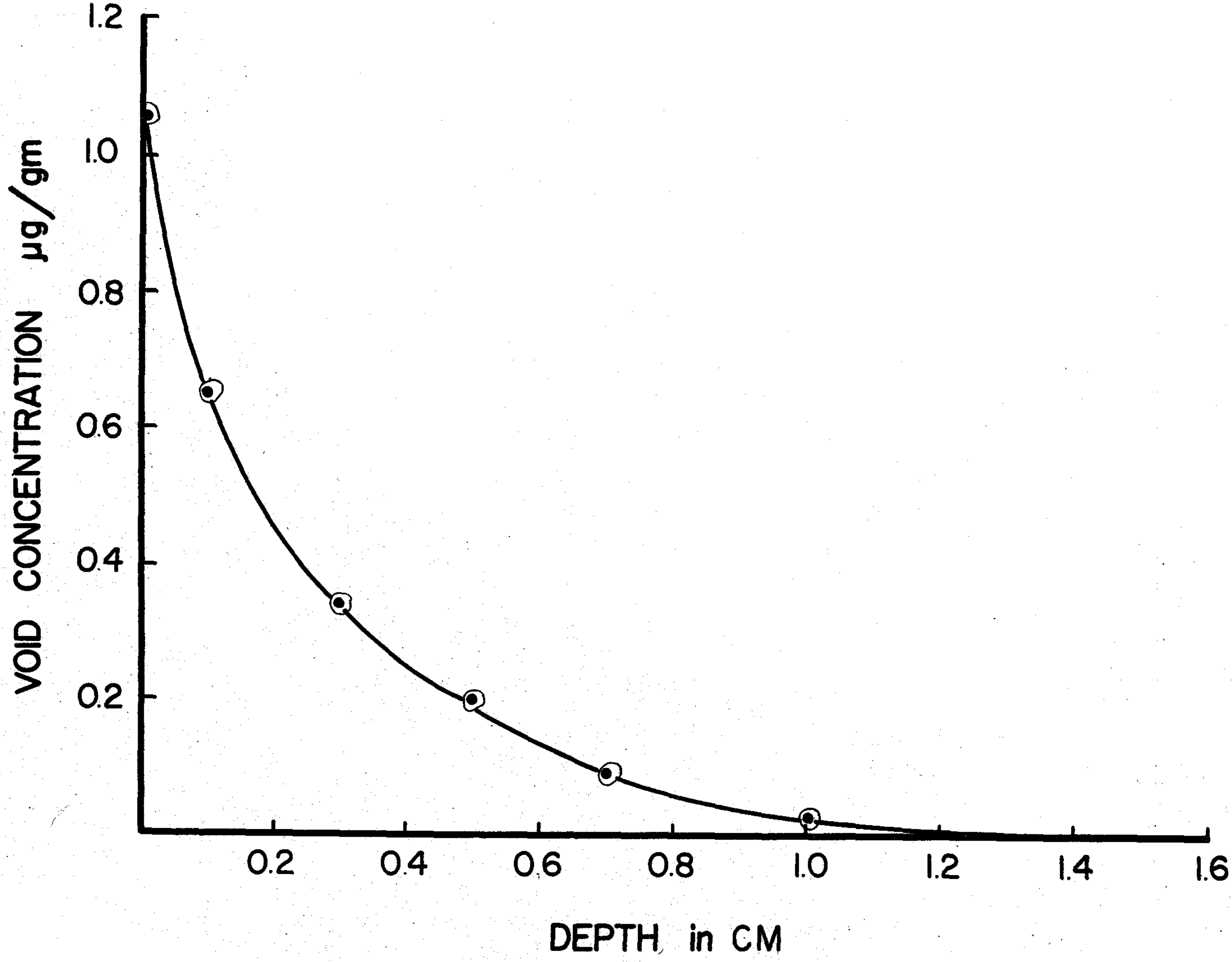

Figure B-1. Graph of relative void concentration versus depth at two days diffusion time into Jory soil.

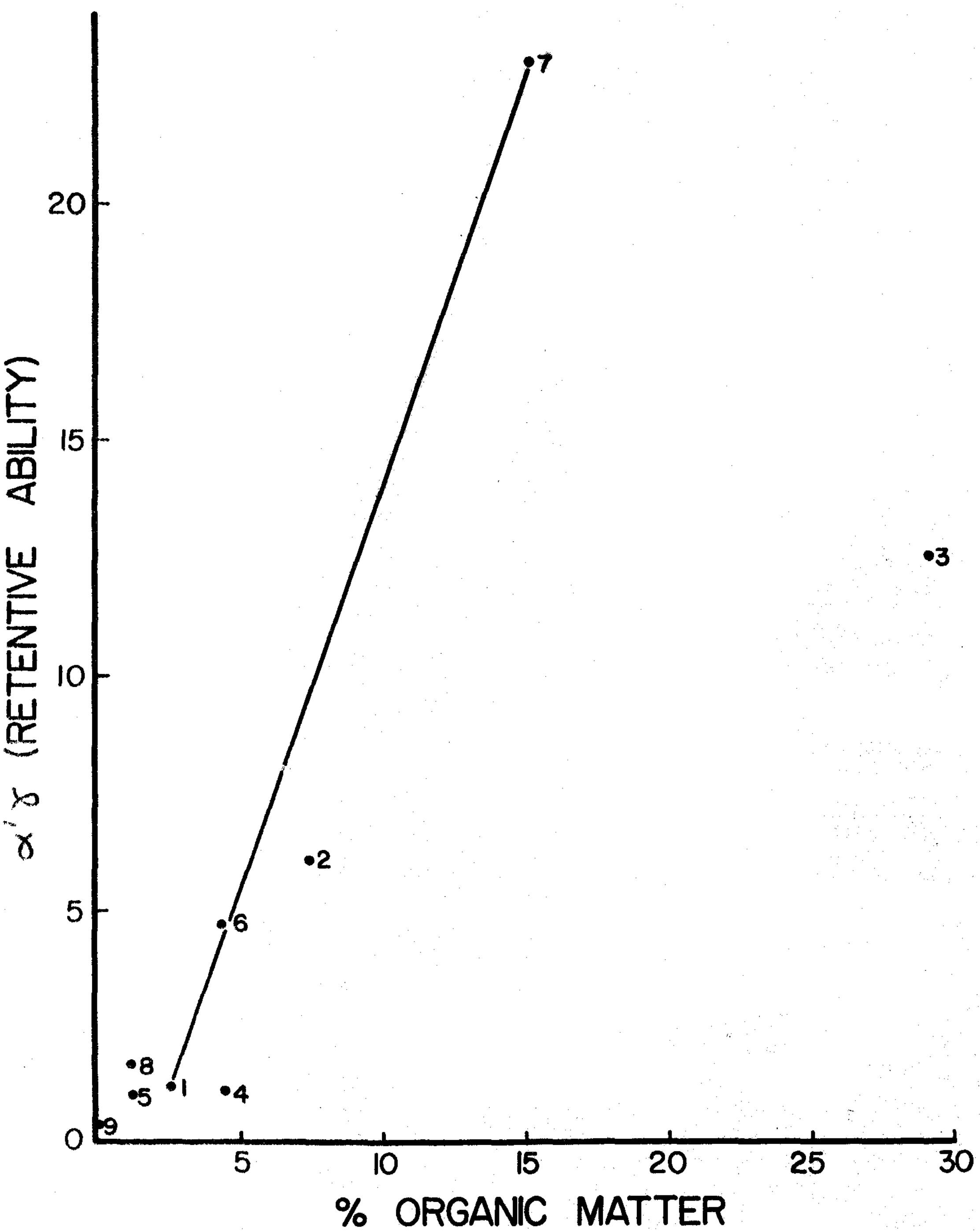

Figure B-2. Graph showing retentive ability of the nine soils used in the experimental test as a function of the % organic matter in the soils.

nine Oregon soils used in the experiments.

Table B-2 shows values for both the true and reduced diffusion coefficient for 2, 4-D chemical in the nine water saturated Oregon soils. The value of each $\alpha\gamma$ product is also shown.

Table B-1. Physical and chemical properties of the nine soils for which diffusion coefficients were determined.

Soil Type	Fe_2O_3	Cation Exchange Capacity	Exchang. Aluminum	Extract Aluminum	pH	Organic Matter	Clay
1. Dayton Silty-loam	1.1	7.7	.35	2.1	5.1	2.6	14.0
2. Jory (Aiken) Silty-clay	7.9	11.9	$\cong$ 0	6.3	5.9	6.9	33.3
3. Hembre Loam	3.5	18.3	3.3	16.8	5.0	29.0	12.6
4. Kenutchen Clay	1.0	45.2	$\cong$ 0	1.0	6.0	4.7	63.7
5. Deschutes Sandy-loam	0.9	10.9	$\cong$ 0	0.7	6.7	0.9	7.2
6. La Grande Silt	0.4	36.4	$\cong$ 0	.3	8.4	4.1	ne
7. Mulkey Loam(10"-18")	nd	nd	nd	nd	5.0	15.1	13.1
8. Nyssa Silt	0.7	18.8	$\cong$ 0	0.6	7.5	1.1	17.0
9. Quartz Sand(0.3-0.5mm)	nd	nd	nd	nd	7.0	$\cong$ 0	$\cong$ 0

nd = not determined

Table B-2. Values of the diffusion coefficient D_o and the reduced diffusion coefficient D for the nine soils used in the experiments.

Soil type	$D \times 10^{-6}$	$a'\gamma$	ϵ_o	$D_o \times 10^{-6}$
	cm^2/sec			cm^2/sec
1. Dayton Silty-loam	0.8 ± 0.3	1.2 ± 0.5	0.48	2.64
2. Jory (Aiken) Silty-clay	0.3 ± 0.1	6.1 ± 1.2	0.46	3.69
3. Hembre Loam	0.15 ± .04	12.8 ± 3.1	0.49	3.91
4. Kenutchen Clay	0.4 ± 0.1	1.1 ± 0.4	0.48	1.24
5. Deschutes Sandy-loam	1.0 ± 0.3	1.3 ± 0.5	0.41	3.20
6. La Grande Silt	0.4 ± 0.1	4.6 ± 0.9	0.50	4.08
7. Mulkey Loam (10"-18")	0.06 ± .03	23.0 ± 5.0	0.51	2.87
8. Nyssa Silt	1.2 ± 0.4	1.5 ± .6	0.43	4.32
9. Quartz Sand (0.3-0.5mm)	4.3 ± 1.1	0.4 ± 0.2	0.375	7.05

APPENDIX C

Equation (3. 41) was plotted for various values of the parameters. Figure C-1 shows plots of the concentration ratio $U(x, t)/U_o$ at a fixed depth x, chosen to be very near the surface of the soil, as a function of time. The six curves represent different values of the influx velocity with and without sorbtion.

The following values were used in the calculations:

$$x \cong 0; \quad \epsilon_d = 0.4; \quad D_o = 2 \frac{cm^2}{mo}; \quad \alpha = 10^{-4}$$

Table C-1. Values used for Q_o and ΔG in Equation (3. 41).

Curve No.	Q_o: $(\frac{cm}{mo})$	ΔG: Kcal/mole	Sorbtion
1	8	0	no
2	8	6	strong
3	4	0	no
4	4	6	strong
5	1.6	0	no
6	1.6	6	strong

The graphs indicate that the effect of rather strong sorbtion is to prevent rapid increase of the chemical in the soil solution over a period of time. When there is no sorbtion the concentration in the soil solution near the surface quickly reaches the level of the input concentration. It can also be seen in Figure C-1, that at higher velocities the surface layer soil void concentration comes quickly up to the input concentration level.

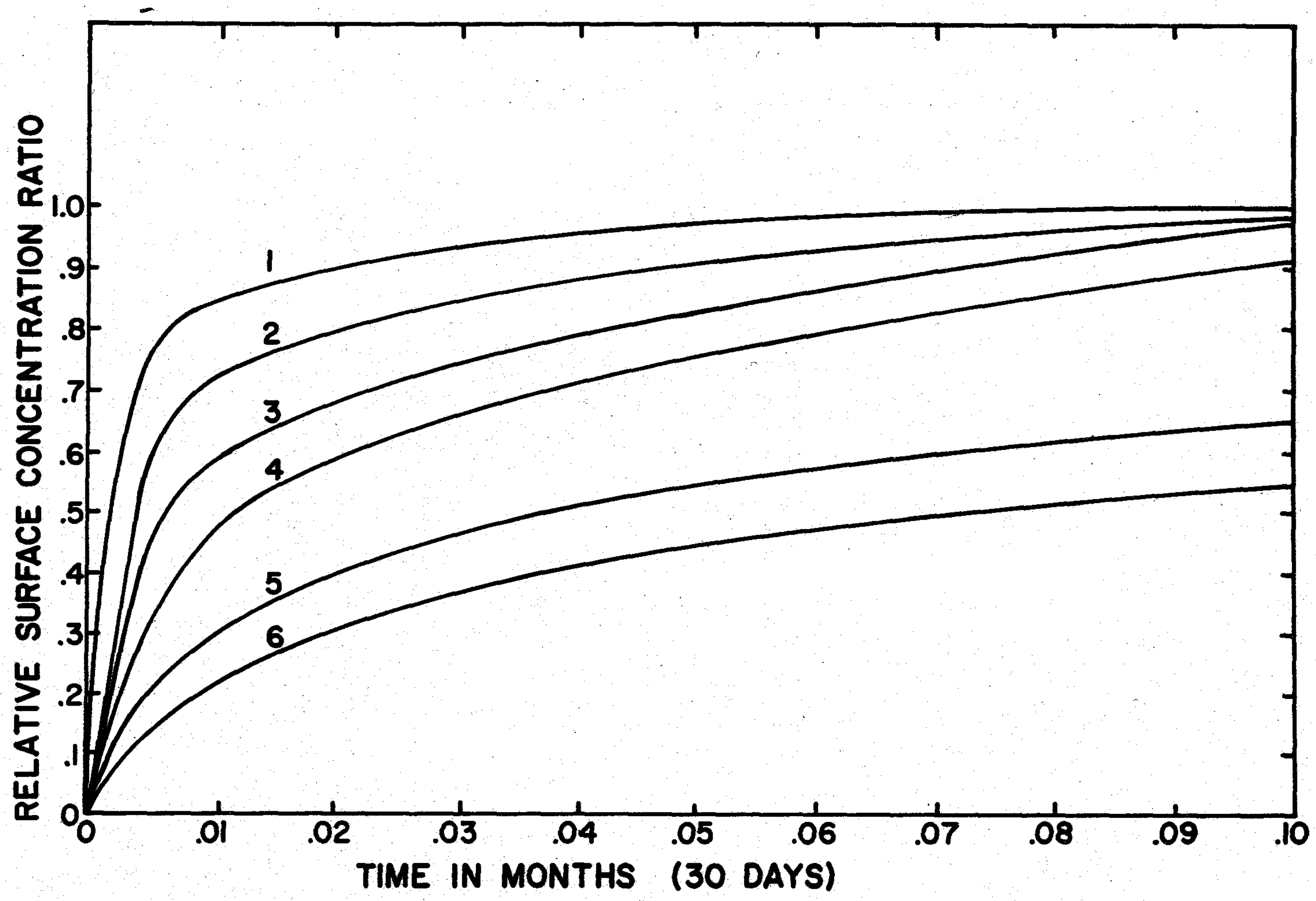

Figure C-1. Graph showing relative surface concentration in voids as a function of time for values of other parameters listed in Table C-1.

The concentration distributions to be expected in the soil solution at different depths after a given period of fluxing are shown in Figure C-2.

Here graphs of the concentration ratio $U(x, t)/U_o$ as a function of depth x, at the time $t = 0.05$ months are presented. The five curves represent different values of the free energy ΔG. Values of the parameters of Equation (3.41) used in the calculations were:

$$Q_o = 40 \text{ cm/mo}; \quad \epsilon_d = 0.4; \quad D_o = 2 \text{ in}^2/\text{mo}; \quad \alpha = 10^{-4}$$

Table C-2. Values used for ΔG in Equation (3.41).

Curve No.	ΔG Kcal/mole	Sorbtion
1	0	no
2	2	weak
3	4	moderate
4	5	moderate to strong
5	6	strong

Figure C-2 shows that with increasing sorbtion energy the rather sharp front of chemical progressing into the soil is retarded in its rate of advance. To obtain these curves the value of ΔG varies from 0 (no sorbtion to 6 Kcal/mole (strong sorbtion) and the value of α used was 10^{-4}). The choice of this value was based on an experiment with a sandy loam, hence the low value. For soils with higher α values the chemical fronts would shift even more toward the influx boundary.

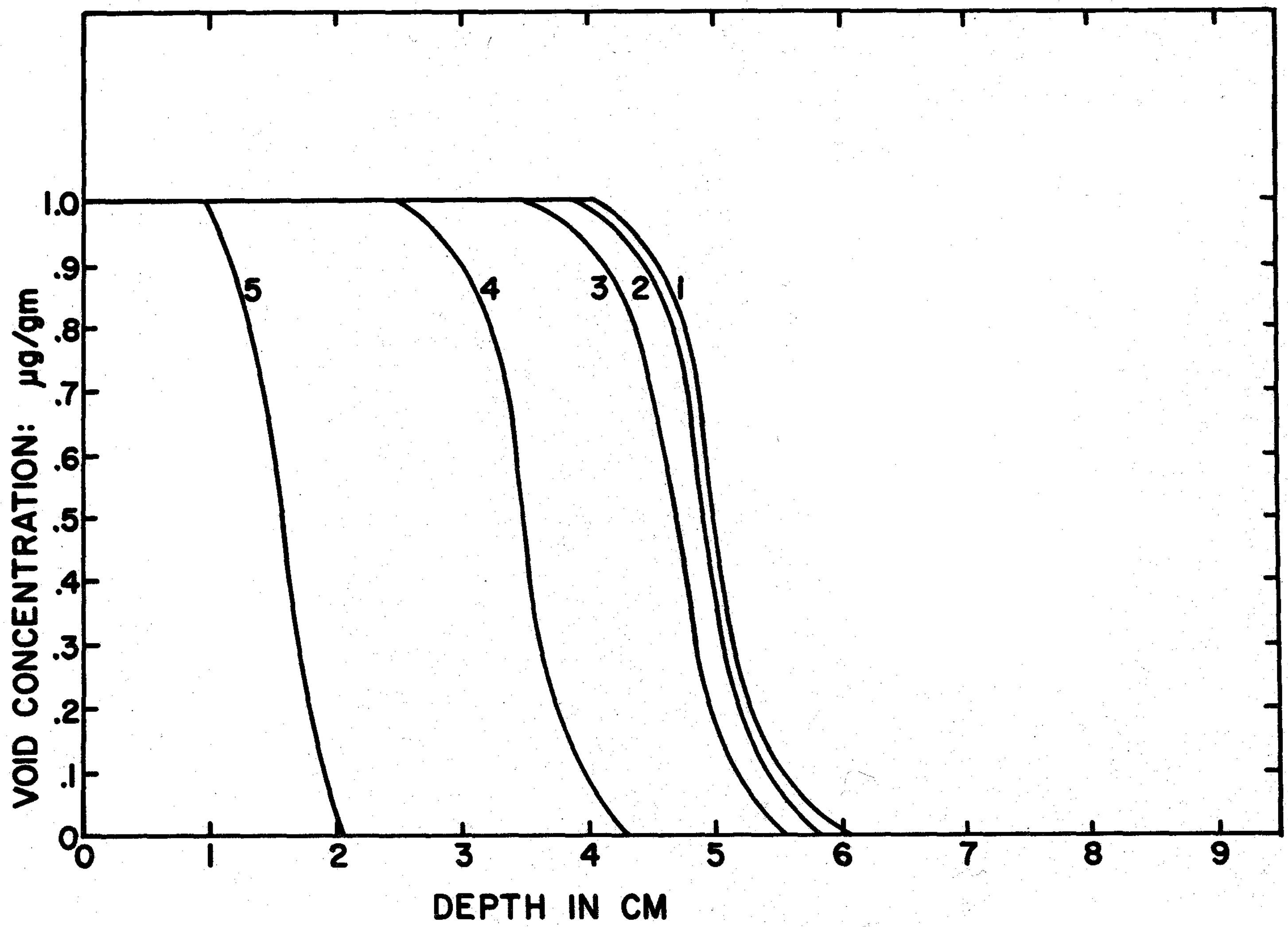

Figure C-2. Graph showing concentration distribution as a function of depth for a fixed time t for values of the parameters listed in Table C-2.

APPENDIX D

Equation (4.11) was evaluated for three different initial distributions. These distributions along with the other necessary information for the calculation are given in Table D-1. Observe that the figures are also designed to show the effect of the effective porosity on the chemical distribution for $t > 0$.

The initial distributions are:

(1) a δ-function;

(2) finite depth Heaviside;

(3) an initially diffused distribution all of which represented the same initial mass in the media.

Table D-1. Showing values of parameters used in Equation (4.11) to generate curves.

Figure No.	Curve	Effective pore ϵ_d	Retention $\alpha\gamma$	Initial dist.
D-1	Top	.125	1	
	Center	.25	1	δ
	Bottom	.33	1	
D-2	Top	.125	1	
	Center	.25	1	Finite
	Bottom	.33	1	
D-3	Top	.125	1	
	Center	.25	1	Diffused
	Bottom	.33	1	
D-4	Top	.25	0, 1, 2	δ
	Center	.25	0, 1, 2	Finte
	Bottom	.25	0, 1, 2	Diffused

Special notes:

1. The values of the other parameters were held constant and are given as follows:
   (i) $V_o = 1.5$ cm/day,
   (ii) $D_o = 0.34$ cm^2/day,
   (iii) $\epsilon_o = 0.5$,
   (iv) $T = 25^oC$.

2. In Figures D-1, D-2, D-3 the numbers (1), (2), (3) refer to 1, 2, and 3 days "leaching" time respectively.

3. In Figure D-4 the leaching time is fixed at 3 days for all curves and the numbers (1), (2), (3) here represent $\alpha\gamma = 0, 1, 2$ respectively.

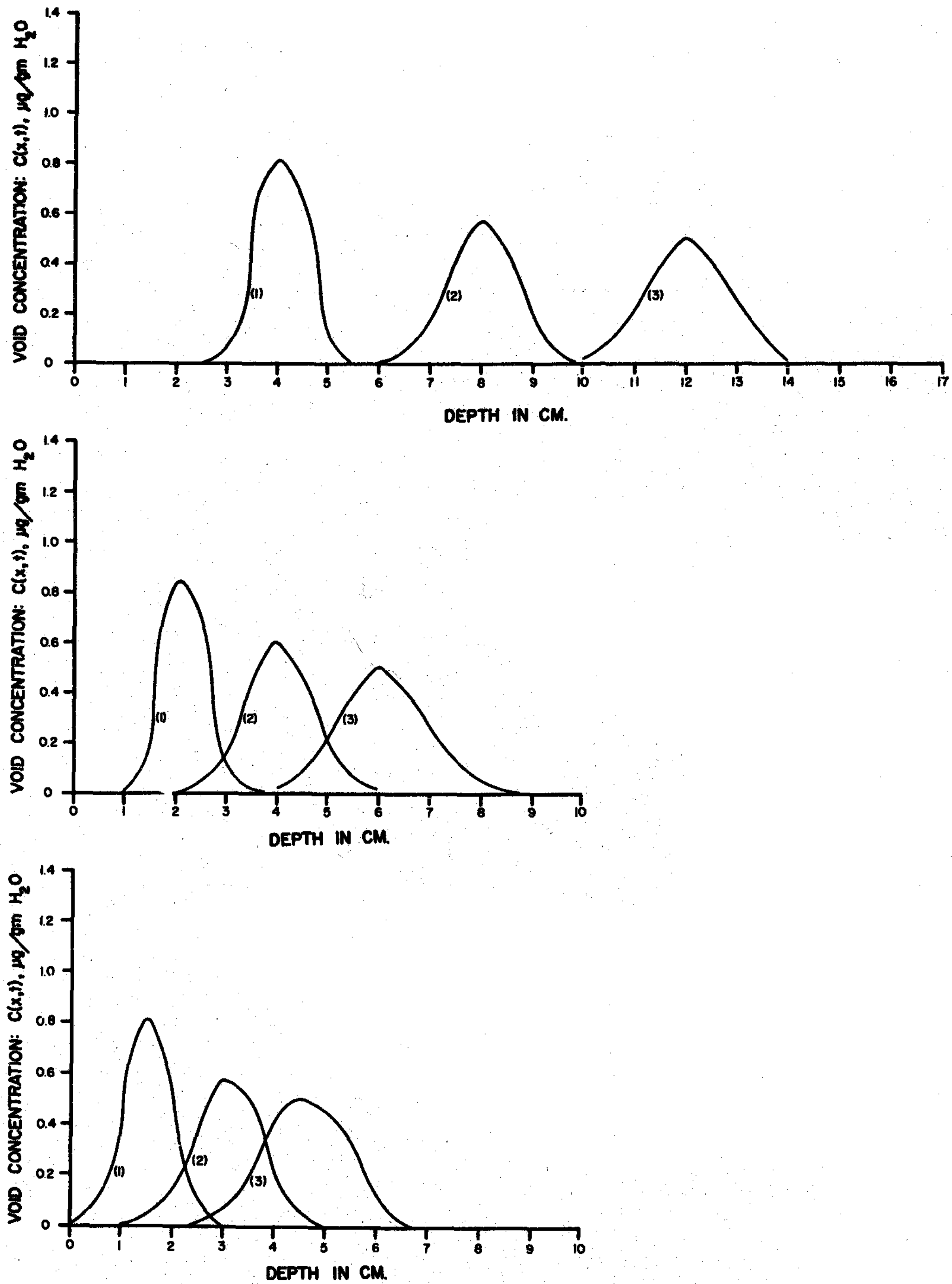

Figure D-1. Comparison graphs for δ function initial distribution.

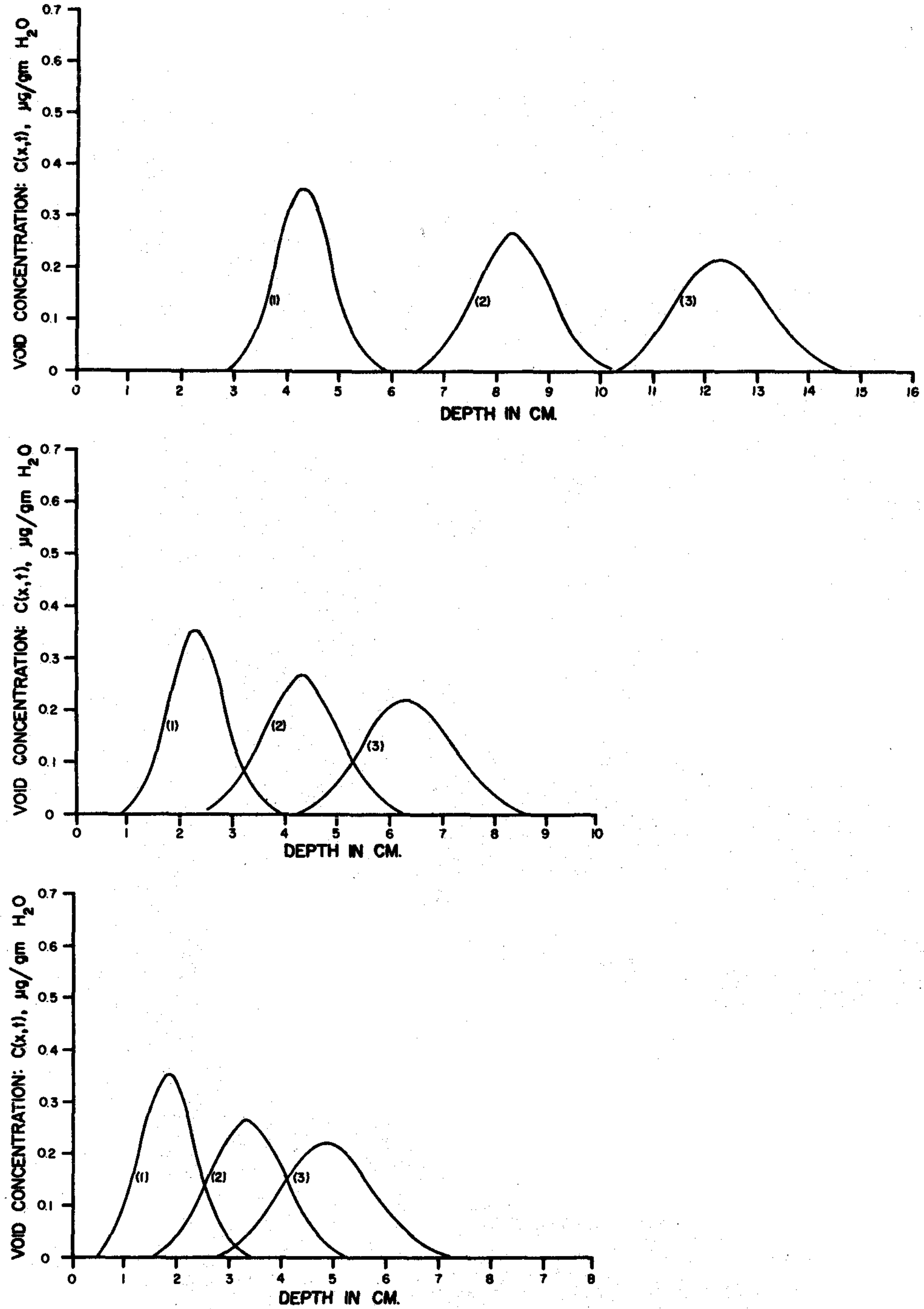

Figure D-2. Comparison graphs for step function initial distribution.

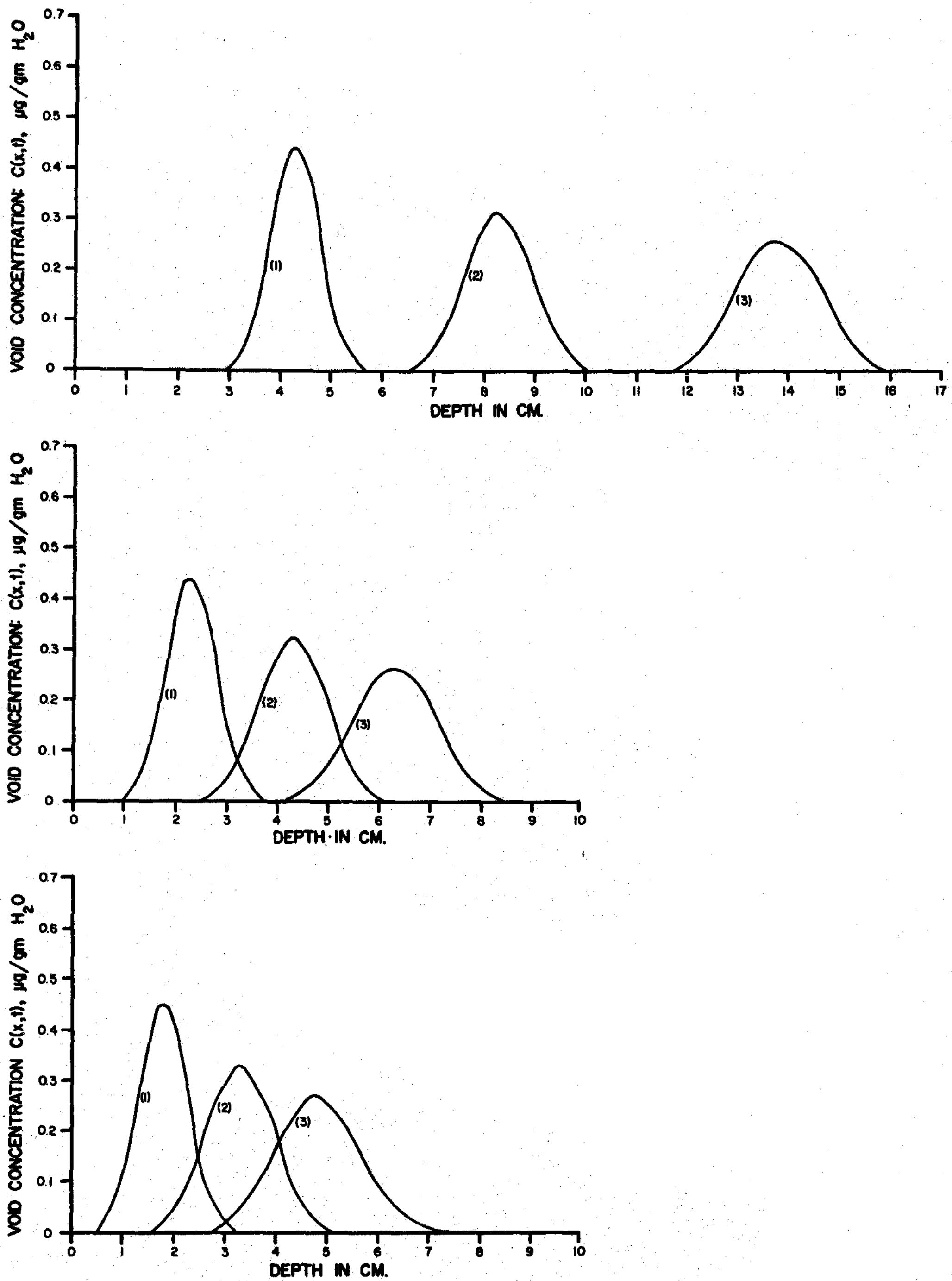

Figure D-3. Comparison graphs for a diffused initial distribution.

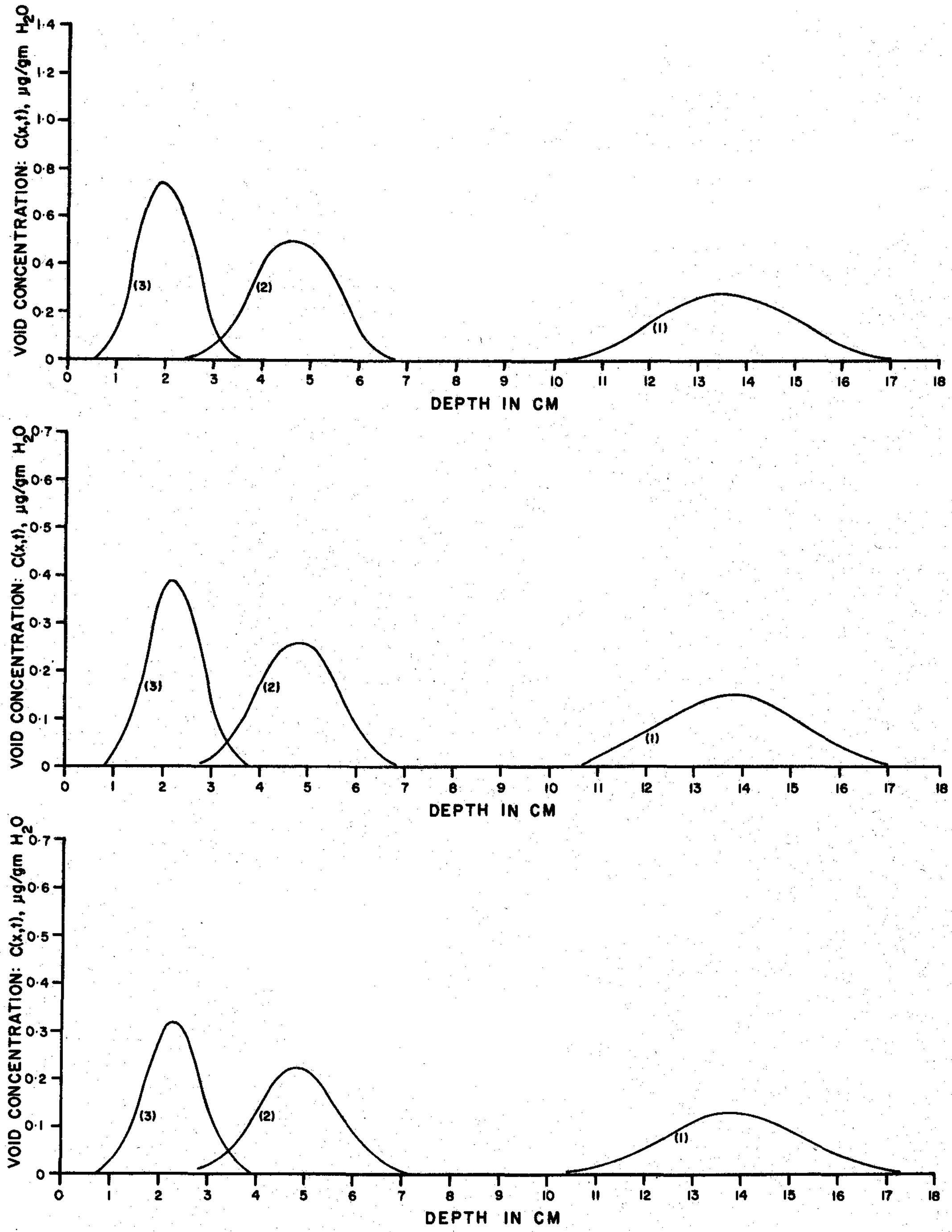

Figure D-4. Comparison graphs of all three initial distributions as a function of adsorption strength (retentive ability).

APPENDIX E

Figure E-1 shows a plot of the solution of the system of equations (5.25) at $n = 20$ i.e., $t = 1$ day ("leaching"). The numerically integrated solution (4.11) for the same initial distribution (a one day diffused type) is also shown. Observe that for the values of h and k defined below the difference between curves (1) and (5) for every point chosen along the depth coordinate is well within $O(h^2+k^2)$ i.e., for $\beta \rightarrow 0$ Equation (4.11) is the limiting case of (5.25).

The values of the parameters used in generating the curves are listed in Table E-1.

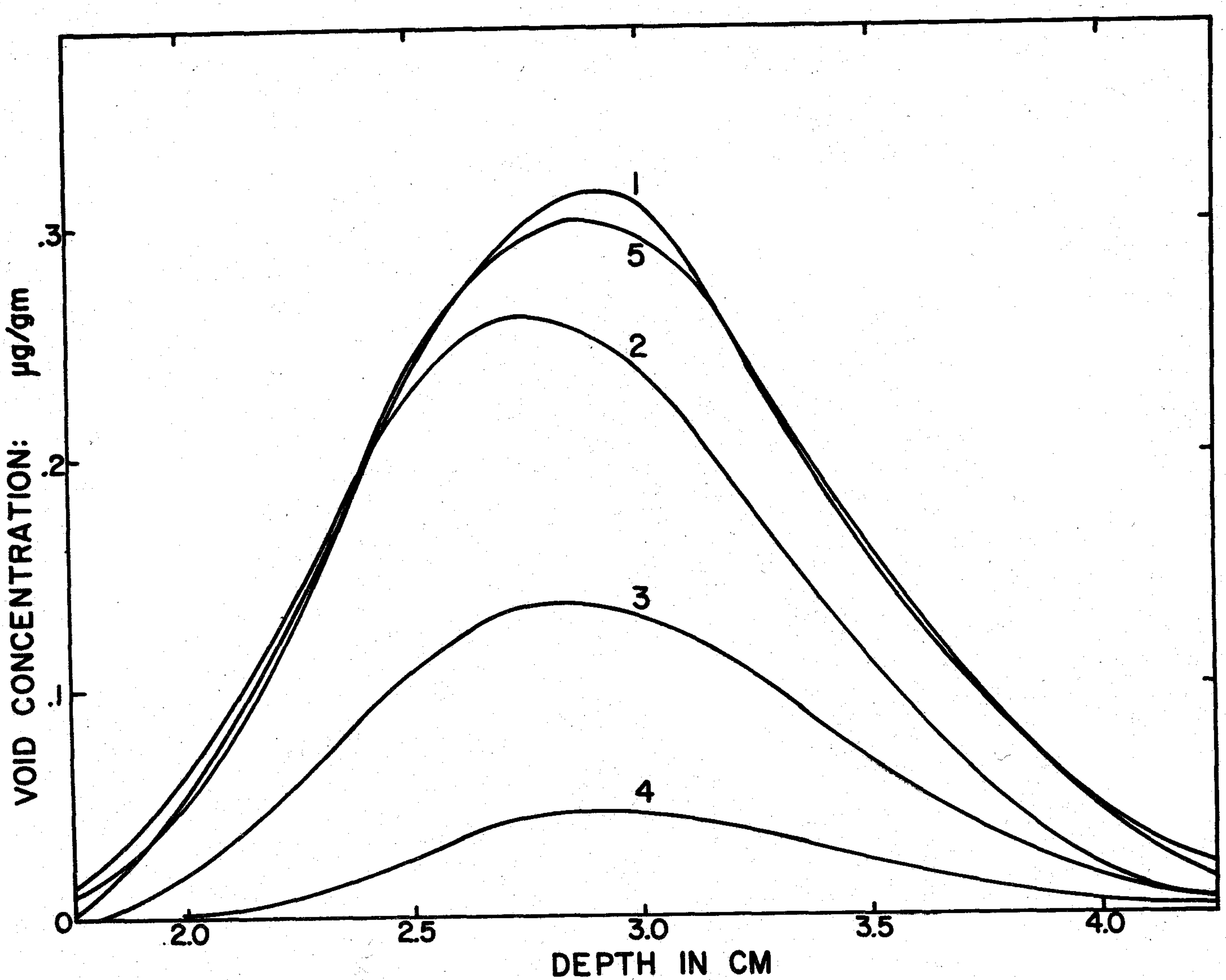

Figure E-1. Graph showing solution of Equation (5. 25) at t = 1 day for four values of β using a diffused type initial distribution.

Table E-1. Mass transport coefficient used in Equation (5.25).

Curve Number	β (mass transfer coefficient)
1	0
2	0.1
3	0.2
4	0.3
5	formal solution of (4.11)

Special notes:

The values of the other parameters used in (5.25) are as follows

$$D_o = 0.33 \frac{cm^2}{day}$$

$$V_o = 6.0 \frac{cm}{day}$$

$$\alpha\gamma = 1$$

$$\epsilon_o = .5$$

$$D_{o1} = 0.18 \frac{cm^2}{day}$$

$$\epsilon_d = .25 \text{ cm}$$

$$L = 0.25 \text{ cm}$$

$$\bar{\lambda} = 2.0 \frac{cm}{day}$$

$$U_o = 1 \text{ (mg/gm)}$$

$$h = .05 \text{ cm}$$

$$k = 0.1 \text{ day}$$

APPENDIX F

Let $\{\sin \beta_n x\}$, $0 \leq x \leq 1$, β_n being the n-th zero of the equation

$$\text{(F. 1)} \qquad \beta \cot \beta + B_o = 0,$$

be a complete orthogonal set which spans $H[0, 1]$. We denote $H[0, 1]$ to be the completion of $L^2[0, 1]$ functions. The expansion of $f(x) = x$, $0 < x \leq 1$ in terms of $\{\sin \beta_n x\}$ is now to be determined. Let

$$\text{(F. 2)} \qquad f(x) = x = \sum_{n=1}^{\infty} \beta_n \sin \beta_n x$$

Multiplying both sides by $\sin \beta_m x$ and integrating $[0, 1]$ gives

$$\text{(F. 3)} \qquad \int_0^1 x \sin \beta_m x dx = \sum_{n=1}^{\infty} a_n \int_0^1 \sin \beta_m x \sin \beta_n x dx.$$

We know by the orthogonality property that

$$\text{(F. 4)} \qquad \int_0^1 \sin \beta_m x \sin \beta_n x dx = \begin{cases} 0, & m \neq n \\ \frac{1}{2}\{1 - \frac{\sin \beta_n \cos \beta_n}{\beta_n}\}, & m=n \end{cases}$$

Thus,

(F. 5) $$\int_0^1 x \sin \beta_n x dx = \frac{a_n}{2} \{1 - \frac{\sin \beta_n \cos \beta_n}{\beta_n}\} .$$

As,

$$\beta_n \cos \beta_n + B_o \sin \beta_n = 0,$$

We obtain upon substitution,

(F. 6) $$\int_0^1 x \sin \beta_n x dx = \frac{a_n}{2} \{1 + \frac{\cos^2 \beta_n}{B_o}\} .$$

Carrying out the indicated integration in the above equation and after some algebraic substitutions and manipulations yields

(F. 7) $$a_n = - \frac{2B_o(B_o+1)}{\beta_n[\beta_n^2+B_o(B_o+1)] \cos \beta_n} .$$

Hence,

(F. 8) $$x = -2B_o(B_o+1) \sum_{n=1}^{\infty} \frac{\sin \beta_n x}{\beta_n[\beta_n^2+B_o(B_o+1)] \cos \beta_n} .$$

As the series representation in (F. 8) is uniformly convergent we differentiate term wise to find

(F. 9) $$1 = -2B_o(B_o+1)\sum_{n=1}^{\infty}\frac{\cos\beta_n x}{[\beta_n^2+B_o(B_o+1)]\cos\beta_n}$$

Rearrangement gives

(F. 10) $$-\frac{1}{1+B_o} = 2B_o\sum_{n=1}^{\infty}\frac{\cos\beta_n x}{[\beta_n^2+B_o(B_o+1)]\cos\beta_n}$$

or

(F. 10') $$\frac{1}{1+B_o} = 2\sum_{n=1}^{\infty}\frac{\beta_n\cos\beta_n x}{[\beta_n^2+B_o(B_o+1)]\sin\beta_n}$$

APPENDIX G

Let $\{\cos \beta_n x\}$, $0 \leq x \leq 1$, β_n being the n-th zero of the equation

(G. 1) $$\beta \tan \beta = B_o, \quad B_o > 0,$$

be a complete orthogonal set which spans $H[0, 1]$. We denote $H[0, 1]$ to be the completion of $L^2[0, 1]$ functions. We now determine the function $f(x) = 1$, $0 < x \leq 1$, in terms of $\{\cos \beta_n x\}$, let

(G. 2) $$f(x) = 1 = \sum_{n=1}^{\infty} a_n \cos \beta_n x.$$

Multiplying both sides of (G. 2) by $\cos \beta_n x$ and integration gives

(G. 3) $$a_n = \frac{2 \sin \beta_n}{\beta_n + \sin \beta_n \cos \beta_n},$$

where use of the orthogonal property of $\cos \beta_n$ has been made. Observe that we can also write (G. 3) as

(G. 4) $$a_n = \frac{2 \sin \beta_n}{\beta_n (\sin^2 \beta_n + \cos^2 \beta_n) + \sin \beta_n \cos \beta_n}.$$

Substituting into (G. 4), $\beta_n \sin \beta_n = B_o \cos \beta_n$, from (G. 1) yields

(G. 5) $$a_n = \frac{2B_o}{[\beta_n^2 + B_o(B_o+1)]\cos\beta_n} .$$

Substitution of a_n in (G. 5) into (G. 2) gives

(G. 6) $$1 = 2B_o \sum_{n=1}^{\infty} \frac{\cos\beta_n x}{[\beta_n^2 + B_o(B_o+1)]\cos\beta_n} .$$

In particular we have at $x = 1$

(G. 7) $$\frac{1}{2B_o} = \sum_{n=1}^{\infty} \frac{1}{\beta_n^2 + B_o(B_o+1)} .$$