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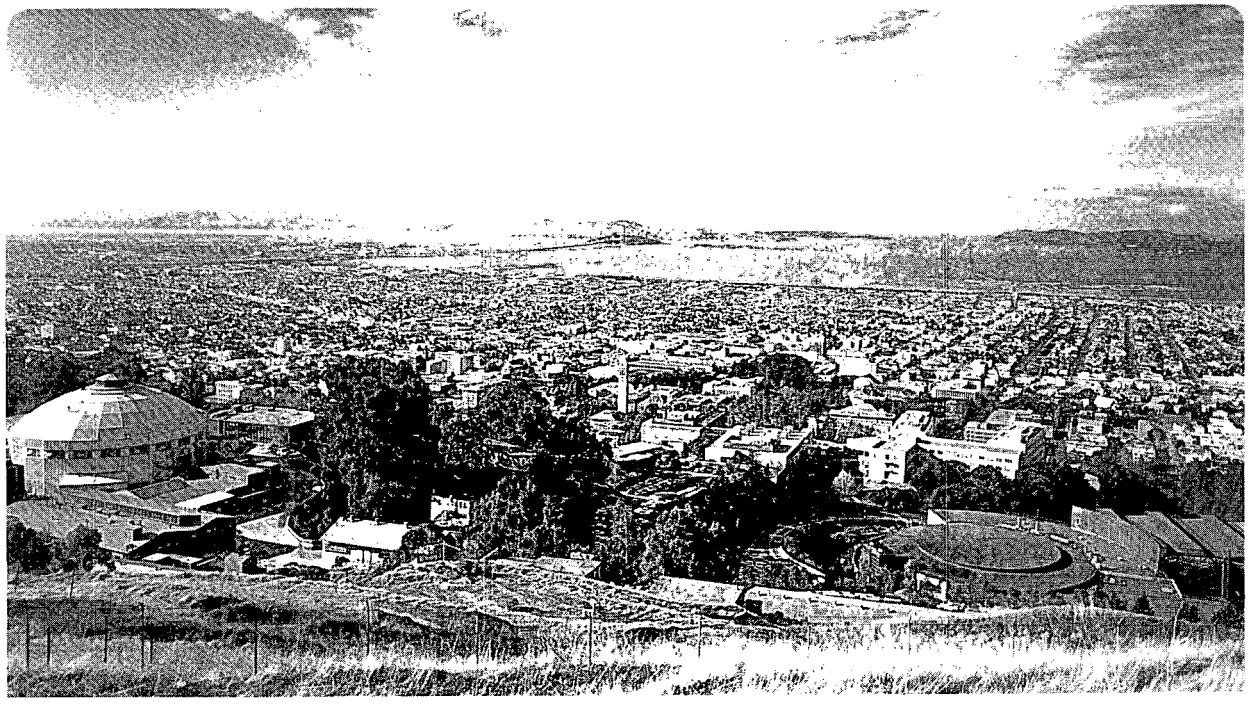
NON-EQUILIBRIUM AND EQUILIBRIUM SORPTION WITH A LINEAR-SORPTION ISOTHERM DURING MASS TRANSPORT THROUGH AN INFINITE, POROUS MEDIUM: SOME ANALYTICAL SOLUTIONS

Chalon L. Carnahan and Janet S. Remer

April 1981



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Non-Equilibrium and Equilibrium Sorption with a Linear-Sorption Isotherm during Mass Transport through an Infinite, Porous Medium: Some Analytical Solutions

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ABSTRACT

Analytical solutions have been developed for the problem of solute transport in a steady, three dimensional field of groundwater flow with non-equilibrium mass transfer of a radioactive species between fluid and solid phases and with anisotropic hydrodynamic dispersion. Interphase mass transport is described by a linear rate expression. Solutions are presented also for the case of equilibrium distribution of solute between fluid and solid phases. Three types of release from a point source were considered: instantaneous release of a finite mass of solute, continuous release at an exponentially decaying rate, and release for a finite period of time. Graphical displays of computational results for point-source solutions show the expected variation of sorptive retardation effects progressing from the case of no sorption, through several cases of non-equilibrium sorption, to the case of equilibrium sorption. The point-source solutions can be integrated over finite regions of a space to provide analytical solutions for regions of solute release having finite spatial extents and various geometrical shapes, thus considerably extending the utility of the point-source solutions.

I. Introduction

The study of transport of chemically reactive solutes by flowing groundwater systems has many applications to current investigations in the fields of hydrology and geochemistry. Processes of mass transport and interphase mass transfer play important roles in natural systems such as ore deposits and geothermal reservoirs. Disturbances of natural systems by human activities also may require evaluation and prediction of rates and extents of mass transport. These disturbances include, for examples, subsurface disposal of radioactive or toxic chemical wastes, acidic drainage from mines, and leaching of landfills, tailings dams, and spoil heaps.

The work reported here is a part of a larger study of non-equilibrium processes in mass transport by flowing groundwater. This work presents analytical solutions for convective-dispersive transport of a radioactive solute which undergoes time-dependent sorption on surfaces of the matrix supporting the flow. The rate of sorption is represented by a linear kinetic rate law, corresponding to the approximation of very low sorbate activity in the fluid phase. These solutions were derived, along with solutions for the case of equilibrium sorption, to serve as references for comparison with numerical results for transport problems using non-linear kinetic rate laws of sorption and with more complex treatments including effects of thermodynamic coupling of transport processes; these investigations are now in progress.

The solutions presented here are geometrically symmetric about an axis parallel to the direction of fluid flow, and include different values of the coefficients of hydrodynamic dispersion in longitudinal and transverse

directions. The medium supporting fluid flow is assumed homogeneous and infinite in extent. Three conditions governing release of solute are considered: (1) an instantaneous release of a finite quantity of solute; (2) a continuous, time-dependent release; and (3) a time-dependent release which is terminated at a finite time.

Our approach has been to derive analytical solutions to the problem of release of solute at a hypothetical, single point in space. The analytical solutions to this problem are useful in two ways. First, the point-source solutions by themselves are useful approximations to solute concentration histories at distances sufficiently far from source regions that the dimensions of the latter can be considered relatively negligible. Second, the point-source solutions can be used as the kernels of integrals over finite volumes of space to provide analytical solutions for source regions having finite spatial extents and a variety of geometrical shapes. This extension allows evaluation of solute concentration histories at source-to-observer distances which are not large relative to source dimensions. The point-source solutions are derived in Section III of this work; the method for their extensions to finite source regions and several examples are presented in Section IV.

The solutions presented here for the cases of non-equilibrium sorption are expressed in closed form as definite integrals in which time is the variable of integration. These integrals appear to be irreducible, and must be evaluated numerically. We have composed a computer code which numerically evaluates the point-source solutions presented here.

II. Previous Work

A large body of literature exists on the subject of mass transport, in a mobile fluid phase, of solutes or components which can be sorbed by a stationary phase supporting the flow of the mobile phase. Published writings on this subject range in content from theoretical studies of ion-exchange chromatography and gas chromatography to predictive analyses of the long-term hydrological safety of sites of underground nuclear explosions. The papers in the relatively small sampling which follows have been selected on the basis of their relationship to the topic of this paper.

Early theoretical treatments of ion-exchange chromatography described one-dimensional, advective transport in sorbing, porous media without hydrodynamic dispersion. Hougen and Marshall (1947) and Thomas (1949) considered non-equilibrium sorption with a linear, reversible rate expression. Hiester and Vermeulen (1952), Goldstein (1953 a, b), and Goldstein and Murray (1959 a, b, c) extended this work to non-linear, reversible, non-equilibrium sorption and to equilibrium sorption characterizable by a non-linear sorption isotherm. Tien and Thodos (1959) provided a numerical solution to the problem of advective transport in an ion exchange column in which sorbent and sorbate are at equilibrium, the sorption process is described by a non-linear isotherm, and the sorbate diffuses in the solid phase.

Lapidus and Amundson (1952) appear to have been the first to provide a complete treatment of the effect of longitudinal dispersion in transport; they considered both equilibrium sorption with a linear isotherm and non-equilibrium sorption with a linear, reversible rate expression. Their work was followed by many papers written by other workers, all dealing with advective-dispersive transport with sorption and differing principally in their treatments of the sorptive process.

Houghton (1963) developed an analytical solution to an approximation of the transport differential equation incorporating equilibrium sorption with a non-linear sorption isotherm.

Lynch (1964) considered transport in fractured flow systems with linear, non-equilibrium sorption. Ogata (1964, 1970), Lindstrom and Narasimhan (1973), Marino (1974, 1978), and Lindstrom (1976) treated the same type of sorption in flow through porous media.

Lindstrom et al. (1967), Holly and Fenske (1968), Cleary and Adrian (1973), and Selim and Mansell (1976) used linear, equilibrium sorption in their treatments of transport. Holly et al. (1971) extended the work of Holly and Fenske to two dimensions using approximation and numerical methods. Both treatments incorporated radioactive decay of the transported material. Burkholder (1976) treated radioactive decay chains arising in the transport of actinide elements.

Numerical methods were used by Lai and Jurinak (1972), Rubin and James (1973), and van Genuchten et al. (1974) in studies of transport with non-linear, equilibrium sorption. The latter workers included hysteresis in sorption-desorption processes and also treated non-linear, non-equilibrium sorption. Numerical methods were used also by Gupta and Greenkorn (1973) to treat non-linear, non-equilibrium sorption.

Several authors have reported studies of transport in two dimensions. Eldor and Dagan (1972) used a perturbation method to derive approximate, analytical solutions for the case of linear, non-equilibrium sorption. Pickens and Lennox (1976) included linear, equilibrium sorption in their numerical treatment of transport in an inhomogeneous, steady flow system. Pickens et al. (1979) extended this work to unsteady flow systems with either equilibrium, or non-equilibrium, linear sorption.

Van Genuchten and Wierenga (1976 a, b) treated one-dimensional models

of transport in which linear, non-equilibrium mass transfer occurs between mobile and immobile fluid phases concurrently with mass transfer between fluid and solid phases. They obtained analytical solutions for the case of linear, equilibrium sorption on the solid phase, and used numerical methods to study effects of hysteresis in non-linear, equilibrium sorption. De Smedt and Wierenga (1979 a, b) later used the same model without fluid-solid mass transfer.

Cameron and Klute (1977) used a model of transport in which linear equilibrium and linear non-equilibrium sorption occur simultaneously at two kinds of sorption sites.

Mansell et al. (1977) fitted experimental data with a numerical model incorporating linear equilibrium, non-linear equilibrium, and non-linear non-equilibrium reversible sorption with irreversible precipitation or chemical immobilization.

Gureghian et al. (1979) used numerical methods to study transport in unsteady flow with non-linear, equilibrium sorption and sequential chemical reactions following linear rate expressions in the fluid phase.

Fenske (1979) presented experimental data on non-linear, non-equilibrium sorption by rock surfaces, and used them in a numerical model of non-dispersive transport with time-dependent sorption based on the binomial probability distribution.

Harada et al. (1980) derived analytical solutions for one-dimensional transport through isotropic, homogeneous or layered, porous media of radionuclides belonging to three- and five-member decay chains. Linear, equilibrium sorption was assumed, and various modes of release of radioactive precursors from a plane source were treated.

III. Development of Analytical Solutions for the Transport Equations.

A. The Equations of Transport and Interphase Transfer

We begin by deriving the differential equations of transport with interphase mass transfer; these will be general expressions of the principle of mass conservation. We then progress toward solutions of the these equations, retaining as much generality as possible. Ultimately, we specify assumptions and conditions leading to specific solutions describing transport of a solute away from a zero-dimensional point of release. We take this approach because of the utility of "point-source" solutions in constructing solutions for other source region geometries, i.e. lines, surfaces, and volumes.

Let us consider an arbitrary volume, V, of a medium having porosity ε and saturated by a fluid phase containing a solute species which may undergo sorption on surfaces of the solid phase. Volume V is fixed with respect to the external coordinate axes. The fluid flows with pore velocity $\vec{v}$. The mass concentrations of solute within V are C mass units per unit volume of fluid and Q mass units per unit volume of solid. Because the system under consideration is not at equilibrium, concentrations C and Q, are not constants but are functions of position and time. The masses of solute associated with the fluid and solid phases within volume V are M_f and M_s respectively, where

$$M_f = \int_V \varepsilon C dV \tag{1}$$

$$M_s = \int_V (1 - \varepsilon) Q dV. \tag{2}$$

The time rates of change of M_f and M_s are given by the time derivatives of (1) and (2). Since the volume V is fixed with respect to the external

coordinate axes, the order of differentiation and integration may be interchanged, so that we have

$$\frac{dM_f}{dt} = \int_V \frac{\partial}{\partial t} (\varepsilon C) dV \tag{3}$$

$$\frac{dM_s}{dt} = \int_V \frac{\partial}{\partial t} [(1 - \varepsilon)Q] dV. \tag{4}$$

Other expressions for dM_f/dt and dM_s/dt may be obtained as follows. The surface of the volume V is divided into infinitesimal elements of area dA. The vector $d\vec{A}$, of magnitude dA, is defined for each element of area. The direction of $d\vec{A}$ is taken perpendicular to the element of surface dA and pointing outward from the volume V. If $\vec{J}$ is the current density or flux of solute mass crossing the surface of volume V, then the rate of change of mass within V due to $\vec{J}$ is

$$- \int_A \vec{J} \cdot d\vec{A}$$

where the integration is taken over the entire surface of V. We now make the assumption that a solute mass flux $\vec{J}$ exists only in the fluid phase, i.e. sorbed solute remains fixed with respect to the solid phase, which in turn is fixed with respect to the external coordinate axes. We next define a solute mass flux in the fluid phase, $\vec{J}_f$, referred to <u>unit area of the fluid phase</u>. Then the rate of change of solute mass M_f within V due to flow of solute through the portion of the surface of V occupied by fluid is

$$- \int_A \varepsilon \vec{J}_f \cdot d\vec{A}.$$

We now consider changes of solute mass arising from internal processes within

volume V. First, we hypothesize that solute mass may be removed from both fluid and solid phases by radioactive decay with a rate constant, λ. Second, we account for interphase mass transfer by hypothesizing a mass transfer rate, S, expressed as mass units of solute per unit time and volume of the solid phase. Adding the changes in M_f and M_s within V due to fluid flow through the boundary of V and to internal processes, we have

$$\frac{dM_f}{dt} = - \int_A \varepsilon \vec{J}_f \cdot d\vec{A} - \int_V \lambda C \varepsilon dV - \int_V S(1 - \varepsilon) dV, \tag{5}$$

$$\frac{dM_s}{dt} = - \int_V \lambda Q(1 - \varepsilon) dV + \int_V S(1 - \varepsilon) dV. \tag{6}$$

(Note that positive S corresponds to a transfer of solute mass from the fluid phase to the solid phase.) The first integral on the right-hand side of (5) may be transformed by use of the divergence theorem (Boas, 1966, p. 247):

$$\int_A \varepsilon \vec{J}_f \cdot d\vec{A} = \int_V \varepsilon \vec{\nabla} \cdot \vec{J}_f \, dV. \tag{7}$$

Combining (3), (5), and (7), and (4) and (6), we find

$$\int_V \left[\varepsilon \frac{\partial C}{\partial t} + \varepsilon \vec{\nabla} \cdot \vec{J}_f + \varepsilon \lambda C + (1 - \varepsilon) S \right] dV = 0, \tag{8}$$

$$\int_V \left[(1 - \varepsilon) \frac{\partial Q}{\partial t} + (1 - \varepsilon) \lambda Q - (1 - \varepsilon) S \right] dV = 0. \tag{9}$$

Since the volume V under consideration is arbitrary, the only way for (8) and (9) to be valid for all volumes V is for the integrands to vanish. Therefore, we obtain the conservation equations

$$\varepsilon\frac{\partial C}{\partial t} = -\varepsilon\vec{\nabla}\cdot\vec{J}_f - \varepsilon\lambda C - (1-\varepsilon)S, \tag{10}$$

$$(1-\varepsilon)\frac{\partial Q}{\partial t} = -(1-\varepsilon)\lambda Q + (1-\varepsilon)S. \tag{11}$$

We now investigate the constitutions of the solute mass flux, $\vec{J}_f$, and the interphase mass transfer rate, S.

The flux of solute is the mass of solute flowing per unit area of fluid phase in unit time, and is equal to the product of mass concentration C and the solute velocity vector, $\vec{v}_s$:

$$\vec{J}_f = C\vec{v}_s. \tag{12}$$

We note that $\vec{v}_s$ is not, in general, equal to the total flow velocity vector $\vec{v}$. We define a dispersive flux, $\vec{j}_f$, of solute relative to the local center of mass as

$$\vec{j}_f = C(\vec{v}_s - \vec{v}). \tag{13}$$

Then the mass flux, $\vec{J}_f$, is related to the dispersive flux, $\vec{j}_f$, by

$$\vec{J}_f = \vec{j}_f + C\vec{v}. \tag{14}$$

The divergence of the mass flux is then

$$\vec{\nabla}\cdot\vec{J}_f = \vec{\nabla}\cdot\vec{j}_f + \vec{v}\cdot\vec{\nabla}C + C\vec{\nabla}\cdot\vec{v}. \tag{15}$$

We make the approximation that $\vec{\nabla}\cdot\vec{v}$ is zero, substitute (15) into (10), and obtain an expression for conservation of solute mass in the fluid phase which contains, explicitly, terms accounting for diffusion and advection:

$$\varepsilon\frac{\partial C}{\partial t} = -\varepsilon\vec{\nabla}\cdot\vec{j}_f - \varepsilon\vec{v}\cdot\vec{\nabla}C - \varepsilon\lambda C - (1-\varepsilon)S. \tag{16}$$

We need to relate the dispersive flux, $\vec{j}_f$, to observable quantities through a constitutive (or phenomenological) relation. For the present purpose, we assume the validity of the expression

$$\vec{j}_f = - \underline{\underline{D}} \cdot \vec{\nabla} C, \tag{17}$$

a form of "Fick's law of diffusion" (Crank, 1975, p. 2) which has been used extensively in studies of solute transport; in this context, the second-rank tensor $\underline{\underline{D}}$ is known as the coefficient of hydrodynamic dispersion and is a function of the velocity of flow, $\vec{v}$ (Scheidegger, 1961; Bachmat and Bear, 1964). With this relation, (16) becomes

$$\varepsilon \frac{\partial C}{\partial t} = \varepsilon \vec{\nabla} \cdot (\underline{\underline{D}} \cdot \vec{\nabla} C) - \varepsilon \vec{v} \cdot \vec{\nabla} C - \varepsilon \lambda C - (1 - \varepsilon) S. \tag{18}$$

The interphase mass-transfer rate, S, may assume many forms. For example, the rate expression for ion exchange in which the ionic solute of interest replaces another ion of equal charge on the solid phase is

$$S = k_1'(Q_{sat} - Q)C - k_2'(C_T - C)Q \tag{19}$$

where Q_{sat} is the ultimate capacity of the solid phase for sorption of the solute, C_T is the total concentration in the fluid phase of the exchanging solutes, and k_1' and k_2' are forward and backward rate constants (Hiester and Vermueulen, 1952). For another example, the rate expression for "Langmuir" adsorption at a surface is

$$S = k_1''(Q_{sat} - Q)C - k_2''Q \tag{20}$$

where k_1'' and k_2'' are rate constants and the other symbols have the same meanings as previously.

Equations (19) and (20) are both non-linear; they may be linearized by assuming in both that $Q \ll Q_{sat}$ and in (19) that $C \ll C_T$. Then the linear, non-equilibrium form of S in both cases is

$$S = k_1 C - k_2 Q \tag{21}$$

in which k_1 equals $k_1' Q_{sat}$ and k_2 equals $k_2' C_T$ for ion exchange, and k_1 equals $k_1'' Q_{sat}$ and k_2 equals k_2'' for Langmuir adsorption. S given by (21) will be used in (10) and (11) for analysis of mass transport with linear, non-equilibrium interphase mass transfer.

If it is assumed that the fluid and solid phases are in a state of chemical equilibrium with respect to transfer of the solute of interest, the net mass transfer rate, S, is identically zero, and we must proceed in the following manner. We add (11) and (18) to obtain a mass conservation equation with respect to a unit volume of porous medium:

$$\varepsilon\frac{\partial C}{\partial t} + (1 - \varepsilon)\frac{\partial Q}{\partial t} = \varepsilon\vec{\nabla}\cdot(\underline{\underline{D}}\cdot\vec{\nabla}C) - \varepsilon\vec{v}\cdot\vec{\nabla}C - \varepsilon\lambda C - (1 - \varepsilon)\lambda Q. \tag{22}$$

If fluid and solid are at equilibrium, the distributed solute concentrations C and Q may be related by

$$\frac{Q}{C} = F(C),$$

where F(C) may be a non-linear function. If our assumptions made about linearity in the non-equilibrium case can be carried over to the equilibrium case, then we may set S equal to zero in (21) and obtain

$$\frac{Q}{C} = \frac{k_1}{k_2}.$$

In either event, we may set the ratio Q/C equal to a function, F, which may be a constant (k_1/k_2) in the linear case or may be a function of C. Then we have

$$Q = FC \tag{23}$$

and

$$\frac{\partial Q}{\partial t} = \frac{\partial}{\partial t}(FC) = (F + F'C)\frac{\partial C}{\partial t} \tag{24}$$

where F' is $\partial F/\partial C$.

Substituting (23) and (24) into (22), dividing by ε, defining α by

$$\alpha = \frac{1 - \varepsilon}{\varepsilon} ,$$

collecting terms, and dividing by $(1 + \alpha F)$, we get

$$\left[1 + \frac{\alpha F' C}{1 + \alpha F}\right]\frac{\partial C}{\partial t} = \vec{\nabla} \cdot \left[\frac{\underline{\underline{D}}}{1 + \alpha F} \cdot \vec{\nabla} C\right] - \frac{\vec{v}}{1 + \alpha F} \cdot \vec{\nabla} C - \lambda C \tag{25}$$

which is the transport equation for the nonlinear, equilibrium case. Passing to the linear equilibrium case, we assume F to be equal to the constant k_1/k_2; then F' is zero and (25) becomes

$$\frac{\partial C}{\partial t} = \vec{\nabla} \cdot \left[\frac{\underline{\underline{D}}}{1 + \alpha F} \cdot \vec{\nabla} C\right] - \frac{\vec{v}}{1 + \alpha F} \cdot \vec{\nabla} C - \lambda C. \tag{26}$$

We note that if F is set to zero in (26) we have the transport equation for a non-sorbed solute. It is apparent that equilibrium sorption causes movement of solute with an effective velocity and effective dispersion coefficient reduced, relative to these quantities in the absence of sorption, by the quantity $(1 + \alpha F)$. This quantity has been called the "retardation factor" in studies of subsurface transport of radionuclides (e.g. Holly et al., 1971, p. 20).

B. Solution of the Equations of Transport

We wish to derive analytical solutions of the transport equations for three cases which cover the entire range of the sorptive behavior that can be described by linear equations: no sorption, linear non-equilibrium sorption, and linear equilibrium sorption. We proceed by making the following assumptions.

1. We are working with a homogeneous, porous medium of infinite extent.
2. The fluid flow field is steady in time, and is uniform throughout space; fluid flows with velocity v parallel to the z axis of a Cartesian coordinate system in the direction of increasing z.

3. The principal axes of the dispersion tensor are oriented parallel to the coordinate axes; the longitudinal dispersion coefficient is D_L in a direction parallel to the z axis, and the lateral (or transverse) dispersion coefficient is D_T in any direction perpendicular to the z axis; D_L and D_T are functions only of the flow velocity, $\vec{v}$.

With these assumptions, the transport equation without sorption is

$$\frac{\partial C}{\partial t} = D_T\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) + D_L \frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \lambda C. \tag{27}$$

For the case of linear equilibrium sorption we have

$$\frac{\partial C}{\partial t} = \frac{D_T}{B}\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) + \frac{D_L}{B}\frac{\partial^2 C}{\partial z^2} - \frac{v}{B}\frac{\partial C}{\partial z} - \lambda C, \tag{28}$$

$$Q = \frac{k_1}{k_2} C, \tag{29}$$

where B is the retardation factor defined by

$$B = 1 + \alpha\frac{k_1}{k_2}. \tag{30}$$

The case of linear non-equilibrium sorption involves two simultaneous equations:

$$\frac{\partial C}{\partial t} = D_T\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) + D_L \frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \lambda C - \alpha(k_1 C - k_2 Q), \tag{31}$$

$$\frac{\partial Q}{\partial t} = -\lambda Q + k_1 C - k_2 Q. \tag{32}$$

We require solutions to (27), (28) and (29), and (31) and (32) subject to the initial conditions:

$$C = 0,\ Q = 0 \text{ for } \rho > 0,\ t = 0, \tag{33}$$

where $\rho^2 = x^2 + y^2 + z^2$,

and the boundary condition:

$$\lim_{\rho\to\infty} C = 0, \; t > 0. \tag{34}$$

Conditions (33) and (34) will determine the required solutions up to a multiplicative constant which will be fixed by the nature of the solute release.

The Laplace transform with respect to time of (28), the case of equilibrium sorption, is

$$\frac{D_T}{B}\left(\frac{\partial^2\bar{C}}{\partial x^2} + \frac{\partial^2\bar{C}}{\partial y^2}\right) + \frac{D_L}{B}\frac{\partial^2\bar{C}}{\partial z^2} - \frac{v}{B}\frac{\partial\bar{C}}{\partial z} - (s + \lambda)\bar{C} = 0 \tag{35}$$

where the overbar indicates the transformed function (or image function) and s is the parameter of transformation. We note that the transform of (27), the case of no sorption, is given by (35) with B = 1. The Laplace transforms of (31) and (32) are

$$D_T\left(\frac{\partial^2\bar{C}}{\partial x^2} + \frac{\partial^2\bar{C}}{\partial y^2}\right) + D_L\frac{\partial^2\bar{C}}{\partial z^2} - v\frac{\partial\bar{C}}{\partial z} - (s + \lambda)\bar{C} - \alpha(k_1\bar{C} - k_2\bar{Q}) = 0, \tag{36}$$

$$s\bar{Q} = -\lambda\bar{Q} + k_1\bar{C} - k_2\bar{Q}. \tag{37}$$

Initial conditions (33) were used in deriving (35), (36), and (37). The transformed boundary condition is

$$\lim_{\rho\to\infty} \bar{C} = 0. \tag{38}$$

Solving (37) for $\bar{Q}$ gives:

$$\bar{Q} = \frac{k_1\bar{C}}{s + \lambda + k_2}. \tag{39}$$

Inserting (39) into (36) and combining terms, we arrive at the following equation for the case of non-equilibrium sorption:

$$D_T\left(\frac{\partial^2\bar{C}}{\partial x^2} + \frac{\partial^2\bar{C}}{\partial y^2}\right) + D_L\frac{\partial^2\bar{C}}{\partial z^2} - v\frac{\partial\bar{C}}{\partial z} - \left(s + \lambda + \alpha k_1 - \frac{\alpha k_1 k_2}{s + \lambda + k_2}\right)\bar{C} = 0. \quad (40)$$

We now note that (35) and (40) may be expressed in the general form:

$$\frac{D_T}{f}\left(\frac{\partial^2\bar{C}}{\partial x^2} + \frac{\partial^2\bar{C}}{\partial y^2}\right) + \frac{D_L}{f}\frac{\partial^2\bar{C}}{\partial z^2} - \frac{v}{f}\frac{\partial\bar{C}}{\partial z} - [s + \lambda + h(s)]\bar{C} = 0 \quad (41)$$

where $h(s) = 0$ for the cases of no sorption and equilibrium sorption,

$h(s) = \alpha k_1 - \dfrac{\alpha k_1 k_2}{s + \lambda + k_2}$ for the case of non-equilibrium sorption,

$f = 1$ for the cases of no sorption and non-equilibrium sorption,

and $f = B$ for the case of equilibrium sorption.

In order to find a complete solution of (41), we need another condition in addition to the boundary condition (38). The second condition will be a statement of conservation of solute mass in all space, and will provide a relationship between solute concentration and the "strength" of a point source releasing solute.

We require that the amount of solute present in all space at any time, t, be equal to the total amount of solute released at the source with correction for conversion of solute to another material by chemical reaction or radioactive decay. Hence, if M(t) is total mass of solute present at time t, it follows that

$$\int_{\substack{\text{all}\\\text{space}}} [\varepsilon C + (1 - \varepsilon)Q]\,dV = M(t). \quad (42)$$

The Laplace transform of (42) is

$$\int_{\substack{\text{all}\\\text{space}}} [\varepsilon\bar{C} + (1 - \varepsilon)\bar{Q}]\,dV = \bar{M}(s) \quad (43)$$

The form of the function M(t), and of its Laplace transform $\bar{M}(s)$, will be determined by the temporal behavior of the solute-emitting source. Leaving this specification open for the time being, we proceed to the solution of (41), subject to conditions (38) and (43), and find:

$$\bar{C} = \frac{(s + \lambda)\bar{M}(s)}{4\pi D_T D_L^{1/2} \varepsilon} \cdot \frac{e^{\frac{vz}{2D_L}}}{\eta} \cdot e^{-\eta f^{1/2}\left(s + \lambda + \frac{v^2}{4D_L f} + h\right)^{1/2}} \tag{44}$$

where $\eta = \left(\frac{r^2}{D_T} + \frac{z^2}{D_L}\right)^{1/2}$

$r^2 = x^2 + y^2$;

h and f remain as defined following (41). A detailed derivation of (44) is given in Appendix A.

Before the solution (44) can be inverted from s-space to t-space, $\bar{M}(s)$ must be specified. In the following sections we consider several release scenarios: (1) an instantaneous release, (2) a continuous, time-dependent release, and (3) a time-dependent release for a finite time period followed by no further release (a "time-dependent pulse").

1. Instantaneous Release

A quantity, M_o, of solute is released instantaneously at time zero at the origin of coordinates. Allowing for disappearance of solute by radioactive decay, the quantity, M(t), of solute present at time t is

$$M(t) = M_o e^{-\lambda t}.$$

The Laplace transform of M(t) is

$$\bar{M}(s) = \frac{M_o}{s + \lambda}. \tag{45}$$

Inserting (45) into (44) gives

$$\bar{C} = \frac{M_o}{4\pi D_T D_L^{1/2}\varepsilon} \frac{e^{\frac{vz}{2D_L}}}{\eta} \cdot e^{-\eta f^{1/2}\left(s + \lambda + \frac{v^2}{4D_L f} + h\right)^{1/2}} \tag{46}$$

We now use (46) to find C and Q for specific cases of sorptive behavior.

a. Equilibrium Sorption

In this case, h(s) = 0 and f = B; the inverse of (46) is then found from tables (e.g., Erdelyi, 1954, p. 245, No. 5.6(1)) to be

$$C = \frac{B^{1/2} M_o e^{-\lambda t}}{8D_T D_L^{1/2}\varepsilon(\pi t)^{3/2}} e^{-\frac{Br^2}{4D_T t} - \frac{B(z - vt/B)^2}{4D_L t}}, \tag{47}$$

and Q is then,

$$Q = \frac{k_1}{k_2} C. \tag{29}$$

b. Non-Equilibrium Sorption

Substituting f = 1 and the appropriate value of h(s) into (46) give:

$$\bar{C} = \frac{M_o}{4\pi D_T D_L^{1/2}\varepsilon} \cdot \frac{e^{\frac{vz}{2D_L}}}{\eta} \cdot e^{-\eta\left(s + \lambda + \frac{v^2}{4D_L} + \alpha k_1 - \frac{\alpha k_1 k_2}{s + \lambda + k_2}\right)^{1/2}} . \tag{48}$$

Then, using (39), we have

$$\bar{Q} = \frac{k_1 M_o}{4\pi D_T D_L^{1/2}\varepsilon} \cdot \frac{e^{\frac{vz}{2D_L}}}{\eta} \cdot \frac{e^{-\eta\left(s + \lambda + \frac{v^2}{4D_L} + \alpha k_1 - \frac{\alpha k_1 k_2}{s + \lambda + k_2}\right)^{1/2}}}{s + \lambda + k_2} . \tag{49}$$

$\bar{C}$ in (48) is inverted by use of (B-13), Appendix B, with

$$\beta_1 = \lambda + \frac{v^2}{4D_L} + \alpha k_1 k_2, \text{ and } \beta_3 = \lambda + k_2.$$

The result is

$$C = \frac{M_o e^{-\lambda t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon} \left\{ \frac{e^{-\frac{r^2}{4D_T t} - \frac{(z - vt)^2}{4D_L t} - \alpha k_1 t}}{t^{3/2}} + (\alpha k_1 k_2)^{1/2} e^{-k_2 t} \int_0^t e^{-\frac{r^2}{4D_T \tau} - \frac{(z - v\tau)^2}{4D_L \tau} - (\alpha k_1 - k_2)\tau} I_1\left[2\sqrt{\alpha k_1 k_2 \tau (t - \tau)}\right] \frac{d\tau}{\tau (t - \tau)^{1/2}} \right\} \tag{50}$$

If we make the substitution $u = \tau/t$, the second term within the curly braces in (50) becomes

$$\left(\frac{\alpha k_1 k_2}{t}\right)^{1/2} e^{-k_2 t} \int_0^1 e^{-\frac{r^2}{4D_T tu} - \frac{(z-vtu)^2}{4D_L tu} - (\alpha k_1 - k_2)\, tu} I_1\left[2t\sqrt{\alpha k_1 k_2 u(1-u)}\right] \frac{du}{u(1-u)^{1/2}},$$

a form useful for numerical evaluation.

To invert $\bar{Q}$ in (49), we note that *

$$L^{-1}\left\{\frac{e^{-\eta\left(s + \lambda + \frac{v^2}{4D_L} + \alpha k_1 - \frac{\alpha k_1 k_2}{s + \lambda + k_2}\right)^{1/2}}}{s + \lambda + k_2}\right\}$$

$$= e^{-\lambda t - k_2 t} L^{-1}\left\{\frac{e^{-\eta\left(s + \frac{v^2}{4D_L} + \alpha k_1 - k_2 - \frac{\alpha k_1 k_2}{s}\right)^{1/2}}}{s}\right\}$$

Then, using (B-11), Appendix B, with

$$\beta_1 = \frac{v^2}{4D_L} + \alpha k_1 - k_2,\ \beta_2 = \alpha k_1 k_2,\ \text{and}\ \beta_3 = 0,$$

we find

$$Q = \frac{k_1 M_o e^{-(\lambda + k_2)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon} \int_0^t e^{-\frac{r^2}{4D_T\tau} - \frac{(z - v\tau)^2}{4D_L\tau} - (\alpha k_1 - k_2)\tau} I_o\left[2\sqrt{\alpha k_1 k_2 \tau(t - \tau)}\right] \frac{d\tau}{\tau^{3/2}}, \tag{51}$$

or

$$Q = \frac{k_1 M_o e^{-(\lambda + k_2)t}}{8\pi^{3/2} D_T (D_L t)^{1/2} \varepsilon} \int_0^1 e^{-\frac{r^2}{4D_T tu} - \frac{(z-vtu)^2}{4D_L tu} - (\alpha k_1 - k_2)tu} I_o[2t\sqrt{\alpha k_1 k_2 u(1-u)}] \frac{du}{u^{3/2}}.$$

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* Symbols L and L^{-1} signify the operations of Laplace transformation and inversion, respectively; see Appendix B.

2. Continuous, Time-Dependent Release

Solute is released continuously at the origin beginning at time zero. The rate of release is m_o mass units per unit time at time zero, and decreases exponentially with time with a time constant, γ; simultaneously, solute disappears by radioactive decay with a decay constant, λ. Then at time t the net rate of change of solute mass, M(t), in space is:

$$\frac{dM(t)}{dt} = m_o e^{-(\gamma + \lambda)t} - \lambda M(t), \tag{52}$$

with the initial condition

$$M(0) = 0. \tag{53}$$

Laplace transforming (52), using (53), and solving for $\bar{M}(s)$ gives:

$$\bar{M}(s) = \frac{m_o}{(s + \lambda)(s + \gamma + \lambda)} . \tag{54}$$

Inserting (54) into (44) gives:

$$\bar{C} = \frac{m_o}{4\pi D_T D_L^{1/2} \varepsilon} \frac{e^{\frac{vz}{2D_L}}}{\eta} \cdot \frac{e^{-\eta f^{1/2}\left(s + \lambda + \frac{v^2}{4D_L f} + h\right)^{1/2}}}{s + \gamma + \lambda} . \tag{55}$$

a. Equilibrium Sorption

With h(s) = 0 and f = B, (55) becomes

$$\bar{C} = \frac{m_o}{4\pi D_T D_L^{1/2} \varepsilon} \frac{e^{\frac{vz}{2D_L}}}{\eta} \cdot \frac{e^{-\eta B^{1/2}\left(s + \lambda + \frac{v^2}{4D_L B}\right)^{1/2}}}{s + \gamma + \lambda} . \tag{56}$$

Using the convolution property and a table of inverse transforms (Erdelyi, 1954, p. 245, no. 5.6(1)), the inverse of (56) is found to be:

$$C = \frac{B^{1/2} m_o e^{-(\gamma + \lambda)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon} e^{\frac{vz}{2D_L}} \int_0^t e^{-\frac{\eta^2 B}{4\tau} - \left(\frac{v^2}{4D_L B} - \gamma\right)\tau} \frac{d\tau}{\tau^{3/2}} . \tag{57}$$

We make the substitution $u = \tau^{-1/2}$ for τ in (57); then, using the following indefinite integral given by Gautschi (1964, p. 304, no. 7.4.33), valid for $a \neq 0$:

$$\int e^{-a^2u^2 - b^2u^{-2}} du = \frac{\pi^{1/2}}{4a} \left[e^{2ab} \operatorname{erf}\left(au + \frac{b}{u}\right) + e^{-2ab} \operatorname{erf}\left(au - \frac{b}{u}\right) \right] + \text{constant}, \tag{58}$$

we find:

$$C = \frac{m_o e^{-(\gamma + \lambda)t}}{8\pi D_T D_L^{1/2} \varepsilon} \frac{e^{\frac{vz}{2D_L}}}{\eta} \left\{ e^{-\eta B^{1/2}\left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2}} \operatorname{erfc}\left[\frac{B^{1/2}\eta}{2t^{1/2}} - \left(\frac{v^2 t}{4D_L B} - \gamma t\right)^{1/2}\right] + e^{+\eta B^{1/2}\left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2}} \operatorname{erfc}\left[\frac{B^{1/2}\eta}{2t^{1/2}} + \left(\frac{v^2 t}{4D_L B} - \gamma t\right)^{1/2}\right] \right\} . \tag{59}$$

Then

$$Q = \frac{k_1}{k_2} C.$$

In the event that $\frac{v^2}{4D_L B} - \gamma < 0$ we use (D-4), Appendix D, which gives the result:

$$C \cong \frac{m_o e^{-(\gamma+\lambda)t}}{4\pi D_T D_L^{1/2}\varepsilon} \; \frac{e^{\frac{vz}{2D_L}}}{\eta} \left\{ \operatorname{erfc}\left(\frac{B^{1/2}\eta}{2t^{1/2}}\right) \cdot \cos \eta B^{1/2}\left(\gamma - \frac{v^2}{4D_L B}\right)^{1/2} \right.$$

$$+ \frac{t^{1/2}}{\pi B^{1/2}\eta} e^{\frac{-B\eta^2}{4t}} \left[1 - \cos \eta B^{1/2}\left(\gamma - \frac{v^2}{4D_L B}\right)^{1/2}\right]$$

$$\left. + \frac{2B^{1/2}\eta}{\pi t^{1/2}} e^{\frac{-B\eta^2}{4t}} \sum_{m=1}^{\infty} \frac{e^{-m^2/4}}{m^2 + \frac{B\eta^2}{t}} \left[\cosh m \left(\gamma - \frac{v^2}{4D_L B}\right)^{1/2} - \cos \eta B^{1/2}\left(\gamma - \frac{v^2}{4D_L B}\right)^{1/2}\right]\right\}$$

If $\frac{v^2}{4D_L B} = \gamma \neq 0$, (57) can be integrated using the substitution $u = \tau^{-\frac{1}{2}}$ to give:

$$C = \frac{m_o e^{\frac{vz}{2D_L} - (\gamma+\lambda)t}}{4\pi D_T D_L^{1/2}\varepsilon\eta} \operatorname{erfc}\left(\frac{B^{1/2}\eta}{2t^{1/2}}\right) .$$

Note that both C and Q are unbounded positively at $\eta = 0$.

b. <u>Non-Equilibrium Sorption</u>

In this case (55) becomes

$$\bar{C} = \frac{m_o}{4\pi D_T D_L^{1/2}\varepsilon} \; \frac{e^{\frac{vz}{2D_L}}}{\eta} \; \frac{e^{-\eta\left(s + \lambda + \frac{v^2}{4D_L} + \alpha k_1 - \frac{\alpha k_1 k_2}{s + \lambda + k_2}\right)^{1/2}}}{s + \gamma + \lambda} , \qquad (60)$$

and (39) becomes

$$\bar{Q} = \frac{k_1 m_o}{4\pi D_T D_L^{1/2} \varepsilon} \; \frac{e^{\frac{vz}{2D_L}}}{\eta} \; \frac{e^{-\eta\left(s + \lambda + \frac{v^2}{4D_L} + \alpha k_1 - \frac{\alpha k_1 k_2}{s + \lambda + k_2}\right)^{1/2}}}{(s + \gamma + \lambda)(s + \lambda + k_2)} \quad . \tag{61}$$

To invert $\bar{C}$ in (60), we note that

$$L^{-1}\left\{\frac{e^{-\eta\left(s + \lambda + \frac{v^2}{4D_L} + \alpha k_1 - \frac{\alpha k_1 k_2}{s + \lambda + k_2}\right)^{1/2}}}{s + \gamma + \lambda}\right\} =$$

$$e^{-(\gamma + \lambda)t} \; L^{-1}\left\{\frac{1}{s} e^{-\eta\left(s + \frac{v^2}{4D_L} + \alpha k_1 - \gamma - \frac{\alpha k_1 k_2}{s + k_2 - \gamma}\right)^{1/2}}\right\} .$$

Then we use (B-10), Appendix B, with

$$\beta_1 = \frac{v^2}{4D_L} + \alpha k_1 - \gamma, \; \beta_2 = \alpha k_1 k_2, \text{ and } \beta_3 = k_2 - \gamma,$$

and find*

$$C = \frac{m_o e^{-(\lambda + \gamma)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon} \int_0^t e^{-\frac{r^2}{4D_T\tau} - \frac{(z - v\tau)^2}{4D_L\tau} + \left(\frac{\alpha k_1}{k_2 - \gamma} + 1\right)\gamma\tau} \; J\left[\frac{\alpha k_1 k_2 \tau}{k_2 - \gamma}, (k_2 - \gamma)(t - \tau)\right] \frac{d\tau}{\tau^{3/2}} \quad . \tag{62}$$

*The function J(x,y) is defined in Appendix B.

The following form of (62) is convenient for numerical evaluations

$$C = \frac{m_o e^{-(\lambda+\gamma)t}}{8\pi^{3/2} D_T (D_L t)^{1/2} \varepsilon} \int_0^1 e^{-\frac{r^2}{4D_T tu} - \frac{(z - vtu)^2}{4D_L tu} + \left(\frac{\alpha k_1}{k_2 - \gamma} + 1\right)\gamma tu} J\left[\frac{\alpha k_1 k_2 tu}{k_2-\gamma}, t(k_2-\gamma)(1-u)\right] \frac{du}{u^{3/2}} .$$

To invert $\bar{Q}$ in (61), we note that

$$L^{-1}\left\{\frac{e^{-\eta\left(s + \lambda + \frac{v^2}{4D_L} + \alpha k_1 - \frac{\alpha k_1 k_2}{s + \lambda + k_2}\right)^{1/2}}}{(s + \gamma + \lambda)(s + \lambda + k_2)}\right\}$$

$$= \frac{e^{-(\gamma + \lambda)t}}{k_2 - \gamma} L^{-1}\left\{\frac{1}{s} e^{-\eta\left(s + \frac{v^2}{4D_L} + \alpha k_1 - \gamma - \frac{\alpha k_1 k_2}{s + k_2 - \gamma}\right)^{1/2}}\right\}$$

$$- \frac{e^{(\lambda + k_2)t}}{k_2 - \gamma} L^{-1}\left\{\frac{1}{s} e^{-\eta\left(s + \frac{v^2}{4D_L} + \alpha k_1 - k_2 - \frac{\alpha k_1 k_2}{s}\right)^{1/2}}\right\} .$$

Then using (B-10), Appendix B, with

$$\beta_1 = \frac{v^2}{4D_L} + \alpha k_1 - \gamma, \ \beta_2 = \alpha k_1 k_2, \text{ and } \beta_3 = k_2 - \gamma,$$

and (B-11), Appendix B, with

$$\beta_1 = \frac{v^2}{4D_L} + \alpha k - k_2, \ \beta_2 = \alpha k_1 k_2, \ \beta_3 = 0,$$

we find

$$Q = \frac{k_1}{k_2 - \gamma}\left\{C - \frac{m_o e^{-(\lambda + k_2)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon}\int_0^t e^{-\frac{r^2}{4D_T\tau} - \frac{(z - v\tau)^2}{4D_L\tau} - (\alpha k_1 - k_2)\tau} I_o\left[2\sqrt{\alpha k_1 k_2 \tau(t - \tau)}\right]\frac{d\tau}{\tau^{3/2}}\right\} \tag{63}$$

$$= \frac{k_1}{k_2-\gamma}\left\{C - \frac{m_o e^{-(\lambda+k_2)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon}\int_0^1 e^{-\frac{r^2}{4D_T tu} - \frac{(z-vtu)^2}{4D_L tu} - (\alpha k_1 - k_2)tu} I_o[2t\sqrt{\alpha k_1 k_2 u(1-u)}]\frac{du}{u^{3/2}}\right\},$$

where C is given by (62). In the event that $\gamma = 0$, corresponding to a rate of release of solute affected only by radioactive decay, (63) becomes

$$Q = \frac{k_1}{k_2}\frac{m_o e^{-\lambda t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon}\int_0^t e^{-\frac{r^2}{4D_T\tau} - \frac{(z - v\tau)^2}{4D_L\tau}}\left\{1 - J\left[k_2(t - \tau), \alpha k_1 \tau\right]\right\}\frac{d\tau}{\tau^{3/2}}, \tag{64}$$

in which (B-8), Appendix B, has been used.

If $\gamma = k_2 \neq 0$, the following expressions are obtained for C and Q:

$$C = \frac{m_o e^{-(\lambda+k_2)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon}\int_0^t e^{-\frac{r^2}{4D_T\tau} - \frac{(z-v\tau)^2}{4D_L\tau} - (\alpha k_1 - k_2)\tau} I_o[2\sqrt{\alpha k_1 k_2 \tau(t-\tau)}]\frac{d\tau}{\tau^{3/2}},$$

$$Q = \frac{k_1 m_o e^{-(\lambda+k_2)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon}\int_0^t d\tau \int_0^\tau e^{-\frac{r^2}{4D_T u} - \frac{(z-vu)^2}{4D_L u} - (\alpha k_1 - k_2)u} I_o[2\sqrt{\alpha k_1 k_2 u(1-u)}]\frac{du}{u^{3/2}}.$$

Note that C and Q are unbounded positively at $\eta = 0$.

3. Time-Dependent Pulse Release

Solute is released at the origin beginning at time zero. The rate of release is m_o mass units per unit time at time zero, and decreases exponentially with time with a decay constant, γ; simultaneously, solute disappears by radioactive decay with a decay constant, λ. The release proceeds from time zero until time T, when it stops; transport of previously released solute continues after time T. At any time, t, the net rate of change of solute mass, M(t), in all space is:

$$\frac{dM(t)}{dt} = m_o e^{-(\gamma + \lambda)t}[U(t) - U(t - T)] - \lambda M(t) \tag{65}$$

with the initial condition

$$M(0) = 0. \tag{66}$$

U(t) is the unit step function, defined by:

$$U(t) = \begin{cases} 0 \text{ for } t < 0 \\ 1 \text{ for } t > 0. \end{cases}$$

We form the Laplace transform of (65), using (66), and solve for $\bar{M}(s)$:

$$\bar{M}(s) = \frac{m_o}{(s + \lambda)(s + \gamma + \lambda)}\left[1 - e^{-T(s + \gamma + \lambda)}\right]. \tag{67}$$

Inserting (67) into (44) gives:

$$\bar{C} = \frac{m_o}{4\pi D_T D_L^{1/2} \varepsilon} \frac{e^{\frac{vz}{2D_L}}}{\eta} \frac{e^{-\eta f^{1/2}\left(s + \lambda + \frac{v^2}{4D_L f} + h\right)^{1/2}}}{s + \gamma + \lambda}\left[1 - e^{-T(s + \gamma + \lambda)}\right]. \tag{68}$$

It is evident that at any time, t, less than or equal to the "shut-off time", T, concentrations in fluid and solid phases are given by the appropriate expressions in Section III.B.2 for a continuous, time-dependent release.

For a time t greater than T, the concentration in a phase is composed of the difference of two terms, one term being the hypothetical concentration that would be computed for a continuous release up to time t and the other term being a correction to account for the cessation of release at time T.

a. Equilibrium Sorption

The fluid concentration at time t, t > T, is

$$C = C_c - C_p,$$

where C_c is given by (59) and C_p is given by:

$$C_p(t) = e^{-(\lambda+\gamma)T} \; C_c(t-T);$$

thus,

$$C_p = \frac{m_o e^{-(\gamma+\lambda)t}}{8\pi D_T D_L^{1/2}\varepsilon} \frac{e^{\frac{vz}{2D_L}}}{\eta} \left\{ e^{-B^{1/2}\eta\left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2}} \operatorname{erfc}\left[\frac{B^{1/2}\eta}{2(t-T)^{1/2}} - \left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2}(t-T)^{1/2}\right] \right.$$

$$\left. + e^{+B^{1/2}\eta\left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2}} \operatorname{erfc}\left[\frac{B^{1/2}\eta}{2(t-T)^{1/2}} + \left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2}(t-T)^{1/2}\right] \right\}. \tag{69}$$

Then the solid concentration is

$$Q = \frac{k_1}{k_2} \; C.$$

At a time t, t>T, (59) and (69) cannot be evaluated at the point r=z=0 (η=0) because η appears in the denominators of these expressions. In this case, C is evaluated by direct integration of a modified version of (57):

$$C = \frac{B^{1/2} m_o e^{-(\gamma+\lambda)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon} \int_{t-T}^{t} e^{-\left(\frac{v^2}{4D_L B} - \gamma\right)\tau} \frac{d\tau}{\tau^{3/2}}$$

$$= \frac{B^{1/2} m_o e^{-(\gamma+\lambda)t}}{4\pi^{3/2} D_T D_L^{1/2} \varepsilon} \left\{ \frac{e^{-\left(\frac{v^2}{4D_L B} - \gamma\right)(t-T)}}{(t-T)^{1/2}} - \frac{e^{-\left(\frac{v^2}{4D_L B} - \gamma\right)t}}{t^{1/2}} \right. \tag{70}$$

$$\left. + \pi^{1/2} \left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2} \operatorname{erf}\left[\left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2} (t-T)^{1/2}\right] - \pi^{1/2} \left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2} \operatorname{erf}\left[\left(\frac{v^2}{4D_L B} - \gamma\right)^{1/2} t^{1/2}\right] \right\} .$$

If $\frac{v^2}{4D_L B} - \gamma < 0$, we use (D-5), Appendix D, in (70) to give:

$$C = \frac{B^{1/2} m_o e^{-(\gamma+\lambda)t}}{4\pi^{3/2} D_T D_L^{1/2} \varepsilon} \left\{ \frac{e^{\left(\gamma - \frac{v^2}{4D_L B}\right)(t-T)}}{(t-T)^{1/2}} - \frac{e^{\left(\gamma - \frac{v^2}{4D_L B}\right)t}}{t^{1/2}} \right.$$

$$+ \frac{\gamma - \frac{v^2}{4D_L B}}{\pi^{1/2}} \left(\sqrt{t} - \sqrt{t-T}\right) + \frac{2}{\pi^{1/2}} \left(\gamma - \frac{v^2}{4D_L B}\right)^{1/2} \sum_{m=0}^{\infty} \frac{e^{-m^2/4}}{m} \tag{71}$$

$$\left. \cdot \left[\sinh m \left(\gamma - \frac{v^2}{4D_L B}\right)^{1/2} \sqrt{t} - \sinh m \left(\gamma - \frac{v^2}{4D_L B}\right)^{1/2} \sqrt{t-T}\right] \right\} .$$

b. Non-Equilibrium Sorption

The fluid concentration at time t, t > T, is

$$C = C_c - C_p,$$

where C_c is given by (62) and C_p is given by:

$$C_p(t) = e^{-(\lambda+\gamma)T}\, C_c(t-T);$$

thus,

$$C_p = \frac{m_o e^{-(\gamma+\lambda)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon} \int_0^{t-T} e^{-\frac{r^2}{4D_T\tau} - \frac{(z-v\tau)^2}{4D_L\tau} + \left(\frac{\alpha k_1}{k_2-\gamma}+1\right)\gamma\tau} J\left[\frac{\alpha k_1 k_2 \tau}{k_2-\gamma},\ (k_2-\gamma)(t-T-\tau)\right] \frac{d\tau}{\tau^{3/2}}\,. \tag{72}$$

The solid concentration at time t, t > T, is

$$Q = Q_c - Q_p,$$

where Q_c is given by (63) and Q_p is given by:

$$Q_p(t) = e^{-(\lambda+\gamma)T}\, Q(t-T);$$

thus,

$$Q_p = \frac{k_1}{k_2-\gamma}\left\{ C_p - \frac{m_o e^{-(\lambda+k_2)t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon} e^{(k_2-\gamma)T} \int_0^{t-T} e^{-\frac{r^2}{4D_T\tau} - \frac{(z-v\tau)^2}{4D_L\tau} - (\alpha k_1 - k_2)\tau} I_o\left[2\sqrt{\alpha k_1 k_2 \tau(t-T-\tau)}\right] \frac{d\tau}{\tau^{3/2}} \right\}. \tag{73}$$

where C_p is given by (74). In the event that $\gamma = 0$, Q_c is given by (64) and Q_p by

$$Q_p = \frac{k_1}{k_2} \frac{m_o e^{-\lambda t}}{8\pi^{3/2} D_T D_L^{1/2} \varepsilon} \int_0^{t-T} e^{-\frac{r^2}{4D_T\tau} - \frac{(z-v\tau)^2}{4D_L\tau}} \left\{1 - J\left[k_2(t-T-\tau), \alpha k_1 \tau\right]\right\} \frac{d\tau}{\tau^{3/2}}\,. \tag{74}$$

IV. Computational Results

Calculations were made for the solutions given in Section III corresponding to each type of solute release and sorptive behavior. Values found in the literature on mass transport through porous media (e.g. Bredehoeft and Pinder, 1973) were used as a guide for the choice of the following parameter values used in the calculations.

$D_L = 7\ m^2/yr$
$D_T = 2\ m^2/yr$
$v = 1\ m/yr$
$\varepsilon = 0.2$
$\lambda = 0$

The source decay constant γ was not included in the computer program, so the calculations correspond to solutions for $\gamma = 0$.

Figures 1 to 3 show the results of contouring the concentration data at a contour level of 10^{-10} moles/liter in the fluid phase. To compare the effects of different types of sorptive behavior, results for the cases of no sorption, equilibrium sorption and non-equilibrium sorption, the latter with varying rate constants, have been superimposed in each figure. Figure 1 shows the level curves for the three types of sorptive behavior ten years after an instantaneous release of one mole of solute at $r = 0$, $z = 0$. Figure 2 shows the resulting level curves after ten years of continuous solute release at $r = 0$, $z = 0$ at the rate of one mole per year, and Figure 3 shows the same at a time nine years after the cessation of a one-year period of solute release at the rate of one mole per year.

It is clear from the figures that the level curves for non-equilibrium sorption for varying rate constants fall between the level curves for the cases of no sorption and equilibrium sorption. In a non-sorbing medium, transport of the solute is not retarded at all relative to motion of the fluid phase. In the presence of non-equilibrium sorption, interphase

transfer occurs at a rate determined by the magnitudes of the forward and backward reaction rate constants, k_1 and k_2, as shown in (21). At the leading edge of a solute front the ratio Q/C, and thus also the retardation calculated from this ratio, increase with increasing magnitudes of the rate constants and with increasing residence time of a parcel of fluid within an elemental volume of the fluid-solid system. In the equilibrium state Q/C and the retardation factor, B, achieve their maximum values given by (29) and (30).

It is difficult to show from the analytical solutions that the non-equilibrium solution tends to the equilibrium solution as the rate constants increase. Consider instead the expression for the mass transfer rate S re-written in terms of Q, obtained by rearranging (21):

$$Q = \frac{k_1}{k_2} C - \frac{1}{k_2} S \cdot$$

Then as k_1 and k_2 increase while the ratio k_1/k_2 is kept constant, $1/k_2$ goes to zero and the expression for Q approaches that of the equilibrium case, (29).

Figures 1-3 show that as the values of the rate constants increase while the ratio k_1/k_2 is kept constant, the non-equilibrium solution tends to the equilibrium solution. The calculations for the equilibrium case were made for $k_1 = 0.01$ and $k_2 = 0.001$ so $k_1/k_2 = 10$. Note that the rate constants k_1 and k_2 do not appear individually in the equilibrium solution, but only in the ratio k_1/k_2. For the non-equilibrium sorption solution, calculations were made for $k_1 = 0.01$, 0.1 and 1.0 , where k_2 was determined by the ratio $k_1/k_2 = 10$.

The influence of the flow field (v = 1m/yr in the direction of the positive z-axis) and of the different longitudinal and lateral dispersion

coefficients can be seen in the location and shape of the curves. Without a flow field, the curves would be circular and centered at r = 0, z = 0. Though not shown on the figures, the 10^{-20} mole/liter level curve for the no sorption case would fall within a rectangle formed by r = 50 m and z = $\pm$ 110 m, whereas a rectangle formed by r = 14 m, z = $\pm$ 16 m would contain the 10^{-20} mole/liter level curve for the equilibrium case. In accordance with the discussion above, all of the 10^{-20} mole/liter level curves for non-equilibrium cases with varying rate constants fall between those for the no sorption and equilibrium cases.

A comparison of Figure 2 to Figure 1 and to Figure 3 shows only a slight difference between sets of level curves. This is unexpected in light of the fact that the concentration in the continuous release case (Figure 2) is the result of a solute release ten times as large as the amount released in the instantaneous release (Figure 1) or one-year continuous release case (Figure 3). Examination of concentration values near the point of release reveals that the concentration is one to two orders of magnitude higher for the continuous release case than for either of the other release types. For the continuous release case, the concentration near the point of release, at r=2, z=0 m, is between 0.2×10^{-4} and 0.7×10^{-4}, in the instantaneous release case, at r=0, z=0, the range is 0.2×10^{-6} to 0.4×10^{-5} and for the one-year continuous release case, 0.1×10^{-6} to 0.5×10^{-5} also at r=0, z=0. Calculations for times larger than ten years would show more appreciable differences between results for different release mechanisms.

V. Extension of Solutions to Finite Sources.

The point source solutions developed in earlier sections can be used to construct solutions resulting from non-point sources. The term non-point source is used to denote one-, two-, or three-dimensional regions which contain a uniform distribution of point sources. The concentration at a point outside the source region is the sum of the contributions from each point source in the source region. This method has been widely used to solve heat conduction problems (e.g., Carslaw and Jaeger, 1959, Chapter 10) in which temperature is analogous to concentration and the quantity of heat released is analogous to the mass of solute released.

In the development of the point source solutions earlier in this work, the point source was assumed to be located at (0,0,0) and the concentration was calculated at a point (x,y,z). If the point source is instead located at (x', y', z'), the variables x, y and z in the point source solutions must be replaced by x-x', y-y', and z-z'. The spatial integrations are then with respect to x', y' and z'. For example, if point sources are distributed along the x-axis from x_1 to x_2, then the integration is with respect to x' with lower and upper limits of integration x_1 and x_2. If the source region is a circular disk of radius R in the x-y plane, then one integration is first performed with respect to x' with limits of integration from $-\sqrt{R^2 - y'^2}$ to $+\sqrt{R^2 - y'^2}$ followed by an integration with respect to y' from -R to R. If a radial coordinate system is used instead of a Cartesian coordinate system and the appropriate change of variable is made in the integrand, then the integration is from 0 to R with respect to r' and from 0 to 2π with respect to θ'. The last example shows how a change of coordinate system may simplify the integration. The integration may also be simplified by aligning the source region with the coordubate axes and by making use of a plane

or axis of symmetry if it exists.

In a Cartestian coordinate system, the integration will be with respect to x', y' and/or z'. One or more of the following integrations will occur in almost every solution:

$$\int_{x_1}^{x_2} e^{-\frac{B(x - x')^2}{4D_T t}} dx' = \left(\frac{\pi D_T t}{B}\right)^{1/2} \left[\operatorname{erf} \frac{B^{1/2}(x - x_1)}{2(D_T t)^{1/2}} - \operatorname{erf} \frac{B^{1/2}(x - x_2)}{2(D_T t)^{1/2}}\right] \tag{75}$$

$$\int_{y_1}^{y_2} e^{-\frac{B(y-y')^2}{4D_T t}} dy' = \left(\frac{\pi D_T t}{B}\right)^{1/2} \left[\operatorname{erf} \frac{B^{1/2}(y-y_1)}{2(D_T t)^{1/2}} - \operatorname{erf} \frac{B^{1/2}(y-y_2)}{2(D_T t)^{1/2}}\right] \tag{76}$$

$$\int_{z_1}^{z_2} e^{-\frac{B(z - z' - vt/B)^2}{4D_L t}} dz' = \left(\frac{\pi D_L t}{B}\right)^{1/2} \left[\operatorname{erf} \frac{B^{1/2}(z - z_1 - vt/B)}{2(D_L t)^{1/2}} - \operatorname{erf} \frac{B^{1/2}(z - z_2 - vt/B)}{2(D_L t)^{1/2}}\right]. \tag{77}$$

Multiple integrations will result in products of error functions. The arguments of the error function will in most cases involve the time variable and therefore the error function will be a part of the integrand in the integration with respect to time. Though the integrands are quite complicated, there are many available software routines which compute error functions and Bessel functions quickly and efficiently.

Approximation of volume sources by point sources is reasonable when the distance between the source region and the point of calculation is large. A spherical source could be approximated by a point source and a cylinder source by a line source. It is difficult, however, to determine the range of validity of such an approximation by means other than direct calculations.

Examples of non-point source solutions illustrating the method and some of the points mentioned above are given in the next section. The case of an instantaneous release with equilibrium sorption is emphasized in the examples because the exponential term involving spatial variables which occurs in this case also occurs in all other cases. Aside from this, the selection of examples is eclectic.

A. Line Source

Consider a line source consisting of a distribution of point sources along a line parallel to the x-axis between x_1 and x_2 and intersecting the y-z plane at the point (y',z'). Then the concentration is given by

$$\underset{\text{line source}}{C(x,y,z;t)} = \int_{x_1}^{x_2} \underset{\text{point source}}{C(x-x', y-y', z-z';t)}\,dx' .$$

Specifically, in the case of instantaneous release with equilibrium sorption

$$C = \frac{M_o' e^{-\lambda t}}{8\pi (D_T D_L)^{1/2} \varepsilon t} e^{-\frac{B(y-y')^2}{4D_T t} - \frac{B(z-z'-vt/B)^2}{4D_L t}} \left[\operatorname{erf} \frac{B^{1/2}(x-x_1)}{2(D_T t)^{1/2}} - \operatorname{erf} \frac{B^{1/2}(x-x_2)}{2(D_T t)^{1/2}} \right] \tag{78}$$

where M_o' is the mass release per unit length, $M_o' = M_o/(x_2-x_1)$. If the center of the line source is located at the origin of the coordinate system then in (78) $y' = 0$, $z' = 0$, $x_1 = -L/2$ and $x_2 = L/2$, where L is the length of the line source. If the line source is infinite then

$$C = \frac{M_o' e^{-\lambda t}}{4\pi (D_T D_L)^{1/2} \varepsilon t} e^{-\frac{B(y-y')^2}{4D_T t} - \frac{B(z-z'-vt/B)^2}{4D_L t}} \tag{79}$$

The solution for a line source along the z-axis is slightly different in form. For the instantaneous release, equilibrium case

$$C = \frac{M_o' e^{-\lambda t}}{8\pi D_T \varepsilon t} e^{-\frac{B(x^2+y^2)}{4D_T t}} \left[\operatorname{erf} \frac{B^{1/2}(z-z_1-vt/B)}{2(D_L t)^{1/2}} - \operatorname{erf} \frac{B^{1/2}(z-z_2-vt/B)}{2(D_L t)^{1/2}} \right] \tag{80}$$

where the line source extends from $z = z_1$ to $z = Z_2$;

B. Disk Source

Next consider a disk source of radius R in the x-y plane centered at $z = z'$. After changing to a radial coordinate system

$$\underset{\text{disk source}}{C(r,z,\Theta;t)} = \int_0^R r'dr' \int_0^{2\pi} d\Theta' \; \underset{\text{point source}}{C(r-r',z-z',\Theta-\Theta';t)}$$

In the case of instantaneous release with equilibrium sorption

$$C = \frac{B^{1/2} M_o'' e^{-\lambda t}}{8D_T D_L^{1/2} \varepsilon (\pi t)^{3/2}} e^{-\frac{B(z-z'-vt/B)^2}{4D_L t}} e^{-\frac{Br^2}{4D_T t}}$$

$$\int_0^R r' e^{-\frac{Br'^2}{4D_T t}} dr' \int_0^{2\pi} e^{-\frac{Brr'}{2D_T t}\cos(\theta'-\theta)} d\theta' \tag{81}$$

where M_o'' is the mass instantaneously released per unit area, $M_o'' = M_o/(2\pi R^2)$. As long as the integration with respect to Θ' is over a period of 2π, the limits of integration can be replaced by Θ and $\Theta+2\pi$. After a change of variable, $\Theta'' = \Theta' - \Theta$, the solution becomes

$$C = \frac{B^{1/2} M_o'' e^{-\lambda t}}{4D_T (\pi D_L)^{1/2} \varepsilon t^{3/2}} e^{-\frac{B(z-z'-vt/B)^2}{4D_L t}} e^{-\frac{Br^2}{4D_T t}} \int_0^R e^{-\frac{Br'^2}{4D_T t}} I_o\left(\frac{Brr'}{2D_T t}\right) r'dr' \tag{82}$$

where the integral with respect to Θ'' is given by Watson (1966, p.79, no.3.7 (9)). This form shows the radial symmetry of the solution, a result not unexpected from the geometry of the problem. Using the definition of the

function J(x,y) in (B-7), Appendix B, the final solution can be written

$$C = \frac{M_o'' e^{-\lambda t}}{2(BD_L \pi t)^{1/2} \varepsilon} e^{-\frac{B(z-z'-vt/B)^2}{4D_L t}} \left[1-J\left(\frac{BR^2}{4D_T t}, \frac{Br^2}{4D_T t}\right)\right] . \tag{83}$$

C. Spherical Source

The solution for a spherical source region with radius R, centered at the origin of coordinates, is most easily developed by superposition of disk sources in the x-y plane, centered on the z-axis at z=z' and with radii R' given by $R'^2 = R^2 - z'^2$. Thus, in cylindrical coordinates,

$$\underset{\text{spherical source}}{C(r,z;t)} = \int_{-R}^{R} dz' \int_0^{\sqrt{R^2-z'^2}} r'dr' \int_0^{2\pi} d\theta' \underset{\text{point source}}{C(r-r',z-z',\theta-\theta';t)} .$$

For the case of instantaneous release with equilibrium sorption, superposition of disk sources gives:

$$C = \frac{M_o''' e^{-\lambda t}}{2(\pi BD_L t)^{1/2} \varepsilon} \int_{-R}^{R} e^{-\frac{B(z-z'-vt/B)^2}{4D_L t}} \left\{1-J\left[\frac{B(R^2-z'^2)}{}, \frac{Br^2}{4D_T t}\right]\right\} dz'$$

$$= \frac{M_o''' e^{-\lambda t}}{2B\varepsilon} \left\{ \mathrm{erf}\left[\frac{B^{1/2}(z+R-vt/B)}{2(D_L t)^{1/2}}\right] - \mathrm{erf}\left[\frac{B^{1/2}(z-R-vt/B}{2(D_L t)^{1/2}}\right] \right. \tag{84}$$

$$\left. -\left(\frac{B}{\pi D_L t}\right)^{1/2} \int_{-R}^{R} e^{-\frac{B(z-z'-vt/B)^2}{4D_L t}} J\left[\frac{B(R^2-z'^2)}{4D_T t}, \frac{Br^2}{4D_T t}\right] dz' \right\},$$

where M_o''' is the mass instantaneously released per unit volume, $M_o''' = M_o/(4\pi R^3/3)$.

D. Cylindrical Sources

For a cylindrical source of length L and radius R, centered at the origin

of coordinates with axis along the z-axis,

$$\underset{\substack{\text{cylindrical}\\ \text{source}}}{C(r,\theta,z;t)} = \int_{-L/2}^{L/2} dz' \int_0^R r'dr' \int_0^{2\pi} d\theta' \cdot \underset{\substack{\text{point}\\ \text{source}}}{C(r-r',\theta-\theta',\ z-z';t)} \quad .$$

The necessary integration with respect to z' is that used in the line source example and the integrations with respect to θ' and r' are those used in the disk source example. The final expression for the concentration for the case of instantaneous release with equilibrium sorption involves the product of those integrations

$$C = \frac{M_o''' e^{-\lambda t}}{2B\varepsilon}\left[1-J\left(\frac{BR^2}{4D_T t}, \frac{Br^2}{4D_T t}\right)\right]\left[\operatorname{erf}\frac{B^{1/2}(z+L/2-vt/B)}{2(D_L t)^{1/2}} - \operatorname{erf}\frac{B^{1/2}(z-L/2-vt/B)}{2(D_L t)^{1/2}}\right] \tag{85}$$

where M_o''' is the mass instantaneously released per unit volume, $M_o''' = M_o/(\pi R^2 L)$.

For a further example, we state the solutions for C and Q in the case of a continuous, time dependent release with non-equilibrium sorption, using the same geometry as that just considered:

$$C = \frac{m_o''' e^{-(\lambda+\gamma)t}}{2\varepsilon}\int_0^t \left[1-J\left(\frac{R^2}{4D_T\tau}, \frac{r^2}{4D_T\tau}\right)\right]\left[\operatorname{erf}\left(\frac{z+L/2-v\tau}{2\sqrt{D_L\tau}}\right)-\operatorname{erf}\left(\frac{z-L/2-v\tau}{2\sqrt{D_L\tau}}\right)\right]$$

$$\cdot e^{\left(\frac{\alpha k_1}{k_2-\gamma}+1\right)\gamma\tau} \quad J\left[\frac{\alpha k_1 k_2 \tau}{k_2-\gamma}, (k_2-\gamma)(t-\tau)\right] d\tau, \tag{86}$$

$$Q = \frac{k_1}{k_2-\gamma}\left\{C - \frac{m_o'''e^{-(\lambda+k_2)t}}{2\varepsilon}\int_0^t \left[1-J\left(\frac{R^2}{4D_T\tau},\frac{r^2}{4D_T\tau}\right)\right]\left[\mathrm{erf}\left(\frac{z+L/2-v\tau}{2\sqrt{D_L\tau}}\right)-\mathrm{erf}\left(\frac{z-L/2-v\tau}{2\sqrt{D_L\tau}}\right)\right]\right.$$

$$\left.\cdot e^{-(\alpha k_1-k_2)\tau} I_o\left[2\sqrt{\alpha k_1 k_2\tau(t-\tau)}\right]d\tau\right\} \tag{87}$$

where m_o''' is the rate of release of mass per unit volume, $m_o''' = m_o/(\pi R^2 L)$.

Finally, consider a cylindrical source region having length L and radius R, centered at the origin of coordinates, with its axis coincident with the y-axis. Here,

$$\underset{\substack{\text{cylindrical}\\\text{source}}}{C(x,y,z;t)} = \int_{-L/2}^{L/2} dy' \int_{-R}^{R} dz' \int_{-\sqrt{R^2-z'^2}}^{\sqrt{R^2-z'^2}} dx' \; \underset{\text{point source}}{C(x-x',y-y',z-z';t)}\cdot$$

For the case of an instantaneous release with equilibrium sorption, it follows that

$$C = \frac{M_o'''e^{-\lambda t}}{8\varepsilon(B\pi D_L t)^{1/2}}\left\{\mathrm{erf}\left[\frac{B^{1/2}(y+L/2)}{2\sqrt{D_T t}}\right]-\mathrm{erf}\left[\frac{B^{1/2}(y-L/2)}{2\sqrt{D_T t}}\right]\right\}$$

$$\int_{-R}^{R} e^{-\frac{B(z-z'-vt/B)^2}{4D_L t}}\left\{\mathrm{erf}\left[\frac{B^{1/2}\left(x+\sqrt{R^2-z'^2}\right)}{2\sqrt{D_T t}}\right]-\mathrm{erf}\left[\frac{B^{1/2}\left(x-\sqrt{R^2-z'^2}\right)}{2\sqrt{D_T t}}\right]\right\}dz'. \tag{88}$$

VI. Discussion

We have derived analytical solutions to the transport equation under the assumption that the number of sites, on surfaces of the solid phase, available for either ion exchange or the Langmuir type of sorption is very large relative to the number of sites occupied by sorbate ions or molecules. This assumption leads to a kinetic law for the rate of mass transfer between fluid and solid phases which is linear in concentrations of sorbate in both phases. Thus, our analysis is strictly applicable only to sorption upon a solid phase in which the concentration of sorbate is small relative to the saturation concentration or, equivalently, to sorptive systems characterized by a linear isotherm for sorption.

Our point-source solutions will serve as standards for checking of, and comparison with, numerical models of non-linear, sorptive systems now under development. Additionally, the point- and line-source solutions are useful approximations, in the far field, to solutions of linear transport problems involving source functions for which a total rate of release of sorbate can be specified. Finally, the point-source solutions are directly applicable to the development of analytical solutions of problems involving source functions occupying finite regions of the space in which transport takes place. This application is possible because the transport equation and, in the cases of non-equilibrium sorption, the associated mass transfer equation are linear equations, and the principle of superposition can be used to construct the analytical expressions for finite sources.

It is a characteristic of point-source solutions that they may become infinite at the point where mass is introduced into the transport system. In our derivations, this point is the origin of coordinates ($r = 0$, $z = 0$). In the following paragraphs we discusss the behavior of our point-source

solutions at this point for each type of mass release.

Instantaneous release: In this case, the expression (47) for equilibrium sorption is finite everywhere when $t > 0$, and as $t \to 0$ (47) tends to zero at all points except the origin where it becomes infinite, as expected. For non-equilibrium sorption, equation (50) for C exhibits identical behavior; however, the integrand in this expression appears to become infinite for $r = z = 0$, at the lower limit of integration when $t > 0$. This apparent singularity can be removed by a change of the variable of integration from τ to τ^2, and by using the limiting form of the modified Bessel function for vanishingly small values of its argument. On the other hand, the integrand in the expression for Q in (51) has a non-removable singularity at the lower limit of integration ($\tau = 0$) when $r = z = 0$ and $t > 0$. This behavior appears to be a consequence of our assumption that the sorptive capacity of the solid phase is unbounded.

Continuous release: As expected, all solutions become infinite at $r = z = 0$ when $t > 0$.

Pulse release: Here the solutions for equilibrium sorption clearly are bounded at the point $r = z = 0$ when $t > T$. For non-equilibrium sorption, the integrands in the expression for C formed by subtracting (72) from (62) appear to become infinite at their lower limits when $r = z = 0$ and $t > T$, contrary to expectation. However, it can be shown (by two partial integrations) that this apparent singularity is removable. On the other hand, the integrands in the complete expression for Q have non-removable singularities at their lower limits when $r = z = 0$ and $t > T$, again apparently because of the assumption of infinite sorptive capacity in the solid phase.

The singularities in Ω in the cases of non-equilibrium sorption following an instantaneous release and cessation of a pulse release are not significant limitations to application of the point-source solutions. First, in the use of these solutions as approximations of solute concentration histories in the far field there will be little, if any, interest in the point $r = z = 0$. Secondly, when the point-source solutions are integrated in space to form solutions for spatially finite source regions all singularities, both real and apparent, disappear.

It should be noted that solutions for finite source regions, derived from our point-source solutions, describe transport away from source regions which have physical and chemical properties identical to those of the surrounding medium, except that mass is introduced within the source regions. In particular, the source regions do not perturb the fluid flow field. Thus, for example, these solutions do not describe transport of a solute which is introduced at the surface of a region of space which is impervious to fluid flow.

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LIST OF SYMBOLS

Following each symbol is a brief definition and dimensions. Dimensions are mass (M), length (L), and time (t).

A	elemental area in porous medium $[L^2]$
B	retardation factor [1]
C	concentration of solute in fluid phase $[ML^{-3}]$
$\bar{C}$	Laplace transform (image) of C $[ML^3]$
C_c	concentration, C, from continuous release for $t < T$ $[ML^{-3}]$
C_p	correction to concentration, C, for $t > T$ $[ML^{-3}]$
C_T	total concentration in fluid phase of exchanging solutes $[ML^{-3}]$
$\underline{D}$	rank 2 tensor coefficient of hydrodynamic dispersion $[L^2t^{-1}]$
D_L	coefficient of longitudinal dispersion $[L^2t^{-1}]$
D_T	coefficient of transverse dispersion $[L^2t^{-1}]$
f	constant defined below eqn. (41) [1]
F	ratio of Ω to C at equilibrium [1]
g	function of s defined below eqn. (A-6) [1]
h	function of s defined below eqn. (41) $[t^{-1}]$
$I_n(x)$	modified Bessel function of the first kind of order n with argument x [1]
j_f	solute flux per unit area of fluid phase relative to motion of local center of mass $[ML^{-2}t^{-1}]$
J	solute flux per unit area of porous medium $[ML^{-2}t^{-1}]$
J_f	solute flux per unit area of fluid phase $[ML^{-2}t^{-1}]$
$J(x,y)$	function defined in Appendix B [1]
k_1	forward rate constant for linear sorption reaction $[t^{-1}]$
k_2	backward rate constant for linear sorption reaction $[t^{-1}]$
k_1'	forward rate constant for ion exchange reaction $[M^{-1}L^3t^{-1}]$
k_2'	backward rate constant for ion exchange reaction $[M^{-1}L^3t^{-1}]$
k_1''	forward rate constant for Langmuir sorption reaction $[M^{-1}L^3t^{-1}]$
k_2''	backward rate constant for Langmuir sorption reaction $[t^{-1}]$
L	Laplace transformation operator [t]
L^{-1}	Laplace inversion operator $[t^{-1}]$
m_o	rate of release of solute from point source at zero time $[Mt^{-1}]$

m_o'''	rate of release of solute from differential element of volume source at zero time $[ML^{-3}t^{-1}]$
M	total mass of solute in all space at time t [M]
$\bar{M}$	Laplace transform (image) of M [Mt]
M_f	mass of solute in fluid phase within volume V [M]
M_s	mass of solute in solid phase within volume V [M]
M_o	mass of solute released from point source [M]
M_o'	mass of solute released from differential element of line source $[ML^{-1}]$
M_o''	mass of solute released from differential element of plane source $[ML^{-2}]$
M_o'''	mass of solute released from differential element of volume source $[ML^{-3}]$
p	function of s defined by eqn. (A-5) $[t^{-1}]$
Q	concentration of solute in solid phase $[ML^{-3}]$
$\bar{Q}$	Laplace transform (image) of Q $[ML^{-3}t]$
Q_{sat}	sorptive capacity of solid phase $[ML^{-3}]$
s	Laplace transform variable $[t^{-1}]$
S	rate of transfer of solute from fluid phase to solid phase $[ML^{-3}t^{-1}]$
T	time of cessation of release of solute [t]
U	unit step function defined below eqn. (66) [1]
v	average velocity of fluid $[Lt^{-1}]$
v_s	average velocity of solute $[Lt^{-1}]$
V	elemental volume of porous medium $[L^3]$
α	ratio of solid volume to fluid volume [1]
β_i	constants used in Appendix B, i = 1,2,3,4 $[t^{-1}]$
γ	time constant for decay of release rate $[t^{-1}]$
ε	porosity [1]
η	reduced coordinate defined below eqn. (44) $[t^{1/2}]$
λ	time constant for radioactive decay of solute $[t^{-1}]$

FIGURES

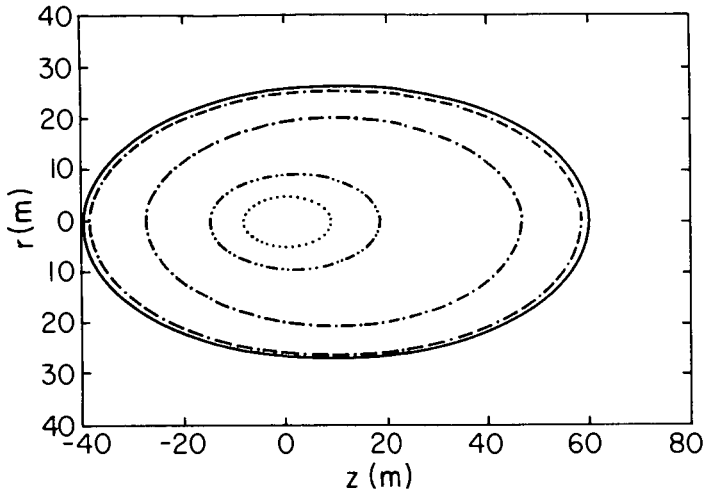

FIGURE 1

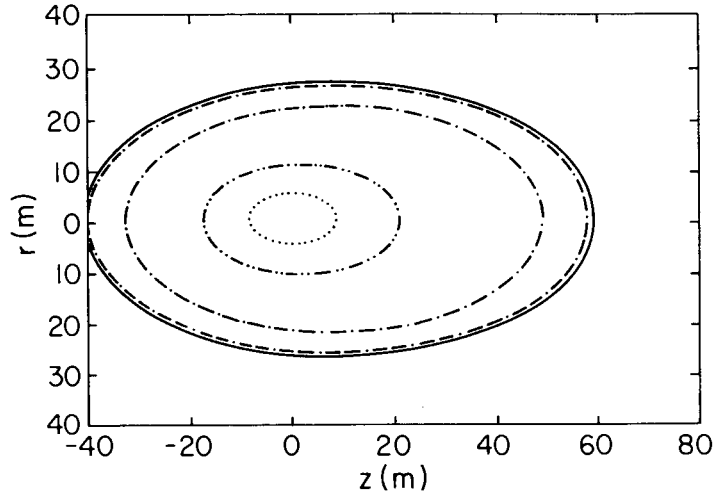

FIGURE 2

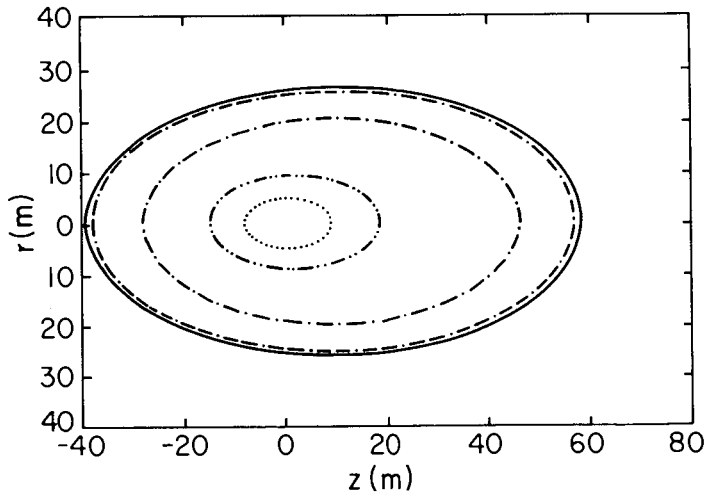

FIGURE 3

Legend

No sorption

Equilibrium sorption

$k_1 = 0.01$, $k_2 = 0.001$

Non - equilibrium sorption

$k_1 = 0.01$, $k_2 = 0.001$

$k_1 = 0.1$, $k_2 = 0.01$

$k_1 = 1$, $k_2 = 0.1$

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Appendix A. Derivation of Equation (44).

We make the following changes of variables:

$$\bar{u} = \bar{C}e^{-\frac{vz}{2D_L}}, \quad x_1 = \left(\frac{D_L}{D_T}\right)^{1/2} x, \quad y_1 = \left(\frac{D_L}{D_T}\right)^{1/2} y.$$

Then (41) becomes

$$\frac{\partial^2 \bar{u}}{\partial x_1^2} + \frac{\partial^2 \bar{u}}{\partial y_1^2} + \frac{\partial^2 \bar{u}}{\partial z^2} - \frac{f}{D_L}\left(s + \lambda + \frac{v^2}{4D_L f} + h\right)\bar{u} = 0, \tag{A-1}$$

and the boundary condition (38) becomes

$$\lim_{\rho_1 \to \infty} \bar{u} = 0, \text{ where } \rho_1^2 = x_1^2 + y_1^2 + z^2. \tag{A-2}$$

(A-1) is spherically symmetric in the coordinate system with axes x_1, y_1, z; therefore (A-1) can be recast in the form:

$$\frac{d^2\bar{u}}{d\rho_1^2} + \frac{2}{\rho_1}\frac{d\bar{u}}{d\rho_1} - \frac{f}{D_L}\left(s + \lambda + \frac{v^2}{4D_L f} + h\right)\bar{u} = 0, \tag{A-3}$$

where ρ_1 is the radial coordinate defined in (A-2). The general solution of (A-3) consistent with (A-2) is

$$\bar{u} = \frac{A}{\rho_1} e^{-\rho_1\left(\frac{f}{D_L}\right)^{1/2}\left(s + \lambda + \frac{v^2}{4D_L f} + h\right)^{1/2}},$$

where A is a constant of integration. Then $\bar{C}$ is given by

$$\bar{C} = A\,\frac{e^{\frac{vz}{2D_L}}}{D_L^{1/2}\eta} \cdot e^{-(fp)^{1/2}\eta}, \tag{A-4}$$

where η was defined following (44), and

$$p = s + \lambda + \frac{v^2}{4D_L f} + h \ . \tag{A-5}$$

We next evaluate A using the mass balance expressed by (43), and noting that $\bar{Q}$ can be related to $\bar{C}$ by:

$$\bar{Q} = g \cdot \bar{C}, \tag{A-6}$$

where g is a function of the transformation parameter s and is given by:

$$g(s) = \frac{k_1}{s + \lambda + k_2} \quad \text{for the case of non-equilibrium sorption;}$$

$$g(s) = \frac{k_1}{k_2} \quad \text{for the case of equilibrium sorption; and}$$

$$g(s) = 0 \quad \text{for the case of no sorption.}$$

We substitute (A-4) and (A-6) into (43) and use the volume element $dV = 2\pi r dr dz$; the result is

$$\frac{2\pi\varepsilon}{D_L^{1/2}} (1 + \alpha g) A \int_{-\infty}^{\infty} dz \int_0^{\infty} r dr \cdot \frac{e^{\frac{vz}{2D_L} - (fp)^{1/2} \left(\frac{r^2}{D_T} + \frac{z^2}{D_L}\right)^{1/2}}}{\left(\frac{r^2}{D_T} + \frac{z^2}{D_L}\right)^{1/2}} = \bar{M}(s). \tag{A-7}$$

To integrate (A-7), let $\eta = \left(\frac{r^2}{D_T} + \frac{z^2}{D_L}\right)^{1/2}$; then (A-7) becomes

$$\frac{2\pi\varepsilon D_T}{D_L^{1/2}} (1 + \alpha g) A \int_{-\infty}^{\infty} e^{\frac{vz}{2D_L}} dz \int_{\frac{|z|}{D_L^{1/2}}}^{\infty} e^{-(fp)^{1/2}\eta} d\eta = \bar{M}(s) \tag{A-8}$$

The result of the integration with regard to η in (A-8) is broken into a sum of two integrals with regard to z; i.e.,

$$\bar{M}(s) = \frac{2\pi\varepsilon D_T}{(fpD_L)^{1/2}}(1 + \alpha g)A \int_{-\infty}^{\infty} e^{\frac{vz}{2D_L}} \cdot e^{-\left(\frac{fp}{D_L}\right)^{1/2}|z|} dz$$

$$= \frac{2\pi\varepsilon D_T}{(fpD_L)^{1/2}}(1 + \alpha g)A \left[\int_{-\infty}^{0} e^{+\left(f^{1/2}p^{1/2} + \frac{v}{2D_L^{1/2}}\right)\frac{z}{D_L^{1/2}}} dz\right.$$

$$\left. + \int_{0}^{\infty} e^{-\left(f^{1/2}p^{1/2} - \frac{v}{2D_L^{1/2}}\right)\frac{z}{D_L^{1/2}}} dz\right] .$$

Evaluating the integrals and solving for A gives the result:

$$A = \frac{(fp - v^2/4D_L)\bar{M}(s)}{4\pi\varepsilon D_T(1 + \alpha g)} . \qquad \text{(A-9)}$$

Inserting appropriate values of h(s) into (A-5) and of g(s) into (A-9) and substituting (A-5) for p in (A-9) and (A-4) gives (44).

Appendix B. Inversion of some Image-Space Solutions

In this appendix we establish two results which are useful in Section III.B. In the following discussion we use the symbol L to signify the operation of Laplace transforming an original function, F(t), into an image function, $\bar{F}(s)$, and the symbol L^{-1} to signify the inversion of an image function back to an original function; thus,

$$\bar{F}(s) \equiv L\{F(t)\} = \int_0^\infty e^{-st} F(t)dt,$$

$$F(t) \equiv L^{-1}\{F(s)\} = (2\pi i)^{-1} \int_{x-i\infty}^{x+i\infty} e^{ts}\, \bar{F}(s)ds.$$

We begin by considering inversion of an image function, $\bar{F}_1(s)$, given by

$$\bar{F}_1(s) = L\left|F_1(t)\right| = \frac{1}{s}\, e^{-\eta\left(s + \beta_1 - \frac{\beta_2}{s + \beta_3}\right)^{1/2}} \tag{B-1}$$

where β_1, β_2 and β_3 are constants, and $\beta_3 \neq 0$. We define a function $\bar{F}_2(s)$ by

$$\bar{F}_2(s) = e^{-\eta(s + \beta_1)^{1/2}}$$

It is clear that $\bar{F}_1(s)$ has the form

$$\bar{F}_1(s) = \frac{\bar{F}_2\left(s - \frac{\beta_2}{s + \beta_3}\right)}{s}.$$

Then it can be shown (see Appendix C) that the original function, $F_1(t)$, corresponding to the image function, $\bar{F}_1(s)$, is given by

$$F_1(t) = L^{-1}\{\bar{F}_1(s)\} = \int_0^t F_2(\tau) \cdot F_3(t-\tau, \tau)\, d\tau, \tag{B-2}$$

where

$$F_2(t) = L^{-1}\left\{\bar{F}_2(s)\right\} \text{ and } F_3(t,\tau) = L^{-1}\left\{\frac{e^{\frac{\beta_2\tau}{s+\beta_3}}}{s}\right\}.$$

From tables (Erdelyi, 1954, p. 245, no. 5.6(1)), we find:

$$\begin{aligned} F_2(t) &= L^{-1}\left\{e^{-\eta(s+\beta_1)^{1/2}}\right\} \\ &= e^{-\beta_1 t} L^{-1}\left\{e^{-\eta s^{1/2}}\right\} \\ &= \frac{\eta}{2(\pi t^3)^{1/2}}\, e^{-\beta_1 t - \frac{\eta^2}{4t}}. \end{aligned} \tag{B-3}$$

To find $F_3(t,\tau)$, we write:

$$F_3(t,\tau) = L^{-1}\left\{\frac{e^{\frac{\beta_2\tau}{s+\beta_3}}}{s}\right\} = L^{-1}\left\{\left(1+\frac{\beta_3}{s}\right)\frac{e^{\frac{\beta_2\tau}{s+\beta_3}}}{s+\beta_3}\right\}. \tag{B-4}$$

We have from tables (Erdelyi, 1954, p. 245, no. 5.5(35)):

$$L^{-1}\left\{\frac{e^{\frac{\beta_2\tau}{s+\beta_3}}}{s+\beta_3}\right\} = e^{-\beta_3 t}\, L^{-1}\left\{\frac{e^{\frac{\beta_2\tau}{s}}}{s}\right\} = e^{-\beta_3 t}\, I_o\left(2\sqrt{\beta_2\tau t}\right), \tag{B-5}$$

where $I_n(x)$ is the modified Bessel function of the first kind and order n having argument x. Then, using the result (B-5) and the convolution property, (B-4) becomes:

$$F_3(t,\tau) = e^{-\beta_3 t} I_o(2\sqrt{\beta_2 \tau t}) + \beta_3 \int_0^t e^{-\beta_3 \xi} I_o(2\sqrt{\beta_2 \tau \xi})\, d\xi . \qquad \text{(B-6)}$$

The integral in (B-6) is related to the function J(x,y) which was introduced by Anzelius (1926) and has been discussed by Goldstein (1953a), Masters (1955), and Luke (1962). The function J(x,y) is defined by:

$$J(x,y) = 1 - e^{-y} \int_0^x e^{-\sigma} I_o(2\sqrt{y\,\sigma})\, d\sigma \qquad \text{(B-7)}$$

and it has the property:

$$1 - J(x,y) = J(y,x) - e^{-x-y} I_o(2\sqrt{xy}) . \qquad \text{(B-8)}$$

If, in (B-7) and (B-8), the following substitutions are made:

$$x = \beta_3 t, \quad y = \frac{\beta_2 \tau}{\beta_3}, \quad \sigma = \beta_3 \xi,$$

then it is easily shown that (B-6) is equivalent to

$$F_3(t,\tau) = e^{\frac{\beta_2 \tau}{\beta_3}} J\left(\frac{\beta_2 \tau}{\beta_3}, \beta_3 t\right) . \qquad \text{(B-9)}$$

We now substitute (B-3) and (B-9) into (B-2) to obtain

$$F_1(t) = \frac{\eta}{2\pi^{1/2}} \int_0^t e^{-\frac{\eta^2}{4\tau} - \left(\beta_1 - \frac{\beta_2}{\beta_3}\right)\tau} \cdot J\left[\frac{\beta_2 \tau}{\beta_3}, \beta_3 (t-\tau)\right] \frac{d\tau}{\tau^{3/2}} ; \qquad \text{(B-10)}$$

the image, $\bar{F}_1(s)$, of $F_1(t)$ is given by (B-1).

In the special case when $\beta_3 = 0$, (B-6) becomes simply

$$F_3(t,\tau) = I_o(2\sqrt{\beta_2 \tau t}),$$

and (B-10) becomes

$$F_1(t)\big|_{\beta_3=0} = \frac{\eta}{2\pi^{1/2}} \int_0^t e^{-\frac{\eta^2}{4\tau} - \beta_1 \tau} I_o\left[2\sqrt{\beta_2 \tau (t-\tau)}\right] \frac{d\tau}{\tau^{3/2}} \quad . \tag{B-11}$$

Next, we consider inversion of the image function,

$$\bar{F}_4(s) = e^{-\eta\left(s + \beta_1 - \frac{\beta_2}{s + \beta_3}\right)^{1/2}} \quad .$$

We note that

$$\bar{F}_4(s) = s \cdot \bar{F}_1(s) = s \cdot L\{F_1(t)\} \quad . \tag{B-12}$$

Using the rule for transforming the derivative,

$$L\left\{\frac{\partial}{\partial t} F_1(t)\right\} = s \cdot L\left\{F_1(t)\right\} - F_1(0).$$

From (B-10), $F_1(0)$ is zero, so (B-11) becomes

$$\bar{F}_4(s) = L\left\{\frac{\partial}{\partial t} F_1(t)\right\},$$

$$L^{-1}\left\{\bar{F}_4(s)\right\} = \frac{\partial}{\partial t} F_1(t).$$

We perform the indicated differentiation on (B-10) using Leibniz' rule (Boas, 1966, p. 162) and the following properties of the function J(x,y) (Goldstein, 1953a):

$$J(x,0) = e^{-x},$$

$$\frac{\partial}{\partial y} J(x,y) = e^{-x-y} \left(\frac{x}{y}\right)^{1/2} I_1(2\sqrt{xy}).$$

The result is:

$$L^{-1}\left\{e^{-\eta\left(s + \beta_1 - \frac{\beta_2}{s + \beta_3}\right)^{1/2}}\right\} = \frac{\eta}{2(\pi t^3)^{1/2}} e^{-\frac{\eta^2}{4t} - \beta_1 t} + \tag{B-13}$$

$$+ \frac{\eta}{2}\left(\frac{\beta_2}{\pi}\right)^{1/2} e^{-\beta_3 t} \int_0^t e^{-\frac{\eta^2}{4\tau} - (\beta_1 - \beta_3)\tau} I_1\left[2\sqrt{\beta_2 \tau(t-\tau)}\right] \frac{d\tau}{\tau(t-\tau)^{1/2}} .$$

Appendix C: A useful Rule for Inversion of certain Image Functions.

The problem can be stated by the following.

Given: an image function, $\bar{F}_1(s)$, which is the Laplace transform of an original function, $F_1(t)$; and

given: functions $g_1(s)$ and $g_2(s)$ such that the function $\bar{F}_2(s)$, where

$$\bar{F}_2(s) = \frac{e^{-\tau g_1(s)}}{g_2(s)}$$

is the Laplace transform of an original function $F_2(t,\tau)$; then

find: the original function, $F_3(t)$, whose Laplace transform, $\bar{F}_3(s)$, is given by

$$\bar{F}_3(s) = \frac{\bar{F}_1[s + g_1(s)]}{g_2(s)} .$$

From the definitions of $\bar{F}_1(s)$ and $\bar{F}_2(s)$ as Laplace transforms, we have

$$\bar{F}_1(s) = \int_0^\infty e^{-s\tau} F_1(\tau)\,d\tau \tag{C-1}$$

and

$$\bar{F}_2(s) = \frac{e^{-\tau g_1(s)}}{g_2(s)} = \int_0^\infty e^{-s\sigma} F_2(\sigma,\tau)\,d\sigma. \tag{C-2}$$

(C-1) can be regarded also as the definition of the functional form of $\bar{F}_1(s)$; accordingly we may write

$$\bar{F}_1[s + g_1(s)] = \int_0^\infty e^{-[s + g_1(s)]\tau} F_1(\tau)\,d\tau,$$

and then

$$\bar{F}_3(s) = \frac{\bar{F}_1[s + g_1(s)]}{g_2(s)} = \int_0^\infty \frac{1}{g_2(s)} e^{-[s + g_1(s)]\tau} F_1(\tau)d\tau \ . \qquad \text{(C-3)}$$

(C-3) can be rearranged to read:

$$\bar{F}_3(s) = \int_0^\infty \left[\frac{e^{-\tau g_1(s)}}{g_2(s)}\right] e^{-s\tau} F_1(\tau)d\tau \ . \qquad \text{(C-4)}$$

The quantity enclosed in brackets in (C-4) is a Laplace transform defined by (C-2); substitution of (C-2) into (C-4) gives:

$$\bar{F}_3(s) = \int_0^\infty d\tau \ . \ e^{-s\tau} F_1(\tau) \int_0^\infty d\sigma \ . \ e^{-s\sigma} F_2(\sigma, \tau) \ . \qquad \text{(C-5)}$$

Now let a new variable of integration, t, be given by

$$t = \tau + \sigma \quad \text{or} \quad \sigma = t - \tau$$

and substitute $t-\tau$ for σ (holding τ constant) in the integral with regard to σ in (C-5). Then (C-5) becomes

$$\bar{F}_3(s) = \int_0^\infty d\tau \ . \ F_1(\tau) \int_\tau^\infty dt \ . \ e^{-st} F_2(t-\tau, \tau) \ . \qquad \text{(C-6)}$$

In (C-6), the integration with regard to t ranges from $t = \tau$ to $t = \infty$ in strips of width $d\tau$, and the integration with regard to τ sums these strips from $\tau = 0$ $\tau = \infty$. If we visualize the $t-\tau$ plane with the line $\tau = 0$ as the abscissa and the line $t = 0$ as the ordinate, we see that the integrations in (C-6) cover a wedge-shaped area in the first quadrant of the plane, this area lying between the abscissa $t = 0$ and the line $\tau = t$. We now adopt a procedure used by Boas

(1966, pp. 608-609) and reverse the order of integration. We now integrate first with regard to τ so that this integration ranges from $\tau = 0$ to $\tau = t$ in strips of width dt, and the second integration with regard to t sums these strips from $t = 0$ to $t = \infty$; this procedure covers the same area in the t-τ plane that was covered by the integrations in (C-6). The new double integral is:

$$\bar{F}_3(s) = \int_0^\infty dt \cdot e^{-st}\left[\int_0^t d\tau \cdot F_1(\tau) \cdot F_2(t-\tau,\tau)\right]. \tag{C-7}$$

We recognize (C-7) as the Laplace transform of the quantity enclosed in brackets. (Compare (C-1).) Therefore,

$$F_3(t) = L^{-1}\left\{\frac{\bar{F}_1[s + g_1(s)]}{g_2(s)}\right\} = \int_0^t F_1(\tau)F_2(t-\tau,\tau)d\tau$$

where

$$F_1(t) = L^{-1}\{\bar{F}_1(s)\} \quad \text{and} \quad F_2(t,\tau) = L^{-1}\left\{\frac{e^{-\tau g_1(s)}}{g_2(s)}\right\}.$$

As an example of application of the method, we shall derive a known, general inversion formula. Let $\bar{F}_1(s)$ be the transformed image of an original function, $F_1(t)$, and let $g_1(s) = s^{1/2}$ and $g_2(s) = s^{1/2}$. Then by our procedure,

$$F_2(t,\tau) = L^{-1}\left\{\frac{e^{-\tau s^{1/2}}}{s^{1/2}}\right\} = \pi^{-1/2}t^{-1/2}e^{-\frac{\tau^2}{4t}}$$

where we have used a result given by Erdelyi (1954, p. 246, no. 5.6(6)) for the inversion. It must follow that

$$L^{-1}\left\{\frac{\bar{F}_1(s + s^{1/2})}{s^{1/2}}\right\} = \pi^{-1/2} \int_0^t F_1(\tau)(t-\tau)^{-1/2} e^{-\frac{\tau^2}{4(t-\tau)}} d\tau \ . \tag{C-8}$$

The result (C-8) is also given by Erdelyi (1954, p. 227, no. 5.1(2)).

Appendix D. Error Function with Complex Argument

Define the function $\Phi(z)$, where the argument z is the complex variable $z = x + iy$, x and y real, by:

$$\Phi(z) = \int_0^z e^{-u^2} du \ . \tag{D-1}$$

The error function with argument z, erf(z), and its complement, erfc(z), are related to $\Phi(z)$ by

$$\mathrm{erf}(z) = 1 - \mathrm{erfc}(z) = 2\pi^{-1/2}\Phi(z) \tag{D-2}$$

Salzer (1951) has derived the following approximate formula for computation of $\Phi(z)$:

$$\Phi(z) = \Phi(x) + \frac{e^{-x^2}}{4\pi^{\frac{1}{2}}x}\,[1-\cos(2xy) + i\sin(2xy)]$$

$$+ \frac{e^{-x^2}}{\pi^{1/2}} \sum_{m=1}^{\infty} \frac{e^{-m^2/4}}{m^2+4x^2}\,[A_m(x,y) + iB_m(x,y)] + E(z) \tag{D-3}$$

where

$A_m(x,y) = 2x - 2x\cdot\cosh(my)\cdot\cos(2xy) + m\cdot\sinh(my)\cdot\sin(2xy),$

$B_m(x,y) = 2x\cdot\cosh(my)\cdot\sin(2xy) + m\cdot\sinh(my)\cdot\cos(2xy),$

and $|E(z)| \simeq 10^{-16}|\Phi(z)|$.

The following results can be derived from (D-1):

$$e^{-2ixy}\,\mathrm{erfc}\,(x-iy) + e^{2ixy}\,\mathrm{erfc}\,(x+iy) \cong 2\cdot\cos(2xy)\cdot\mathrm{erfc}(x)$$

$$+ \frac{e^{-x^2}}{\pi x}[1-\cos(2xy)] + \frac{8x}{\pi}\,e^{-x^2}\sum_{m=1}^{\infty}\frac{e^{-m^2/4}}{m^2+4x^2}\,[\cosh(my)-\cos(2xy)], \tag{D-4}$$

and

$$i\cdot\mathrm{erf}(iy) \cong -\frac{y}{\pi} - \frac{2}{\pi}\sum_{m=1}^{\infty}\frac{e^{-m^2/4}}{m}\,\sinh(my). \tag{D-5}$$