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ANALYTICAL MODELING OF AQUIFER
DECONTAMINATION BY PULSED PUMPING WHEN
CONTAMINANT TRANSPORT IS AFFECTED BY
RATE-LIMITED SORPTION AND DESORPTION

THESIS

Thomas A. Adams, Captain, USAF
Robert C. Viramontes, Captain, USAF

AFIT/GEE/ENC/93-S1

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ANALYTICAL MODELING OF AQUIFER DECONTAMINATION BY PULSED PUMPING
WHEN CONTAMINANT TRANSPORT IS AFFECTED BY
RATE-LIMITED SORPTION AND DESORPTION

THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air Education and Training Command
In Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Engineering and Environmental Management

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List of Symbols

a	Immobile region radius or half width [L]
a_1	Longitudinal dispersivity [L]
b	Aquifer thickness [L]
$C(r, t)$	Contaminant aqueous concentration [M / L^3]
$C'_i(r, z, t)$	Local solute concentration at points within the immobile region [M / L^3]
$C_i(X, Z, T)$	Dimensionless concentration at points within the immobile region
$\bar{C}_i(X, Z, s)$	Dimensionless Laplace transformed concentration at points within the immobile region
$C'_{im}(r, t)$	Volume-averaged immobile region solute concentration [M / L^3]
$C_{im}(X, T)$	Dimensionless volume-averaged immobile region solute concentration
$\bar{C}_{im}(X, s)$	Dimensionless Laplace transformed volume-averaged immobile region solute concentration
$C'_m(r, t)$	Solute concentration in the mobile region [M / L^3]
$C_m(X, T)$	Dimensionless mobile region solute concentration
$\bar{C}_m(X, s)$	Dimensionless Laplace transformed mobile region solute concentration
C'_0	Initial maximum concentration in the mobile and immobile region [M / L^3]

D_m	Mobile region dispersion coefficient $[L^2 / T]$
D'_e	Immobile region solute diffusion coefficient $[L^2 / T]$
D_e	Dimensionless immobile region solute diffusion coefficient
D'_o	Mobile region molecular diffusion coefficient $[L^2 / T]$
$F'_m(r)$	Initial solute concentration in the mobile region $[M / L^3]$
$F_m(X)$	Dimensionless initial solute concentration in the mobile region
$F'_{im}(r)$	Volume-averaged initial solute concentration in the immobile region $[M / L^3]$
$F_{im}(X)$	Dimensionless volume-averaged initial solute concentration in the immobile region
$F'_i(r, z)$	Initial local solute concentration at points within the immobile region of a certain geometry $[M / L^3]$
$F_i(X, Z)$	Dimensionless initial solute concentration in the immobile region of a certain geometry
K_d	Mobile region distribution coefficient $[L^3 / M]$
Q_w	Extraction well pumping rate $[L^3 / T]$
R_{im}	Immobile region retardation factor
R_m	Mobile region retardation factor
r	Radial distance variable $[L]$

r_w	Extraction well radius [L]
r_i	Radius of initially contaminated zone [L]
s	Laplace transform variable
$S(r, t)$	Sorbed contaminant or sorbed solute concentration
t	Time variable [T]
T	Dimensionless time variable
$V(r)$	Mobile region seepage velocity [L / T]
V_m	Same as $V(r)$ [L / T]
X	Dimensionless radial distance variable
X_w	Dimensionless extraction well radius
X_i	Dimensionless radius of initially contaminated zone
z	Variable used within the immobile region [L]
Z	Dimensionless immobile region variable
α'	First-order rate constant [T ⁻¹]
α	Dimensionless first-order rate constant
β	Solute capacity ratio of immobile to mobile regions
ϵ	Coefficient of leakage of the solute from the contaminated zone to the outer boundary
θ	Total aquifer porosity or water content
θ_m	Mobile region water content
θ_{im}	Immobile region water content
ρ	Bulk density of aquifer material [M / L ³]

Abstract

This research explores radially convergent contaminant transport in an aquifer towards an extraction well. This thesis presents the equations governing the transport of a contaminant during aquifer remediation by pulsed pumping. Contaminant transport is assumed to be affected by radial advection, dispersion, and sorption/desorption. Sorption is assumed to be either equilibrium or rate-limited, with the rate-limitation described by either a first-order law, or by Fickian diffusion of contaminant through layered, cylindrical, or spherical immobile water regions. The equations are derived using an arbitrary initial distribution of contaminant in both the mobile and immobile regions, and they are analytically solved in the Laplace domain using a Green's function solution. The Laplace solution is then converted to a formula translation (FORTRAN) source code and numerically inverted back to the time domain. The resulting model is tested against another analytical Laplace transform model and a numerical finite element and finite difference model. Model simulations are used to show how pulsed pumping operations can improve the efficiency of contaminated aquifer pump-and-treat remediation activities.

**ANALYTICAL MODELING OF AQUIFER DECONTAMINATION BY PULSED
PUMPING WHEN CONTAMINANT TRANSPORT IS AFFECTED
BY RATE-LIMITED SORPTION AND DESORPTION**

I. Introduction

Background

Groundwater is the source of drinking water for approximately 48,000 communities and twelve million individuals across the country. Almost all rural households and thirty-four of the nation's 100 largest cities depend upon groundwater as their drinking water source [Wentz, 1989:271]. Historically, groundwater has been considered an unlimited and safe source of drinking water. However, the widespread contamination of groundwater due to years of accidental or deliberate dumping of various synthetic organic chemicals is becoming an issue of growing importance in the United States. Many of these chemicals are known or potential carcinogens or teratogens and their presence in the groundwater, even at low concentrations, presents serious and substantial health risks [Chiras, 1991:388; Wentz, 1989:270].

It has been estimated that "more than 70 percent of the nearly 1,200 hazardous-waste sites on the Superfund National Priorities List (NPL) are contaminated with chemicals at levels exceeding federal drinking-water standards" [National,

1991:117]. In addition, over 33,000 other sites have been identified and included in the Comprehensive Environmental Response, Compensation, and Liability Information System for ranking and potential inclusion on the NPL. Furthermore, groundwater contamination has been identified or is suspected at more than 1,700 Resource Conservation and Recovery Act facilities. These sites constitute an immense groundwater contamination problem [Olsen and Kavanaugh, 1993:42]. In response, the Air Force is engaged in a program to identify, assess, and remediate hazardous waste sites at military installations throughout the United States [Goltz, 1991:24; Installation Restoration Program Handout, 1992]. This program is known as the Installation Restoration Program (IRP).

IRP cleanups will cost the Air Force an estimated \$7-10 billion over the next ten years [Vest, 1992]. A substantial portion of IRP costs is associated with groundwater contamination remediation. Consequently, site remediations often include aquifer cleanup efforts. Because of the rising cost to perform aquifer remediation, it is critical that decisions made regarding groundwater cleanup be based upon the best available information. One major source of information provided to IRP decision makers comes from contaminant transport models [Goltz, 1991:24].

Contaminant transport modeling plays an important part in aquifer remediation. These mathematical models are used as tools for predicting trends over short or long term periods by

simulating the effects of various processes occurring simultaneously in an aquifer that can affect the transport or concentration of pollutants [Ismail, 1987:274]. The knowledge gained using these models can be applied by IRP planners to determine the effectiveness of various groundwater treatment technologies, estimate risk, and make predictions about the cost and duration of cleanup efforts [Goltz, 1991:24]. One problem with these models involves assumptions that are made to simulate the chemical, biological, or physical processes that are occurring in the aquifer [Goltz, 1991:24]. Model simulations may significantly differ from reality, depending on actual site conditions.

One assumption commonly made when modeling organic contaminant transport is the local equilibrium assumption (LEA) [Goltz, 1991:24]. The LEA is one method used to describe the relationship between the amount of contaminant that is sorbed to soil particles in the aquifer and the amount dissolved in the water (aqueous). Under the LEA, a retardation factor is used to account for the sorption of the contaminant to the soil. The use of this retardation factor implies an instantaneous equilibration between the aqueous and sorbed contaminant [Goltz, 1991:24]. Thus, the LEA assumes the contaminant sorbed to the soil particles is instantaneously desorbed into the clean water as an extraction pump extracts contaminated water and clean water flows in to replace it [Goltz, 1991:24]. Since organic contamination is a main concern at Air Force installations, the

LEA is often used to model contaminant fate and transport at Air Force IRP sites [Goltz, 1991:24]. However, the occurrence of two phenomena in several laboratory and field studies suggests the LEA is often not a valid assumption [Goltz, 1991:24; Goltz and Roberts, 1988; Brusseau and Rao, 1989:41; Weber and others, 1991:505].

The first phenomenon is termed 'tailing', and it is used to describe the asymptotic decrease in the rate of reduction of contaminant concentration in extracted water after a relatively rapid initial decrease. The second phenomenon, termed 'rebound', involves the increase in contaminant concentration that is observed after cessation of pumping. Oftentimes, this behavior is observed several years after the pump or pumps have been stopped and the hazardous site closed [Goltz, 1991:25; Valocchi, 1986; EPA 600/8-90/003, 1990:14; Keely and others, 1987:91; Travis and Doty, 1990:1465; Mackay and Cherry, 1989:633]. Under these conditions, it appears that contaminant in the sorbed and aqueous phases does not instantaneously equilibrate but only slowly reaches equilibrium [Goltz and Oxley, 1991:547]. This rate-limited sorption/desorption can have a significant impact on contaminant transport and lead to differences between reality and model simulations based on the LEA. By making the LEA assumption, the effects of rate-limited sorption/desorption are not considered, possibly resulting in underestimating concentration levels, cost, and duration of cleanup efforts [Goltz and Oxley, 1991:547].

Some researchers have suggested a pumping scheme that enhances the traditional 'pump and treat' (groundwater extraction and treatment) approach by accounting for slow desorption [Goltz, 1991:25; Borden and Kao, 1992:34; Mackay and Cherry, 1989:633; Haley and others, 1991:124]. It has been proposed that a pumping convention that allows for periods of time when pumps are shut off (pulsed pumping) would improve the efficacy of a pump and treat system. During periods when the pump is off, slow desorption would occur, and when the pumps are turned on again, water containing higher concentrations of contaminant would be removed [Goltz, 1991:25; Borden and Kao, 1992:34; Mackay and Cherry, 1989:633; Haley and others, 1991:124; Environmental Protection Agency 540/2-89/054, 1989:5-2].

It appears that slow sorption is 'real' and is evident by the observance of tailing and rebound at IRP sites. Therefore, the Air Force needs a better tool that incorporates this behavior. A pulsed pump model is one approach that may lend itself to account for this phenomena, and as a result provide IRP decision makers with vital information regarding contaminant concentration levels, remediation alternatives, and realistic estimates of cleanup duration.

Specific Problem

The purpose of this research is to analytically model aquifer decontamination by pulsed pumping when contaminant

transport is affected by rate-limited sorption and desorption. This research will extend the work of Goltz and Oxley [Goltz and Oxley, 1991] and Carlson and others [Carlson and others, 1993].

Research Objectives

The specific objectives of this research are to:

1. Derive the governing differential equations and analytical Laplace solutions, as presented by Carlson and other [Carlson and others, 1993], describing contaminant transport by means of radial advection, dispersion, and sorption/desorption in an aquifer undergoing remediation by pulsed pumping. Sorption/desorption is assumed: at local equilibrium, rate-limited modeled by a two-region first-order rate process, and rate-limited due to Fickian diffusion of the contaminant through immobile water regions of simple geometry (rectangular, cylindrical, and spherical).
2. Develop a computer model by coding the analytical Laplace solutions presented by Carlson and others.
3. Perform simulations, using the model, of contaminant concentrations at a pulsed pumped extraction well and along an arbitrary radius of the contaminated area. This will provide insight on the effect of sorption/desorption on contaminant concentrations at the wellhead and other locations due to the assumptions of local equilibrium, two-region first-order rate, and Fickian diffusion.

4. Perform a comparison test with existing models that incorporate rate-limited sorption/desorption. This will provide model verification.

Scope and Limitations

To be solved analytically, model equations must be simple. The simplifying assumptions used in this research are listed below.

1. Contaminant transport is described by steady, uniform, converging radial flow and occurs as a result of advection due to the well when the pump is on. This research assumes the transport due to the natural groundwater gradient is negligible.
2. Only a single, infinite, homogeneous unconfined aquifer of constant height is considered; it is bounded by a horizontal aquitard with no seepage.
3. The drawdown of the aquifer water table due to pumping is negligible.
4. A single, fully penetrating extraction well is considered; it is placed at the center of the contaminated area.
5. In the governing contaminant transport equations, molecular diffusion is considered negligible with respect to mechanical dispersion when the pump is on. However, when the pump is off, contaminant transport is due solely to molecular diffusion.
6. The initial contamination distribution is radially symmetric.

Definitions

Key terms associated with contaminant transport and aquifer remediation, as defined by the Environmental Protection Agency (EPA) unless otherwise specified, are listed below [Environmental Protection Agency, 600/8-90/003, 1990; Environmental Protection Agency, 540/S-92/016, 1993].

1. Absorption: A uniform penetration of the solid by a contaminant.
2. Adsorption: An excess contaminant concentration at the surface of a solid.
3. Advection: The process whereby solutes are transported by the bulk mass of flowing fluid.
4. Aquifer: A geologic unit that contains sufficient saturated permeable material to transmit significant quantities of water.
5. Aquitard: A relatively impermeable layer that greatly restricts the movement of groundwater [Masters, 1991:148].
6. Breakthrough Curve: Contaminant concentration versus time relation [Freeze and Cherry, 1979:391].
7. Cleanup: The attainment of a specified contaminant concentration [Goltz and Oxley, 1991:547].
8. Concentration Gradient: Movement of a contaminant from a region of higher concentration to a region of lower concentration [Freeze and Cherry, 1979:25].
9. Unconfined aquifer: An aquifer in which the water table forms the upper boundary [Freeze and Cherry, 1979:48].
10. Desorption: The reverse of sorption.

11. Diffusion: Mass transfer as a result of random motion of molecules. It is described by Fick's first and second law.
12. Dispersion: The spreading and mixing of the contaminant in groundwater caused by diffusion and mixing due to microscopic variations in velocities within and between pores.
13. Extraction Well: A pumped well used to remove contaminated groundwater.
14. Homogeneous: A geologic unit in which the hydrologic properties are identical from point to point.
15. Pulsed Pumping: A pump and treat enhancement where extraction wells are periodically not pumped to allow concentrations in the extracted water to increase.
16. Retardation: The movement of a solute through a geologic medium at a velocity less than that of the flowing groundwater due to sorption or other removal of the solute.
17. Sorption: The generic term used to encompass the phenomena of adsorption and absorption.
18. Tailing: The slow, nearly asymptotic decrease in contaminant concentration in water flushed through contaminated geologic material.

Overview

IRP planners use contaminant transport models to assess risk, to design remedies, and to estimate remediation cost and cleanup duration at IRP hazardous sites. Chapter I examined one modeling assumption often employed at these sites and discussed

how this assumption does not account for the slow or rate-limited sorption/desorption that has been observed in several laboratory and field studies. A pulsed pumping scheme was proposed as a technique to enhance the effectiveness of groundwater pump and treat systems by accounting for rate-limited sorption/desorption. This chapter concludes with a research proposal to analytically model aquifer decontamination by pulsed pumping when the contaminant transport is affected by rate-limited sorption and desorption.

Chapter II discusses the literature associated with sorbing solute transport modeling. An introduction of the processes thought to control the subsurface movement of contaminants is presented. Then, the chapter reviews the efforts of researchers to develop mathematical models to account for equilibrium sorption and nonequilibrium sorption. Chapter III presents the derivation of Carlson and others analytical solutions [Carlson and others, 1993] describing contaminant transport by means of radial advection, dispersion, and sorption/desorption in an aquifer undergoing pulsed pumping operations. Sorption/desorption is described assuming: linear equilibrium, rate-limitation modeled by a two-region first-order rate process, and rate-limitation due to Fickian diffusion of the contaminant through immobile water of cylindrical, spherical, and rectangular geometry. In Chapter IV, a discussion on some of the numerical techniques used to code the analytical solutions is presented. Then, model simulations are conducted

using pulsed and continuous pumping schemes and varying the initial contaminant concentration distribution. Model simulations are used to show how pulsed pumping operations can improve the efficiency of contaminated aquifer pump and treat remediation activities. Finally, the model is compared with two existing models found in the literature that incorporate rate-limited sorption and desorption. Several breakthrough curves and tables are generated and used to illustrate the simulations and model comparisons. Chapter V summarizes the research, draws conclusions based on the findings, and offers recommendations for further research.

II. Literature Review

Overview

Installation Restoration Program (IRP) site remediations often include aquifer cleanup and frequently involve the operation of a system of extraction wells [Goltz and Oxley, 1991:547; Valocchi, 1986:1696; Keely and others, 1987:91; Mackay and Cherry, 1989:630]. Theoretical research and field observations have found that the contaminant load discharged by the extraction wells asymptotically declines over time and eventually approaches a residual level. Contaminant concentrations slowly decrease once they reach this plateau, resulting in long cleanup times (Figure 2.1).

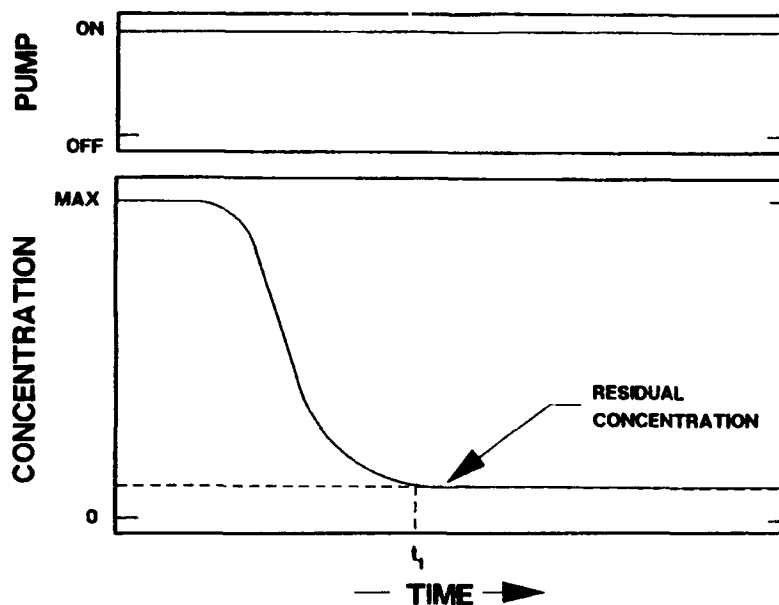


Figure 2.1. Effluent Concentration Pattern for Continuous Wellfield Operations [Keely and others, 1987]

This leveling-off phenomenon is termed 'tailing'. As pumping continues, large volumes of water are extracted and treated to remove only small quantities of contaminants [Goltz and Oxley, 1991:547; Keely and others, 1987:91; Mackay and Cherry, 1989:630; Olsen and Kavanaugh, 1993:44]. Depending on the amount of contaminant remaining in the aquifer, "this may cause remediation to be continued indefinitely, or it may lead to premature cessation of the remediation and closure of the site" [Keely and others, 1987:91]. The cessation of pumping is of concern because once the pumps are turned off, the contaminant concentration in the groundwater has been observed to rise. This phenomenon, termed 'rebound', is particularly of concern if the remediation is discontinued prior to the removal of all residual contaminants (Figure 2.2) [Keely and others, 1987:91; Mackay and Cherry, 1989:633; Travis and Doty, 1990:1465].

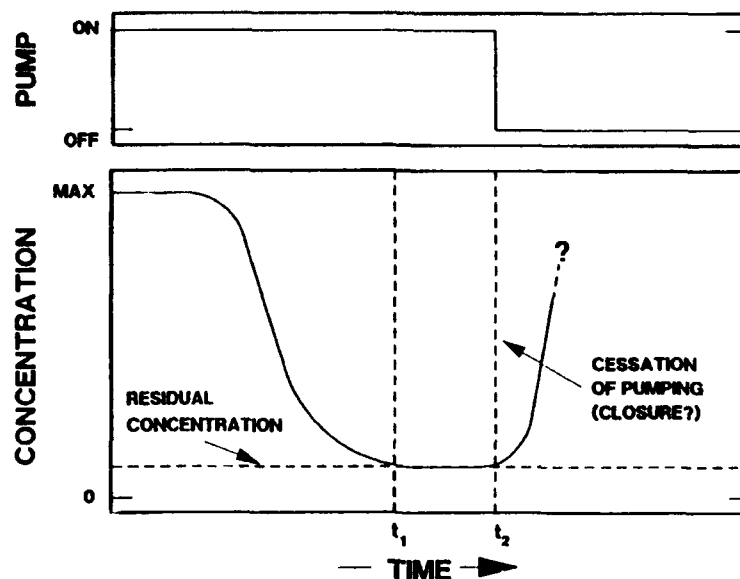


Figure 2.2. Potential Groundwater Contamination Response to Cessation of Continuous Pumping [Keely and others, 1987]

The models presently being used at IRP sites do not account for tailing and rebound. Thus, pollutants may persist longer and at a higher concentration than predicted by current models [Goltz, 1991:24]. Researchers suggest that tailing and rebound could be due to rate-limited sorption and desorption of a contaminant from the solids in an aquifer [Goltz and Oxley, 1991:547; Mackay and Cherry, 1989:633; Keely and others, 1987:94] or due to the molecular diffusion into low permeability regions or regions of immobile water [Goltz and Roberts, 1986; Goltz and Roberts, 1988; Goltz and Oxley, 1991].

This chapter presents a review of the literature related to sorbing solute transport modeling. It begins with an introduction of the processes thought to control contaminant transport in an aquifer. Then, the chapter reviews mathematical

models that account for the sorption process. More specifically, a model review is presented with a discussion focusing on the impact and significance of equilibrium sorption/desorption and rate-limited (nonequilibrium) sorption/desorption in immobile regions of an aquifer. Next, the chapter explores the modeling efforts involving pulsed pumping. Finally, some conclusions are drawn based on the literature review.

Contaminant Transport Processes

To understand contaminant transport modeling, it is first necessary to describe the various processes thought to control the subsurface movement of contaminants. For purposes of this thesis, subsurface refers to the saturated zone (below the water table) in an aquifer. These processes are related to the flow of contaminants dissolved in groundwater [National Research Council, 1990:28]. Dissolved contaminant transport is due to a variety of processes. The National Research Council (NRC) divides these processes into two groups: (1) mass transport and (2) mass transfer [National Research Council, 1990: 37].

Mass Transport. Mass transport are physical processes responsible for fluxes (flow) in the groundwater system. These mass fluxes occur due to advection, diffusion, and hydrodynamic dispersion.

Advection is the primary process responsible for contaminant transport in the subsurface [National Research Council, 1990:37]. Movement of the contaminant mass occurs due to the

movement of the groundwater, and in general, it is assumed that the dissolved mass is transported in the same direction and with the same velocity as the groundwater [National Research Council, 1990:37; Freeze and Cherry, 1979:389].

Diffusion is the process where contaminant mass spreads due to molecular constituents moving in response to a concentration gradient (movement from an area of high concentration to an area of lower concentration) [Freeze and Cherry, 1979:103]. The process of diffusion is often referred to as molecular diffusion or ionic diffusion. Diffusion occurs in the absence of any movement of solution. If the solution is flowing, diffusion is partially responsible for contaminant mass mixing [Freeze and Cherry, 1979:103]. The process of diffusion ceases only when the concentration gradients become nonexistent.

Hydrodynamic dispersion is a process that accounts for the spreading of a solute from a path that it would be expected to follow according to the advective process in a flow system [Freeze and Cherry, 1979:75]. Because of this spreading, dispersion causes dilution of the solute; hence, it is a mixing process. Dispersion can be considered to consist of two components: mechanical dispersion (mechanical mixing during fluid advection) and molecular diffusion of the solute particle [Freeze and Cherry, 1979:75]. Mechanical dispersion occurs as a consequence of local variability in velocity [National Research Council, 1990:41]. On a microscopic scale, this variability may be caused by velocity variations within individual pores or due

to the branching of pore channels [Freeze and Cherry, 1979:75-76; National Research Council, 1990:40-41]. The relationship between mechanical dispersion and molecular diffusion is dependent upon groundwater flow velocities. At modest flows, the common assumption is that the molecular diffusion component of hydrodynamic dispersion is negligible and the mechanical component is responsible for the spreading. At very slow groundwater flow velocities, diffusion may dominate [Environmental Protection Agency 540/4-89/005, 1989:4].

Mass Transfer. Mass transfer processes redistribute contaminant mass within or between phases through chemical and biological reactions [National Research Council, 1990:8]. There is a multitude of these processes, each of them impacting the transport of a contaminant differently. Of the various processes, sorption is considered to be one of the most important since it can have profound effects on contaminant transport, fate, and removal [Brusseau and Rao, 1989:33; Goltz and Oxley, 1991:547; Environmental Protection Agency 540/S-92/016, 1993]. In this thesis, sorption is the only mass transfer process considered.

The Environmental Protection Agency (EPA) defines sorption as

the interaction of a contaminant with a solid. More specifically, the term can be further divided into adsorption and absorption. The former refers to an excess contaminant concentration at the surface of a solid while the latter implies a more or less uniform penetration of the solid by a contaminant. In most environmental settings, this distinction serves little

purpose as there is seldom information concerning the specific nature of the interaction. The term sorption is used in a generic way to encompass both phenomena. [Environmental Protection Agency 540/S-92/016]

The effect of sorption is to retard or slow the movement of contaminants in the groundwater. When sorption occurs, the rate at which the contaminant is transported is lower than would be the case for an unretarded solute. This process not only reduces the movement of contaminants in the groundwater, it also makes it more difficult to remove contaminants from an aquifer. That is,

the slow desorption of contaminants from the solid to the liquid phase can significantly reduce the effectiveness of a pump-and-treat system by progressively lowering contaminant concentrations in water pumped to the surface. It is not uncommon to pump a system until contaminant concentrations in the pumped water meet a mandated restoration level, while the aquifer's solid phase still contains a substantial contaminant mass. [Environmental Protection Agency 540/S-92/016, 1993]

As a result, both the time and cost to remediate to a cleanup level are increased [National Research Council, 1990:45-46; Goltz and Oxley, 1991:547; Mackay and Cherry, 1989:633]. The behavior, transport, and fate of contaminants in the subsurface is dependent upon the mass transport and mass transfer reactions, which in turn, depend on contaminant and aquifer properties [Weber and others, 1991:499].

Advection-Dispersion-Sorption Models

Mathematical models are commonly used in groundwater studies to represent those physical and chemical processes that are

occurring in an aquifer [Goltz, 1991:24; National Research Council, 1990:1,28,38; Freeze and Cherry, 1979:18-19]. These models attempt to simulate the actual behavior of contaminant resulting from these processes by solving mathematical equations [National Research Council, 1990:52]. These models provide a source of information about contaminant transport processes that can assist in the design of remedial programs, risk assessment, and predict cost and cleanup duration at contaminated sites [Goltz, 1991:24].

The following sections examine the efforts of researchers to develop mathematical models to account for the chemical and physical processes that control sorbing solute transport. The mathematical formulation of the sorption processes assumes linear equilibrium, rate-limitation modeled by a two-region first-order rate process, and rate-limitation due to Fickian diffusion of the contaminant through immobile water of cylindrical, spherical, and rectangular geometry.

The mathematical formulation of the physical and chemical processes that govern dissolved sorbing transport of a single contaminant in saturated, homogeneous porous media has traditionally been modeled with advection, dispersion, and a sink term to describe the transfer of contaminant from the aqueous phase to the solid phase [Freeze and Cherry, 1979:402]. Equation (2.1) shows, in cylindrical coordinates, the mass balance equation typically used to account for these processes:

$$\frac{\partial C(r, t)}{\partial t} = D(r) \frac{\partial^2 C(r, t)}{\partial r^2} - V(r) \frac{\partial C(r, t)}{\partial r} - \frac{\rho}{\theta} \frac{\partial S(r, t)}{\partial t} \quad (2.1)$$

where $C(r, t)$ is the contaminant aqueous concentration $[M / L^3]$, r is the radial coordinate $[L]$, t is time $[T]$, $D(r)$ is the mobile region hydrodynamic dispersion coefficient $[L^2 / T]$, $V(r)$ is the mobile region seepage velocity $[L / T]$, ρ is the bulk density of aquifer material $[M / L^3]$, θ is the aquifer porosity [unitless], and $S(r, t)$ is the sorbed contaminant [unitless]. The first, second, and third terms on the right-hand side (rhs) of the Equation (2.1) represent dispersion, advection, and sorption of the contaminant, respectively. This equation is the governing equation for sorbing contaminant transport.

Chen and Woodside presented a mathematical model for the "basic case" of aquifer decontamination by pumping. That is, they developed analytical solutions for a single extraction well operating under a constant pumping rate. Their model describes converging radial transport for various initial distributions of contaminant. Transport was assumed to be controlled by advection and dispersion. Thus, this model does not account for the effects of sorption [Chen and Woodside, 1988; Goltz and Oxley, 1991:547].

The models currently in existence that describe sorbing contaminant transport differ primarily on how the sink term is represented. The two general approaches that are used to model

this term are by assuming sorption equilibrium and sorption nonequilibrium [Brusseau and Rao, 1989:34].

Sorption Equilibrium. These models relate the amount of solute sorbed per unit of sorbent to the amount of solute retained in the aqueous phase [Weber and others, 1991:505]. Three equilibrium models commonly used to describe this relationship are the linear, Langmuir, and Freundlich models.

The most common and simplest model to use to simulate sorbing solute transport assumes an equilibrium, reversible, and linear relationship between contaminant in the sorbed and the aqueous phase [Goltz and Oxley, 1991:548; Weber and others, 1991:505]. The assumptions in this simple model are known as the local equilibrium assumptions (LEA). This implies that the accumulation of solute by the sorbent is directly proportional to the solution phase concentration. Mathematically, this assumption is represented by $S = K_d C$, where K_d is the distribution coefficient [L^3 / M] [Weber and others, 1991:505]. This distribution coefficient describes the distribution of contaminants between aquifer solids and the groundwater. The value of K_d is dependent upon the characteristics of both the contaminant and the aquifer material with the hydrophobicity of the contaminant and the amount of soil organic carbon playing important roles in determining the magnitude of K_d [Environmental Protection Agency 540/S-92/016, 1993]. If we assume only a fraction, ϕ , of the total aquifer porosity is mobile, so $\theta_m = \phi \theta$ where θ_m represents the mobile region

porosity, we may define $C'_m(r, t)$ as the solute concentration in the mobile region $[M / L^3]$, V_m as the mobile region seepage velocity $[L / T]$, and D_m as the mobile region dispersion coefficient $[L^2 / T]$. Substituting the expression $S = K_d C'_m(r, t)$ into the sink term of Equation (2.1) produces

$$\frac{\partial C'_m(r, t)}{\partial t} = \frac{D_m}{R_m} \frac{\partial^2 C'_m(r, t)}{\partial r^2} - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} \quad (2.2)$$

where R_m is the mobile region retardation factor [unitless] where $R_m = 1 + (\rho K_d) / \theta_m$. This LEA model (linear, equilibrium) has been found to describe sorption accurately under certain conditions, most appropriately at very low solute concentrations and for solids of low sorption potential and low flow [Weber and others, 1991:505]. According to Brusseau and Rao,

In order for the LEA to be valid, the rate of the sorption process must be fast relative to the other processes affecting solute concentration (e.g., advection, hydrodynamic dispersion) so that equilibrium may be established between the sorbent and the pore fluid. Initially, it was thought that, because of the generally slow movement of water in the subsurface, equilibrium conditions should prevail and, therefore, the LEA would be valid. Detailed laboratory and field investigations, however, have revealed that, in many cases, this assumption is invalid. [Brusseau and Rao, 1989:41]

When the LEA is justified, the mathematics of sorbing contaminant transport is greatly simplified [Weber and others, 1991:505].

The Langmuir model, a nonlinear model, was originally developed for the case where sorption leads to the deposition of a single layer of solute molecules on the surface of a sorbent. The assumptions governing this model are: (1) the energy of sorption for each molecule is the same and independent of surface coverage, and (2) sorption occurs only on localized sites and involves no interactions between sorbed molecules [Weber and others, 1991:505].

The most widely used nonlinear sorption equilibrium model is the Freundlich model [Weber and others, 1991:506]. This model has been applied to simulate sorption on heterogeneous surfaces. Weber and others indicate that the Langmuir and Freundlich models are equivalent when describing nonlinear sorption over moderate ranges of solution concentrations; however, major differences exist between the models over wide ranges and high levels of concentration [Weber and others, 1991:506].

Sorption Nonequilibrium. It has been proposed that a rate-limited sorption process is responsible for the concentration tailing that has been observed in many laboratory and field observations [Goltz and Oxley, 1991:547; Keely and others, 1987:91; Mackay and Cherry, 1989:630]. In the literature, two approaches have been used to model these sorption kinetics--chemical and physical [Brusseau and Rao, 1989:43; Valocchi, 1986:1694]. That is, sorption nonequilibrium is assumed to be due to either a slow chemical or physical mechanism. In this section both mechanisms are discussed; however, the primary

emphasis of this research is on physical sorption nonequilibrium.

Chemical. These models assume that sorption nonequilibrium results from a rate-limited sorption reaction at the soil-solution interface [Valocchi, 1986:1694; Brusseau and Rao, 1989:43]. Valocchi presented a model describing converging radial transport of a sorbing contaminant. Valocchi's model assumed a chemical rate-limited sorption reaction described by a first-order rate law [Valocchi, 1986].

Physical. The tailing phenomenon has been successfully modeled by dividing the porous medium into regions of mobile and immobile water and modeling advective/dispersive solute transport in the mobile region (Equation (2.1)) with an expression to describe the diffusional transfer of contaminant between the two regions [Goltz and Roberts, 1986:1139; Goltz and Roberts, 1988:40; Goltz and Oxley, 1991:549]. With these models, advective/dispersive solute transport is assumed to occur only in the mobile region and solute transport in the immobile region is assumed to occur only by diffusion. The solute transport between the two regions causes the immobile region to act as a sink or source. Consequently, nonequilibrium sorption is rate-limited due to the slow transfer of solute between the two regions [Valocchi, 1986:1694; Brusseau and Rao, 1989:45]. Mathematically, the transport of a single sorbing solute in a radially flowing aquifer in a porous medium with

immobile water regions may be written as [Goltz and Oxley, 1991:548]

$$\frac{\partial C'_m(r, t)}{\partial t} = \frac{D_m}{R_m} \frac{\partial^2 C'_m(r, t)}{\partial r^2} - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} - \frac{\theta_{im} R_{im}}{\theta_m R_m} \frac{\partial C'_m(r, t)}{\partial t} \quad (2.3)$$

where $C'_m(r, t)$ is volume-averaged immobile region solute concentration $[M / L^3]$, R_m is the immobile region retardation factor [unitless], $\theta_m = \phi \theta$ is the mobile region water content [unitless], and $\theta_{im} = \theta - \theta_m$ is the immobile region water content [unitless]. This expression assumes that sorption onto the solids is linear and reversible, with the effect of sorption incorporated into R_m and R_{im} , where $R_m = 1 + (\rho f K_d) / \theta_m$, $R_{im} = 1 + [\rho (1 - f) K_d] / \theta_{im}$, where f is the fraction of sorption sites adjacent to regions of mobile water [Goltz and Roberts, 1988:40].

Various models have been proposed to describe the transfer of solute between the mobile and immobile regions. The two most common models found in the literature are first-order rate and Fickian diffusion [Goltz and Roberts, 1986:1139; Goltz and Oxley, 1991:548-549; Brusseau and Rao, 1989:46-47].

First-Order Rate. These models assume that solute transfer between the mobile and immobile regions can be described by a first-order rate expression [Goltz and Oxley, 1991:548]:

$$\frac{\partial C'_{im}(r, t)}{\partial t} = \frac{\alpha'}{\theta_{im} R_{im}} [C'_m(r, t) - C'_{im}(r, t)] \quad (2.4)$$

where $\alpha' [1/T]$ is a first-order rate constant. The physical interpretation of Equation (2.4) is based on the assumption that solute transfer is a function of the solute concentration difference between the mobile and immobile regions. This model also assumes that the immobile region is perfectly mixed; thus, the local concentration at all points within the immobile region is the same as the volume-averaged immobile region solute concentration (C'_{im}) [Goltz and Oxley, 1991:548]. This assumption is in contrast to physical diffusion models where a concentration gradient exists. The combination of Equations (2.3) and (2.4) are the governing equations describing two-region first-order sorbing solute transport.

Nkedi-Kizza and others [1984] have shown that the Valocchi's first-order chemical expression is equivalent to physical nonequilibrium models. In other words, Nkedi-Kizza and others have suggested that the difference between physical first-order rate diffusion controlled adsorption and two-site chemical kinetic adsorption, such as Valocchi's [1986], are mathematically equivalent when describing ion exchange during transport through aggregated sorbing media. On a macroscopic level, both models generate the same total concentration distribution in the system [Nkedi-Kizza and others, 1984:1129].

Fickian Diffusion. The transfer of solute between the two regions may be assumed to be governed by Fickian (Fick's second law) diffusion of solute within immobile regions of specified geometry [Goltz and Oxley, 1991:548-549]. This solute transfer mechanism requires the presence of a concentration gradient. As such, the dependent variable in Equation (2.3), C'_{im} , represents a volume-averaged solute concentration within the immobile region [Goltz and Roberts, 1986:1140]. $C'_{im}(r, t)$ is defined by [Goltz and Oxley, 1991:548]

$$C'_{im}(r, t) = \frac{v}{a^v} \int_0^a z^{v-1} C'_i(r, z, t) dz \quad (2.5)$$

where $C'_i(r, z, t)$ is the local concentration at points within the immobile region $[M / L^3]$, $v = 1, 2, 3$ for rectangular (layered), cylindrical, and spherical immobile region geometry, respectively, a is the immobile region radius or half width $[L]$, and z is the coordinate within the immobile region $[L]$. Mathematically, Fick's second law of diffusion, describing contaminant transport within the immobile region, is

$$R_{im} \frac{\partial C'_i(r, z, t)}{\partial t} = \frac{D'_e}{z^{v-1}} \frac{\partial}{\partial z} \left(z^{v-1} \frac{\partial C'_i(r, z, t)}{\partial z} \right) \quad (2.6)$$

where D'_e is the immobile region solute diffusion coefficient $[L^2 / T]$.

Figure 2.3 shows an idealized conceptualization of an aquifer remediation by pumping where the transfer of solute

between mobile and immobile regions may be affected by first-order rate or Fickian diffusion rate-limiting mechanisms [Goltz and Oxley, 1991:549].

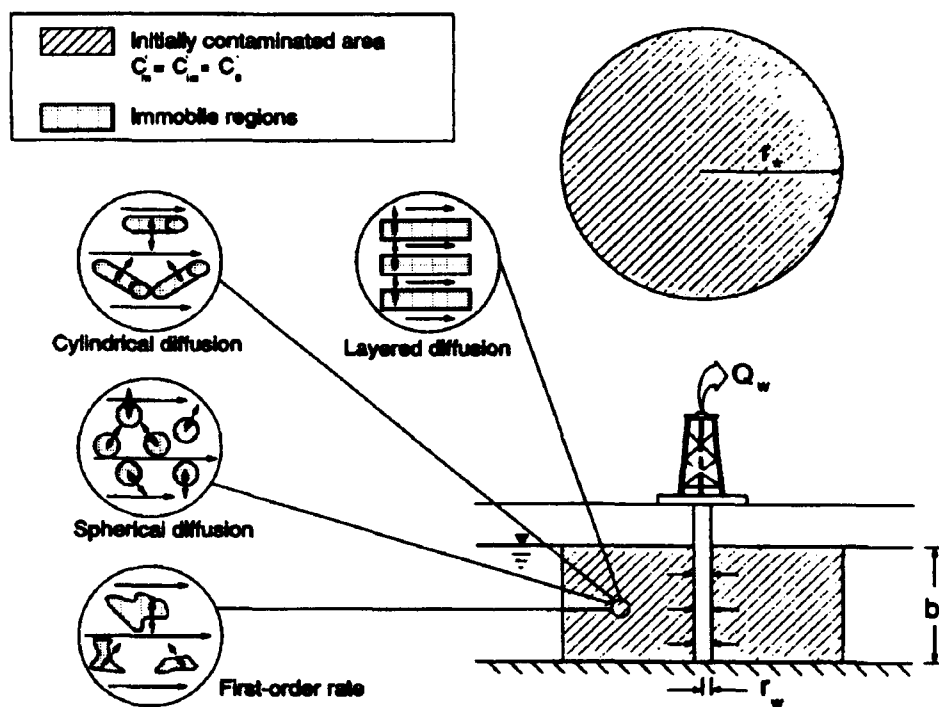


Figure 2.3. Conceptualization of Aquifer Remediation, Where Contaminant Transfer May Be Affected by Rate-Limiting Mechanisms [Goltz and Oxley, 1991]

In summary, the differential equations that govern dissolved sorbing solute transport consist of Equation (2.3) (with the last term not present) for the local equilibrium assumption, Equations (2.3) and (2.4) for the two-region first-order rate

assumption, and Equations (2.3), (2.5), and (2.6) for the diffusion assumptions.

Pulsed Pumping

As previously mentioned, pump and treat is the most commonly used technology for remediating contaminated aquifers. "Approximately 68% of Superfund Records of Decision (RODs) select pumping and treating as the final remedy to achieve aquifer remediation" [Travis and Doty, 1990:1465]. In fact, pump and treat technology is the preferred method to restore contaminated aquifers to drinking water quality [Olsen and Kavanaugh, 1993:42]. The literature reviewed has, for the most part, criticized pump and treat technology primarily due to its ineffectiveness in achieving health-based cleanup standards coupled with extended periods of cleanup duration and high cost. The most significant literature reviewed was an EPA study involving 19 sites where pump and treat remediation had been ongoing for up to 10 years [Environmental Protection Agency 540/2-89/054, 1989]. This study revealed

Of the 19 sites studied in detail, 13 had aquifer restoration as their primary goal, and only 1 has been successful so far. Several of the other systems show promise of eventual aquifer restoration, but typically progress toward this goal is behind schedule. Concentrations often decline rapidly when the extraction system is first turned on, but after the initial decrease continued reductions are usually slower than expected. [Environmental Protection Agency 540/2-89/054, 1989]

The EPA further indicated that although significant removal of contaminant mass was achieved, the concentration levels remaining in the aquifer were generally above health-based standards or site-specific cleanup objectives. As a result, the systems had been operating longer than the predicted time required for cleanup [Environmental Protection Agency 540/2-89/054, 1989:E-1-E-3, 2-13].

The previous section discussed how rate-limited sorption/desorption tends to slow the removal of contaminants from an aquifer as the groundwater is pumped. In turn, pump and treat remediation is often rendered ineffective. Therefore, there is great interest in evaluating alternative pumping schemes that can account for rate-limited sorption/desorption. One proposed approach is pulsed pumping. Under a pulsed pumping scheme, pumps are shut off for periods of time so that slow desorption would occur. When the pumps are turned on again, higher concentrations would be removed [Goltz, 1991:25; Keely and others, 1987; Borden and Kao, 1992:34; Mackay and Cherry, 1989:633; Haley and others, 1991:124; Environmental Protection Agency 540/2-89/054, 1989]. It has been suggested that this cycling of extraction wells on and off in 'active' and 'resting' phases may remove the minimum volume of contaminated groundwater, at the maximum possible concentration, for the most efficient treatment (Figure 2.4) [Keely and others, 1987:94-99].

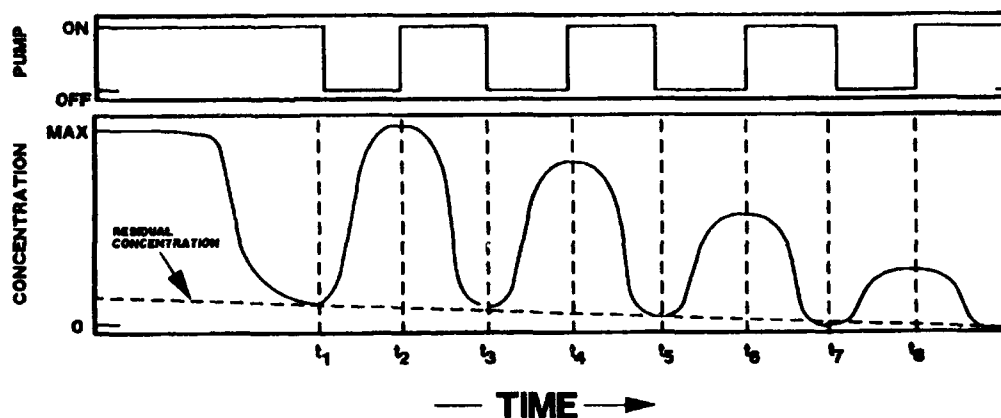


Figure 2.4. Potential Effluent Concentrations for Pulsed Pumping Remediation [Keely and others, 1987]

The literature reviewed has identified sources that qualitatively discuss pulsed pumping as a pump and treat enhancer; however, the only mathematical analysis incorporating pulsed pumping with the advection/dispersion equation is an unpublished document by Carlson and others [Carlson and others, 1993].

Carlson and others mathematically derived the solutions in the Laplace domain for contaminant concentration for the cases of linear equilibrium, two-region first-order rate, and Fickian diffusion. Carlson and others research extends the work of Goltz and Oxley [1991] in that their derivation takes into account conditions when the pump is on and when the pump is off, whereas Goltz and Oxley's solutions required the pump to be continuously on. Unfortunately, Carlson and others did not

numerically evaluate the Laplace domain solution nor convert it back to the time domain.

Summary

Groundwater extraction or pump and treat is the most commonly used remediation technology for aquifer decontamination. However, it has been criticized for its inability to attain health-based cleanup standards, meet projected timelines, and stay within budget. The literature indicates that part of the limitations of pump and treat are due to the various processes occurring in an aquifer. Understanding the physical and chemical processes which dictate the transport, fate, and removal of contaminants in groundwater is essential in designing and implementing more effective and efficient remediation systems at IRP hazardous waste sites. Mathematical models have proven to be excellent tools for representing the effects of the various processes--advection, dispersion, sorption, and diffusion--that can occur simultaneously in an aquifer and affect the transport and concentration of pollutants.

The literature search revealed three commonly used sorbing solute transport models: linear equilibrium, two-region first-order rate, and Fickian diffusion. The significant difference among these models is the underlying assumptions used in their development. The linear equilibrium model assumes an instantaneous equilibrium between the aqueous and sorbed contaminant phases, whereas the two-region first-order rate and

the Fickian diffusion models are based on the premise that a nonequilibrium condition exists, and solute transport is rate-limited due to the transfer of the contaminant between regions of mobile and immobile water. The appropriateness of any one of these models is dependent upon actual site conditions. In fact, rate-limited sorption/desorption has been studied by several researchers who propose that this phenomenon is responsible for the 'tailing' and 'rebound' that have been observed in numerous field and laboratory studies and one 'culprit' responsible for the ineffectiveness of pump and treat systems. As a result, pump and treat enhancers which account for this behavior, such as pulsed pumping, are being investigated.

The literature reviewed has shown that the only significant attempt to model a pulsed pumping scheme under conditions of rate-limited sorption/desorption was the research proposed by Carlson and others. The literature clearly shows a need for continued research in this area. Further efforts are needed to numerically evaluate their solutions.

This thesis will extend Carlson and others work by developing a source code based on their solutions. It is intended that this research may provide IRP decision makers with a better understanding of the physics that can occur in an aquifer, and help them validate more complex numerical models that are used to predict the level of cleanup required, duration of cleanup efforts, and the cost associated with aquifer remediation.

III. Model Formulation

Introduction

The primary objective of this research is to develop a computer model describing contaminant transport by means of radial advection, dispersion, and sorption in an aquifer undergoing pulsed pumping operations. Since this research extends the work of Goltz and Oxley [1991] and Carlson and others [1993], the equations, solutions, notation, and source code will be based on the expressions of sorption presented in their respective papers.

In order to establish the basis of the equation set, model assumptions and aquifer characteristics are reviewed. Then, the governing equations and their solutions, which are used to develop the source code, are presented.

Model Assumptions and Aquifer Characteristics

As stated in Chapter I, in order to model contaminant transport analytically, model equations must be simple. The simplifying assumptions used in this research represent an 'idealized' scenario.

One key assumption used to set up the model was the assumption that contaminant transport is described by steady, uniform, converging radial flow resulting from advection due to the extraction well. Thus, transport due to the natural groundwater gradient is assumed negligible. Coupled with this

assumption, the drawdown of the aquifer water table due to the pumping is also considered negligible.

To take advantage of radial symmetry, we assumed that a single, fully penetrating extraction well is in operation placed at the center of a cylindrically symmetrical contaminated region. In addition, the initial contamination distribution was also assumed to be radially symmetric.

Another significant assumption used to set up the model is a single, infinite, homogeneous, and unconfined aquifer. Furthermore, the aquifer was considered to be of constant thickness and bounded by a horizontal aquitard with no seepage.

In addition to the assumptions listed above, model development was based on the concept of physical sorption nonequilibrium as discussed in Chapter II. Therefore, to understand the formulation of the model, it is necessary to review this concept. Recall that in Chapter II, we discussed how solute transfer can be modeled by dividing the porous medium into regions of mobile and immobile water. Advective and dispersive solute transport occurs in the mobile region, and an additional term is used to describe the diffusional transfer of contaminant between the two regions [Goltz and Roberts, 1986:1139; Goltz and Roberts, 1988:40; Goltz and Oxley, 1991:549]. The transfer of solute between mobile and immobile water may be assumed to be governed by either Fickian diffusion of solute within immobile regions of layered, cylindrical, and spherical geometry or by a first-order rate expression [Goltz

and Oxley, 1991:548-549]. Goltz and Oxley presented a conceptualization of mobile and immobile water regions in an aquifer where contaminant transfer may be affected by Fickian diffusion or a first-order rate process (Figure 2.3).

If we combine the simplifying assumptions and the concept of physical nonequilibrium, we can now describe the aquifer characteristics associated with formulating the model.

Consider an extraction well of radius r_w [L] pumping at a rate Q_w [L^3 / T] placed at the center of a cylindrically symmetric contaminated region of radius r [L] in an aquifer of constant thickness b [L]. In this contaminated region assume there exists mobile and immobile water regions. General properties associated within the mobile region consists of the mobile region water content, θ_m [dimensionless], mobile retardation factor, R_m [dimensionless], and longitudinal dispersivity, α_l [L]. Immobile water region properties consists of the immobile region water content, θ_{im} [dimensionless], immobile retardation factor, R_{im} [dimensionless], and the immobile region solute diffusion coefficient, D'_c [L^2 / T]. If the transfer of solute between the two regions is assumed to be governed by Fickian diffusion, then another property associated with the immobile region is the radius of the spherical or cylindrical regions or half width of the layered region, a [L].

Initially in the contaminated region there exists some maximum concentration in the mobile and immobile regions, C'_0 [M / L^3]. If we define the initial solute concentration

distribution in the mobile region as $F'_m(r) [M / L^3]$, and the volume-averaged initial solute concentration in the immobile region as $F'_i(r) [M / L^3]$, then at a later time, $t [T]$, we now define the mobile region solute concentration as $C'_m(r, t) [M / L^3]$ and the volume-averaged immobile region solute concentration as $C'_i(r, t) [M / L^3]$.

In the case where the immobile region is geometry dependent (Fickian diffusion), initially there exists some local solute concentration at points within this region, $F'_i(r, z) [M / L^3]$. This concentration is not only a function of the radial distance, $r [L]$, but also its radial position within the immobile region, $z [L]$. As time progresses, we define the local solute concentration at points within the immobile region as $C'_i(r, z, t) [M / L^3]$.

Governing Equations and Solutions

Chapter II introduced the theoretical development of the differential equations for sorbing solute transport. This section presents the governing equations and solutions for sorbing solute transport for conditions when an extraction well is on and when an extraction well is off. The model equations allow for arbitrary initial conditions and are developed for the following sorption assumptions: linear equilibrium, rate-limited modeled by a two-region first-order rate process, and rate-limited due to Fickian diffusion of the contaminant through immobile water regions of layered, cylindrical, and spherical

geometry. A more detailed mathematical analysis can be found at Appendix A and a list of the variables or notation used in this thesis on page viii.

Model Formulation: Extraction Well On. As presented in Chapter II, the expression governing contaminant transport within the mobile region of a homogenous, radially flowing aquifer is

$$\frac{\partial C'_m(r, t)}{\partial t} = \frac{D_m}{R_m} \frac{\partial^2 C'_m(r, t)}{\partial r^2} - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} - \frac{\theta_m R_m}{\theta_m R_m} \frac{\partial C'_m(r, t)}{\partial t} \quad (3.1)$$

for $r_w < r < r_e$ and $t > 0$ and $C'_m(r, t)$ is defined by [Goltz and Oxley, 1991:548]

$$C'_m(r, t) = \frac{v}{a^v} \int_0^a z^{v-1} C'_s(r, z, t) dz \quad (3.2)$$

for $r_w < r < r_e$ and $t > 0$ and $0 \leq z \leq a$. Given an aquifer of constant thickness, b [L], and an extraction well pumping at a rate Q_w [L³ / T], then the radial velocity is

$$V_m(r) = \frac{-Q_w}{2\pi b \theta_m r} \quad (3.3)$$

Assuming that the mobile region dispersion coefficient, D_m [L² / T], is given by

$$D_m(r) = a_1 |V_m(r)| \quad (3.4)$$

and that the mobile region molecular diffusion coefficient, $D'_0 \ll D_m$, and defining the dimensionless variables as

$$X = \frac{r}{a_1} \quad (3.5)$$

$$T = \frac{Q_w t}{2 \pi b \theta_m R_m a_1^2} \quad (3.6)$$

$$C_m(X, T) = \frac{C'_m(r, t)}{C'_0} \quad (3.7)$$

$$C_{im}(X, T) = \frac{C'_{im}(r, t)}{C'_0} \quad (3.8)$$

and the dimensionless constant

$$\beta = \frac{\theta_{im} R_{im}}{\theta_m R_m} \quad (3.9)$$

where X is the dimensionless radial distance, T is the dimensionless time, $C_m(X, T)$ is the dimensionless mobile region solute concentration, $C_{im}(X, T)$ is the dimensionless volume-averaged immobile region solute concentration, then Equation (3.1) can be rewritten in dimensionless form as

$$\frac{\partial C_m(X, T)}{\partial T} = \frac{1}{X} \frac{\partial^2 C_m(X, T)}{\partial X^2} + \frac{1}{X} \frac{\partial C_m(X, T)}{\partial X} - \beta \frac{\partial C_{im}(X, T)}{\partial T} \quad (3.10)$$

for $X_w < X < X_c$, where X_w is the nondimensionalized well radius and $X_w = r_w / a_1$, and X_c is the nondimensionalized contaminated area radius and $X_c = r_c / a_1$ for $T > 0$.

The use of the mobile retardation factor, R_m , and immobile retardation factor, R_{im} , is based on the assumption that there is an instantaneous equilibration between the aqueous and sorbed contaminant within the mobile and immobile regions, whereas the sorption rate limitation is due to the slow diffusive release of solute between the two regions [Goltz and Oxley, 1991:548].

The third term on the right-hand side of Equations (3.1) and (3.10) represents the accumulation of the contaminant within immobile regions [Goltz and Oxley, 1991:548]. As previously discussed, this term can be modeled assuming that immobile regions do not exist (local equilibrium), or that two region transfer of solute can be described by a first-order rate expression, or that Fickian diffusion governs the transfer of solute within immobile regions of layered, cylindrical, and spherical geometry [Goltz and Oxley, 1991:548-549].

The simplest model used assumes that contaminant transport is through the mobile region only. Sorption is instantaneous. This model, commonly referred to as the local equilibrium assumption, assumes $\beta = 0$ which implies all the water is mobile and therefore it does not account for immobile water regions [Goltz and Oxley, 1991:548].

Another assumption often made is that the transfer of solute between the mobile and immobile region can be described using a first-order rate expression:

$$\frac{\partial C'_{im}(r, t)}{\partial t} = \frac{\alpha'}{\theta_{im} R_{im}} [C'_m(r, t) - C'_{im}(r, t)] \quad (3.11)$$

where α' is a first-order rate constant $[T^{-1}]$. Defining a dimensionless first-order rate constant α as

$$\alpha = \frac{\alpha' 2 \pi b a_1^2}{Q_w \beta} \quad (3.12)$$

and using Equations (3.5) through (3.8) gives the expression

$$\frac{\partial C_{im}(X, T)}{\partial T} = \alpha [C_m(X, T) - C_{im}(X, T)] \quad (3.13)$$

This model assumes that the immobile region is perfectly mixed; thus, the local concentration at all points within the immobile region is the same as the volume-averaged immobile region solute concentration [Goltz and Oxley, 1991:548].

Finally, it is often assumed that the transfer of solute between the mobile and immobile regions is governed by Fickian (Fick's second law) diffusion within immobile regions of specified geometry [Goltz and Oxley, 1991:548-549]. Mathematically, Fick's second law of diffusion describing contaminant transport within the immobile region is

$$R_{im} \frac{\partial C'_s(r, z, t)}{\partial t} = \frac{D'_e}{z^{v-1}} \frac{\partial}{\partial z} \left(z^{v-1} \frac{\partial C'_s(r, z, t)}{\partial z} \right) \quad (3.14)$$

where $0 < z < a$. When $v = 1$ diffusion is assumed to occur through a rectangular or layered immobile region; when $v = 2$, diffusion is assumed to occur through a cylindrical immobile region; and when $v = 3$ diffusion is assumed to occur through a spherical immobile region [Goltz and Oxley, 1991:549; Goltz and Roberts, 1987]. Defining a dimensionless immobile region solute diffusion coefficient, D_e , as

$$D_e = \frac{D'_e a_1^2 2 \pi b \theta_m R_m}{a^2 Q_w R_{im}} \quad (3.15)$$

and the dimensionless immobile region variable, Z , and dimensionless local solute concentration at points within the immobile region, $C_s(X, Z, T)$, as

$$Z = \frac{z}{a} \quad (3.16)$$

$$C_s(X, Z, T) = \frac{C'_s(r, z, t)}{C'_o} \quad (3.17)$$

changes Equation (3.14) to

$$\frac{\partial C_s(X, Z, T)}{\partial T} = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad (3.18)$$

for $0 < Z < 1$ and Equation (3.8) to

$$C_{im}(X, T) = v \int_0^1 Z^{v-1} C_i(X, Z, T) dZ \quad (3.19)$$

Having described the aquifer characteristics, model assumptions, and dimensionless variables, the following initial and boundary conditions can be formulated for the various models.

Initial conditions. The initial conditions are

$$C_m(X, T = 0) = F_m(X) \quad X_w < X < X_1 \quad (3.20)$$

$$C_{im}(X, T = 0) = F_{im}(X) \quad X_w < X < X_1 \quad (3.21)$$

$$C_m(X, T = 0) = C_{im}(X, T = 0) = 0 \quad X > X_1 \quad (3.22)$$

where $F_m(X)$ and $F_{im}(X)$ are dimensionless arbitrary initial concentration conditions in the mobile region and immobile region, respectively. The diffusion models require the following additional initial conditions to describe transport within the immobile regions [Goltz and Oxley, 1991:549-550]:

$$C_i(X, Z, T = 0) = F_i(X, Z) \quad X_w < X < X_1 \quad (3.23)$$

$$C_i(X, Z, T = 0) = 0 \quad X > X_1 \quad (3.24)$$

where $F_i(X, Z)$ is the dimensionless arbitrary initial concentration condition in the immobile region of a certain geometry. Again, Equations (3.20), (3.21), (3.22), (3.23), and (3.24) state the initial conditions, which assume contamination

of mobile and immobile regions at some arbitrary concentration within a cylindrical region of dimensionless radius $X_.$

Boundary Conditions. The outer boundary condition is derived based on the assumption that the total mass flux inward at the outer boundary ($X = X_.$) must always be zero, since initially, there is no contaminant mass at $X > X_.$ That is,

$$C'_m(r, t) + \frac{\partial C'_m}{\partial r}(r, t) = 0 \quad (3.25)$$

using Equations (3.5) and (3.6) changes this expression into dimensionless form:

$$C_m(X, T) + \frac{\partial C_m}{\partial X}(X, T) = 0 \quad (3.26)$$

The boundary condition at the well radius is based on the assumption that at any time, the concentration inside the well bore is equal to that entering the well from surrounding media [Goltz and Oxley, 1991:549]. This implies a zero concentration gradient at the interface between the well and its immediate adjacent aquifer. Thus,

$$\frac{\partial C'_m}{\partial r}(r_w, t) = 0 \quad (3.27)$$

Again, using Equations (3.5) and (3.6) changes this expression into dimensionless form:

$$\frac{\partial C_m}{\partial X}(X_w, T) = 0 \quad (3.28)$$

The diffusion models require additional boundary conditions to describe transport within the immobile regions of certain geometry. We assume that the concentration gradient within an immobile region of certain geometry is zero at the center due to radial symmetry and is equal to the mobile region concentration at its outer boundary. Therefore,

$$\frac{\partial C'_i}{\partial z}(r, z = 0, t) = 0 \quad r_w < r \quad (3.29)$$

$$C'_i(r, z = 1, t) = C'_m(r, t) \quad r_w < r \quad (3.30)$$

or in dimensionless form, using Equation (3.17), gives us

$$\frac{\partial C_i}{\partial Z}(X, Z = 0, T) = 0 \quad X_w < X \quad (3.31)$$

$$C_i(X, Z = 1, T) = C_m(X, T) \quad X_w < X \quad (3.32)$$

Laplace Transform. In this section we introduce a mathematical technique that is often used in the solution of boundary-value problems. This technique is known as the Laplace transform, which converts a boundary-value problem involving a linear differential equation as a function of time into an algebraic problem involving the Laplace transform variable s [Ross, 1980:427]. Ross defines the Laplace transform by

$$F(s) = \int_0^{\infty} e^{-st} f(t) dt \quad (3.33)$$

for all values of s for which the integral exists, where f is a real-valued function of the real variable t , defined for $t > 0$ and s is a variable that is assumed to be real [Ross, 1980:427]. The function F defined by the integral is called the Laplace transform of the function f . The Laplace transform F of f is denoted by $\mathcal{L}\{f\}$ and $F(s)$ by $\mathcal{L}\{f(t)\}$ [Ross, 1980:427].

One of the basic properties of the Laplace transform used in developing the model equations is the Laplace transform of the derivative of f . That is, if f is a real function that is continuous for $t \geq 0$ and of exponential order e^{at} , and f' , the derivative of f , is piecewise continuous in every finite closed interval $0 \leq t \leq b$ then $\mathcal{L}\{f'(t)\}$ exists for $s > a$ [Ross, 1980:435]. Thus,

$$\mathcal{L}\{f'(t)\} = s \mathcal{L}\{f(t)\} - f(0) \quad (3.34)$$

Laplace Solution. In this section we present the general Laplace solution for when an extraction well is on. Details of the derivation can be found at Appendix A.

Taking the Laplace transform of Equation (3.10) together with the appropriate conditions for the various models, yields

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - \gamma X \bar{C}_m = \bar{F}(X, s) \quad (3.35)$$

where the overbar indicates the transformed function and γ and $\bar{F}(X, s)$ are given for the various models as follows.

Local Equilibrium Model (LEA):

$$\gamma = s \quad (3.36)$$

$$\bar{F}(X, s) = -X F_m(X) \quad (3.37)$$

First-Order Rate Model:

$$\gamma = s \left(1 + \frac{\beta \alpha}{s + \alpha} \right) \quad (3.38)$$

$$\bar{F}(X, s) = -X \left(F_m(X) + \frac{\beta \alpha F_m(X)}{s + \alpha} \right) \quad (3.39)$$

Layered Diffusion:

$$\gamma = s \left(1 + \frac{\beta \sinh \omega}{\omega \cosh \omega} \right) \quad (3.40)$$

$$\bar{F}(X, s) = -X \left[F_m(X) + \frac{\beta}{\cosh \omega} \int_0^1 \cosh(\omega \xi) F_s(X, \xi) d\xi \right] \quad (3.41)$$

where $\omega = (s / D_e)^{1/2}$.

Cylindrical Diffusion:

$$\gamma = s \left[1 + \frac{2\beta I_1(\omega)}{\omega I_0(\omega)} \right] \quad (3.42)$$

$$\bar{F}(X, s) = -X \left[F_m(X) + \frac{2\beta}{I_0(\omega)} \int_0^1 \xi I_0(\omega \xi) F_s(X, \xi) d\xi \right] \quad (3.43)$$

where $\omega = (s / D_e)^{1/2}$, and I_0 and I_1 denote the modified Bessel functions of the first kind of order zero and one, respectively.

Spherical Diffusion:

$$\gamma = s \left[1 + \frac{3\beta i_1(\omega)}{\omega i_0(\omega)} \right] \quad (3.44)$$

$$\bar{F}(X, s) = -X \left[F_m(X) + \frac{3\beta}{i_0(\omega)} \int_0^1 \xi^2 i_0(\omega\xi) F_i(X, \xi) d\xi \right] \quad (3.45)$$

where $\omega = (s / D_e)^{1/2}$, and i_0 and i_1 denote the modified spherical Bessel functions of the first kind of order zero and one, respectively.

Green's Function. Now assume that Equation (3.35) has a solution of the form

$$\bar{C}_m(X, s) = \phi(X, s) e^{-\frac{1}{2}X} \quad (3.46)$$

Substituting Equation (3.46) into Equation (3.35) yields

$$\frac{d^2\phi}{dX^2} - \gamma \phi \left[X + \frac{1}{4\gamma} \right] = e^{\frac{1}{2}X} \bar{F}(X, s) \quad (3.47)$$

and upon letting $y = \gamma^{\frac{1}{3}} [X + (1 / 4\gamma)]$, and

$$\Phi(y, s) = \phi(X, s) = \phi\left(\gamma^{-\frac{1}{3}} y - 1 / (4\gamma), s\right) \quad , \text{Equation (3.35)}$$

becomes

$$\frac{d^2\Phi}{dy^2} - y\Phi = \gamma^{-2/3} \exp\left[\frac{1}{2}\left(\gamma^{-\frac{1}{3}} y - \frac{1}{4\gamma}\right)\right] \bar{F}\left(\gamma^{-\frac{1}{3}} y - \frac{1}{4\gamma}, s\right) \equiv \mathcal{J}(y, s) \quad (3.48)$$

for $y_w < y < y_*$ where Φ is now a function of y and s . If we also substitute Equation (3.46), and use the above definitions for $y = y_w$, $y = y_*$, into Equations (3.26) and (3.28) we get the boundary conditions

$$-\frac{1}{2} \Phi(y_w) + \gamma^{\frac{1}{3}} \frac{d\Phi}{dy}(y_w) = 0 \quad (3.49)$$

$$\frac{1}{2} \Phi(y_*) + \gamma^{\frac{1}{3}} \frac{d\Phi}{dy}(y_*) = 0 \quad (3.50)$$

It is well known that Equation (3.48) has a solution of the form [Ritger and Rose, 1968]

$$\Phi(y, s) = \int_{y_w}^{y_*} g(y, \eta, s) \mathcal{J}(\eta, s) d\eta \quad (3.51)$$

where $g(y, \eta, s)$ is the Green's function given by

$$g(y, \eta, s) = \begin{cases} \frac{\Phi_1(y) \Phi_2(\eta)}{W[\Phi_1, \Phi_2](\eta)} & y \leq \eta \leq y. \\ \frac{\Phi_1(\eta) \Phi_2(y)}{W[\Phi_1, \Phi_2](\eta)} & y_w \leq \eta \leq y \end{cases} \quad (3.52)$$

where Φ_1 satisfies Equations (3.48) and (3.49), Φ_2 satisfies Equations (3.48) and (3.50), $W[\Phi_1, \Phi_2](\eta)$ is the Wronskian of Φ_1 and Φ_2 . If we define the following operators, G and H , as

$$G[Ai](y_w) = -\frac{1}{2} Ai(y_w) + \gamma^{\frac{1}{3}} \frac{dAi}{dy}(y_w) \quad (3.53)$$

$$G[Bi](y_w) = -\frac{1}{2} Bi(y_w) + \gamma^{\frac{1}{3}} \frac{dBi}{dy}(y_w) \quad (3.54)$$

$$H[Ai](y.) = \frac{1}{2} Ai(y.) + \gamma^{\frac{1}{3}} \frac{dAi}{dy}(y.) \quad (3.55)$$

$$H[Bi](y.) = \frac{1}{2} Bi(y.) + \gamma^{\frac{1}{3}} \frac{dBi}{dy}(y.) \quad (3.56)$$

where Ai and Bi are Airy and Bairy functions, respectively, then,

$$\Phi_1(y) = G[Bi](y_w) Ai(y) - G[Ai](y_w) Bi(y) \quad (3.57)$$

$$\Phi_2(y) = H[Bi](y.) Ai(y) - H[Ai](y.) Bi(y) \quad (3.58)$$

and the value of the Wronskian is

$$W[\Phi_1, \Phi_2](y) = \left[\frac{G[Ai](y_w)}{G[Bi](y_w)} - \frac{H[Ai](y.)}{H[Bi](y.)} \right] \frac{1}{\pi} \quad (3.59)$$

Substituting Equations (3.57), (3.58), and (3.59) into Equation (3.52) yields

$$g(y, \eta) = \begin{cases} \frac{\pi[G[Bi](y_w)Ai(y) - G[Ai](y_w)Bi(y)][H[Bi](y.)Ai(\eta) - H[Ai](y.)Bi(\eta)]}{G[Ai](y_w)H[Bi](y.) - G[Bi](y_w)H[Ai](y.)} \\ \frac{\pi[G[Bi](y_w)Ai(\eta) - G[Ai](y_w)Bi(\eta)][H[Bi](y.)Ai(y) - H[Ai](y.)Bi(y)]}{G[Ai](y_w)H[Bi](y.) - G[Bi](y_w)H[Ai](y.)} \end{cases} \quad (3.60)$$

where the top expression is defined for the interval $y < \eta \leq y.$
and the bottom expression is defined for the interval
 $y_w \leq \eta < y.$ Since $y = \gamma^{\frac{1}{3}}[X + (1/4\gamma)]$ then

$$\eta = \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]; d\eta = \gamma^{\frac{1}{3}} d\xi \quad (3.61)$$

Thus, Equation (3.51) becomes

$$\phi(X) = \int_{x_w}^{x.} g\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right], \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \mathcal{F}\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \gamma^{\frac{1}{3}} d\xi \quad (3.62)$$

or alternatively, using $\bar{C}_m(X, s) = \phi(X, s) e^{-\frac{1}{2}X}$ from Equation (3.46)

$$\bar{C}_m(X, s) = e^{-\frac{1}{2}X} \int_{x_0}^{x_1} g\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right], \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \gamma^{-\frac{1}{3}} e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \quad (3.63)$$

If we define

$$b(X, \xi, s) = g\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right], \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \quad (3.64)$$

then

$$\bar{C}_m(X, s) = e^{-\frac{1}{2}X} \int_{x_0}^{x_1} b(X, \xi, s) \gamma^{-\frac{1}{3}} e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \quad (3.65)$$

Substituting in the constructed Green's function from Equation (3.60) gives us

$$\bar{C}_m(X, s) = \left\{ \frac{\pi e^{-\frac{1}{2}X} \gamma^{-\frac{1}{3}}}{G[Ai](y_w)H[Bi](y_*) - G[Bi](y_w)H[Ai](y_*)} \right\} \cdot$$

$$\begin{aligned} & \left\{ G[Bi](y_w)H[Bi](y_*)Ai\left[\gamma^{\frac{1}{3}}\left(X + \frac{1}{4\gamma}\right)\right] \int_{x_*}^x Ai\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \right. \\ & - G[Bi](y_w)H[Ai](y_*)Bi\left[\gamma^{\frac{1}{3}}\left(X + \frac{1}{4\gamma}\right)\right] \int_{x_*}^x Ai\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \\ & + G[Ai](y_w)H[Ai](y_*)Bi\left[\gamma^{\frac{1}{3}}\left(X + \frac{1}{4\gamma}\right)\right] \int_{x_*}^x Bi\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \\ & - G[Ai](y_w)H[Bi](y_*)Ai\left[\gamma^{\frac{1}{3}}\left(X + \frac{1}{4\gamma}\right)\right] \int_{x_*}^x Bi\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \\ & + G[Bi](y_w)H[Bi](y_*)Ai\left[\gamma^{\frac{1}{3}}\left(X + \frac{1}{4\gamma}\right)\right] \int_x^{x_*} Ai\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \\ & - G[Ai](y_w)H[Bi](y_*)Bi\left[\gamma^{\frac{1}{3}}\left(X + \frac{1}{4\gamma}\right)\right] \int_x^{x_*} Ai\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \\ & + G[Ai](y_w)H[Ai](y_*)Bi\left[\gamma^{\frac{1}{3}}\left(X + \frac{1}{4\gamma}\right)\right] \int_x^{x_*} Bi\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \\ & \left. - G[Bi](y_w)H[Ai](y_*)Ai\left[\gamma^{\frac{1}{3}}\left(X + \frac{1}{4\gamma}\right)\right] \int_x^{x_*} Bi\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \right\} \end{aligned}$$

(3.66)

Model Formulation: Extraction Well Off. If we now consider turning off the extraction well ($Q_w = 0$) after a certain period of time, say $\hat{T}$, then the mobile region dispersion coefficient, $D_m = 0$ (Equation (3.1)), and the molecular diffusion coefficient, D'_o , becomes the dominant transport mechanism. As a result, Equation (3.1) becomes

$$\frac{\partial C'_m(r, t)}{\partial t} = \frac{D'_o}{R_m} \frac{1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial C'_m(r, t)}{\partial r} \right] - \beta \frac{\partial C'_{im}(r, t)}{\partial t} \quad (3.67)$$

If we define the dimensionless variables

$$X = \frac{r}{a} \sqrt{\frac{D'_o R_m}{D'_o R_{im}}} \quad (3.68)$$

$$T = \frac{D'_o t}{R_{im} a^2} \quad (3.69)$$

then Equation (3.67) becomes

$$\frac{\partial C_m(X, T)}{\partial T} = \frac{\partial^2 C_m(X, T)}{\partial X^2} + \frac{1}{X} \frac{\partial C_m(X, T)}{\partial X} - \beta \frac{\partial C_{im}(X, T)}{\partial T} \quad (3.70)$$

Notice that this X and T are different from those defined in Equations (3.5) and (3.6). Similarly, if we define

$$Z = \frac{z}{a} \quad (3.71)$$

which is the same as previously defined in Equation (3.16), then Equation (3.14) becomes

$$\frac{\partial C_s(X, Z, T)}{\partial T} = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (3.72)$$

To attain a form of the solution when the extraction well is off, we will assume that the arbitrary initial conditions are of the same form as the initial conditions when the well is on, except for two significant differences. First, the initial conditions are at some later time, $T = \hat{T}$, rather than at time $T = 0$. This time ($\hat{T}$) reflects the contaminant concentration in the mobile and immobile regions at the time the extraction well is turned off. Thus, the initial conditions at $\hat{T}$ are the terminal conditions for the pump on. Second, the dimensionless variables, X , X_w , X_i , and T take on a different meaning and form from the pump on case. From Equation (3.68) we have

$$X_w = \frac{r_w}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{im}}} \quad (3.73)$$

$$X_i = \frac{r_i}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{ia}}} \quad (3.74)$$

Thus, the form of Equations (3.20), (3.21), (3.22), (3.23), and (3.24) are applicable as the initial conditions for when an extraction well is off.

The boundary condition at the well for the pump on case is still assumed to be applicable when the pump is off (Equation (3.28)). That is, we assume that the concentration inside the well bore is equal to that entering the well from the surrounding media. Similarly, the boundary conditions within the immobile regions of layered, cylindrical, and spherical geometry remain as stated in Equations (3.31) and (3.32).

The outer boundary condition is modified to allow for leakage of the contaminant, since molecular diffusion is assumed to be the dominant mechanism responsible for transport. Thus, we assume that the total mass flux outward at the outer boundary of the contamination region (r_o) is proportional to the amount of the contaminant mass present in the mobile region. Mathematically, this boundary condition is represented as

$$\epsilon \frac{\partial C_m(X_o, \hat{T})}{\partial X} - C_m(X_o, \hat{T}) = 0 \quad (3.75)$$

where ϵ represents the coefficient of leakage [dimensionless] of the contaminant through the outer boundary. Refer to Appendix A for the derivation of this boundary condition.

Laplace Solution. As previously discussed, using the Laplace transform, the general Laplace solution for when an extraction well is off is derived. Details of the derivation can be found at Appendix A.

Combining the Laplace transform of Equation (3.70) together with the appropriate conditions for the various models, yields

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \gamma \bar{C}_m = \bar{F}(X, s) \quad (3.76)$$

where the overbar indicates the transformed function and γ and $\bar{F}(X, s)$ are given for the various models as follows.

Local Equilibrium Model (LEA):

$$\gamma = s \quad (3.77)$$

$$\bar{F}(X, s) = -F_m(X) \quad (3.78)$$

First-Order Rate Model:

$$\gamma = s \left(1 + \frac{\beta \alpha}{s + \alpha} \right) \quad (3.79)$$

$$\bar{F}(X, s) = - \left(F_m(X) + \frac{\beta \alpha F_m(X)}{s + \alpha} \right) \quad (3.80)$$

Layered Diffusion:

$$\gamma = s \left(1 + \frac{\beta \sinh \omega}{\omega \cosh \omega} \right) \quad (3.81)$$

$$\bar{F}(X, s) = - \left[F_m(X) + \frac{\beta}{\cosh \omega} \int_0^1 \cosh(\omega \xi) F_s(X, \xi) d\xi \right] \quad (3.82)$$

where $\omega = (s)^{1/2}$.

Cylindrical Diffusion:

$$\gamma = s \left[1 + \frac{2\beta I_1(\omega)}{\omega I_0(\omega)} \right] \quad (3.83)$$

$$\bar{F}(X, s) = -[F_m(X) + \frac{2\beta}{I_0(\omega)} \int_0^1 \xi I_0(\omega \xi) F_*(X, \xi) d\xi] \quad (3.84)$$

where $\omega = (s)^{1/2}$, and I_0 and I_1 denote the modified Bessel functions of the first kind of order zero and one, respectively.

Spherical Diffusion:

$$\gamma = s \left[1 + \frac{3\beta i_1(\omega)}{\omega i_0(\omega)} \right] \quad (3.85)$$

$$\bar{F}(X, s) = -[F_m(X) + \frac{3\beta}{i_0(\omega)} \int_0^1 \xi^2 i_0(\omega \xi) F_*(X, \xi) d\xi] \quad (3.86)$$

where $\omega = (s)^{1/2}$, and i_0 and i_1 denote the modified spherical Bessel functions of the first kind of order zero and one, respectively.

Green's Function. As before, we construct a Green's function by assuming that Equation (3.76) has a solution of the form

$$\bar{C}_m(X, s) = \phi(X, s) \quad (3.87)$$

such that this solution satisfies the differential equation (Equation (3.76)) and the boundary conditions (Equations (3.28) and (3.75)). Substituting Equation (3.87) into Equation (3.76) yields

$$\frac{d^2\phi(X, s)}{dX^2} + \frac{1}{X} \frac{d\phi(X, s)}{dX} - \gamma \phi(X, s) = \bar{F}(X, s) \quad (3.88)$$

and upon letting $y = \gamma^{1/2} X$, and $\phi(X, s) = \phi(\gamma^{1/2} y, s) \equiv \Phi(y, s)$, Equation (3.88) becomes

$$\frac{d^2\Phi(y, s)}{dy^2} + \frac{1}{y} \frac{d\Phi(y, s)}{dy} - \Phi(y, s) = \frac{1}{\gamma} \mathcal{F}(y, s) \quad (3.89)$$

for $y_w < y < y_*$, where $\mathcal{F}(y, s) = \bar{F}(\gamma^{1/2} y, s)$ and Φ is now a function of y and s . If we also substitute Equation (3.87), and use the above definitions for $y = y_w$, $y = y_*$, into Equations (3.28) and (3.75) we get the boundary conditions

$$\frac{d\Phi}{dy}(y_w, s) = 0 \quad (3.90)$$

$$\epsilon \gamma^{1/2} \frac{d\Phi}{dy}(y_*, s) - \Phi(y_*, s) = 0 \quad (3.91)$$

It is well known that Equation (3.89) has a solution of the form [Ritger and Rose, 1968]

$$\Phi(y, s) = \int_{y_w}^{y_*} g(y, \eta, s) \mathcal{F}(\eta, s) d\eta \quad (3.92)$$

where $g(y, \eta, s)$ is the Green's function given by

$$g(y, \eta, s) = \begin{cases} \frac{\Phi_1(y) \Phi_2(\eta)}{W[\Phi_1, \Phi_2](\eta)} & y \leq \eta \leq y. \\ \frac{\Phi_1(\eta) \Phi_2(y)}{W[\Phi_1, \Phi_2](\eta)} & y_w \leq \eta \leq y \end{cases} \quad (3.93)$$

where Φ_1 satisfies Equation (3.89) and (3.90), Φ_2 satisfies Equation (3.89) and (3.91) and $W[\Phi_1, \Phi_2](\eta)$ is the Wronskian of Φ_1 and Φ_2 . Thus,

$$\Phi_1(y, s) = -K'_0(y_w) I_0(y) + I'_0(y_w) K_0(y) \quad (3.94)$$

$$\Phi_2(y, s) = H[K_1, K_0](y.) I_0(y) + G[I_1, I_0](y.) K_0(y) \quad (3.95)$$

where K_0 and I_0 are modified Bessel functions of the third kind order zero and first kind order zero, respectively, and I_1 is a Bessel function of the first kind order one and is equal to I'_0 , and K_1 is a Bessel function of the third kind order one and is equal to $-K'_0$ [Abramowitz and Stegun, 1970]. Also, G and H are operators defined by

$$G[I_1, I_0](y.) = \epsilon \gamma^{\frac{1}{2}} I_1(y.) - I_0(y.) \quad (3.96)$$

$$H[K_1, K_0](y.) = \epsilon \gamma^{\frac{1}{2}} K_1(y.) + K_0(y.) \quad (3.97)$$

and the value of the Wronskian is

$$W[\Phi_1, \Phi_2](y) = \frac{1}{y} [I_1(y_w) H[K_1, K_0](y.) - K_1(y_w) G[I_1, I_0](y.)] \quad (3.96)$$

Substituting Equations (3.94), (3.95), and (3.98) into Equation (3.93) yields

$$g(y, \eta, s) = \begin{cases} \frac{\eta [K_1(y_w) I_0(y) + I_1(y_w) K_0(y)] [H[K_1, K_0](y.) I_0(\eta) + G[I_1, I_0](y.) K_0(\eta)]}{I_1(y_w) H[K_1, K_0](y.) - K_1(y_w) G[I_1, I_0](y.)} \\ \frac{\eta [K_1(y_w) I_0(\eta) + I_1(y_w) K_0(\eta)] [H[K_1, K_0](y.) I_0(y) + G[I_1, I_0](y.) K_0(y)]}{I_1(y_w) H[K_1, K_0](y.) - K_1(y_w) G[I_1, I_0](y.)} \end{cases} \quad (3.99)$$

where the top expression is defined for the interval $y \leq \eta \leq y.$ and the bottom expression is defined for the interval $y_w \leq \eta \leq y.$ Since $\Phi(y) = \phi(X)$ then

$$\eta = \gamma^{\frac{1}{3}} \xi; d\eta = \gamma^{\frac{1}{3}} d\xi \quad (3.100)$$

Thus, Equation (3.89) becomes

$$\phi(y, s) = \int_{x_w}^{x.} g\left(\gamma^{\frac{1}{2}} X, \gamma^{\frac{1}{2}} \xi, s\right) \mathcal{F}\left(\gamma^{\frac{1}{2}} \xi, s\right) \gamma^{\frac{1}{2}} d\xi \quad (3.101)$$

Since $\bar{C}_m(X, s) = \phi(y, s)$ (Equation (3.87)), then

$$\bar{C}_m(X, s) = \int_{x_0}^{x_1} g\left(\gamma^{\frac{1}{2}} X, \gamma^{\frac{1}{2}} \xi, s\right) \gamma^{-\frac{1}{2}} \bar{F}(\xi, s) d\xi \quad (3.102)$$

If we define

$$b(X, \xi, s) = g\left(\gamma^{\frac{1}{2}} X, \gamma^{\frac{1}{2}} \xi, s\right) \quad (3.103)$$

then

$$\bar{C}_m(X, s) = \int_{x_0}^{x_1} b(X, \xi, s) \gamma^{-\frac{1}{2}} \bar{F}(\xi, s) d\xi \quad (3.104)$$

Substituting in the constructed Green's function (Equation (3.99)) gives us

$$\bar{C}_m(x, s) = \left\{ \frac{1}{I_1(y_w)H[K_1, K_0](y_*) - K_1(y_w)G[I_1, I_0](y_*)} \right\} \cdot$$

$$\begin{aligned} & \left\{ \left[H[K_1, K_0](y_*)I_0(\gamma^{\frac{1}{2}}X) + G[I_1, I_0](y_*)K_0(\gamma^{\frac{1}{2}}X) \right] K_1(y_w) \int_{x_*}^x \xi I_0(\gamma^{\frac{1}{2}}\xi) \bar{F}(\xi, s) d\xi \right. \\ & + \left[H[K_1, K_0](y_*)I_0(\gamma^{\frac{1}{2}}X) + G[I_1, I_0](y_*)K_0(\gamma^{\frac{1}{2}}X) \right] I_1(y_w) \int_{x_*}^x \xi K_0(\gamma^{\frac{1}{2}}\xi) \bar{F}(\xi, s) d\xi \\ & + \left[K_1(y_w)I_0(\gamma^{\frac{1}{2}}X) + I_1(y_w)K_0(\gamma^{\frac{1}{2}}X) \right] H[K_1, K_0](y_*) \int_x^{x_*} \xi I_0(\gamma^{\frac{1}{2}}\xi) \bar{F}(\xi, s) d\xi \\ & \left. + \left[K_1(y_w)I_0(\gamma^{\frac{1}{2}}X) + I_1(y_w)K_0(\gamma^{\frac{1}{2}}X) \right] G[I_1, I_0](y_*) \int_x^{x_*} \xi K_0(\gamma^{\frac{1}{2}}\xi) \bar{F}(\xi, s) d\xi \right\} \end{aligned}$$

(3.105)

IV. Analysis and Evaluation of Results

Introduction

This chapter presents results using a computer model based on the analysis developed in Chapter III. First, a discussion of the numerical techniques and difficulties encountered in coding the analytical solutions is presented. Then, model simulations, showing the transport and fate of a contaminant undergoing pulsed and continuous pumping, are presented for varying initial conditions. Finally, model verification is attempted by comparing model results with two existing models that incorporate rate-limited sorption and desorption.

Numerical Evaluation

Because of the complex nature of the Laplace solutions presented in Chapter III (Equations (3.66) and (3.105)), the formula translation (FORTRAN) language was used. Being one of the older scientific computer languages, the FORTRAN language has the advantage of accessing large mathematical libraries. Incorporating sophisticated, well-tested functions and routines from these libraries, the model is able to numerically solve the Laplace solutions. Specifically, the model uses the Stehfest algorithm [Stehfest, 1970], Gauss-Quadrature integration [Press and others, 1992], and the International Mathematical and Statistical Library (IMSL) function package SFUN [International Mathematical and Statistical Library, 1989]. For detailed

information concerning the model's numerical and logical architecture, refer to the systems level flowchart at Appendix B and the FORTRAN source code at Appendix C.

Laplace Inversion. As stated in Chapter III, the primary objective of this research is to develop a working computer model describing contaminant transport by means of radial advection, dispersion, and sorption/desorption in an aquifer undergoing pulsed pumping operations.

As shown in Chapter III, the solutions used to develop the code are in the Laplace domain. Therefore, the primary purpose of the model is to numerically invert these analytical Laplace solutions. The Stehfest algorithm was selected for this purpose since it was easy to implement and was successfully used in a previous analytical model [Goltz and Oxley, 1991].

The Stehfest algorithm approximates the inverse of a function, $P(s)$, according to the approximation equation

$$F_i = \frac{\ln(2)}{T} \sum_{i=1}^N V_i P\left(\frac{\ln(2)}{T} i\right) \quad (4.1)$$

where T is the time, N is an even numbered integer variable affecting the precision, and V_i is a weight function defined by

$$V_i = (-1)^{\left(\frac{N}{2} + i\right)} \sum_{k=\left[\frac{i+1}{2}\right]}^{\min\left(i, \frac{N}{2}\right)} \frac{k^{\frac{N}{2}+1} (2k)!}{\left(\frac{N}{2} - k\right)! k! (k-1)! (i-k)! (2k-i)!} \quad (4.2)$$

The even number integer variable N has been shown to offer maximum precision at a value of 18 for double precision calculations [Stehfest, 1970]. However, precision is also affected by function smoothness. Function discontinuities, sharp fluctuations, or ill-behaved oscillatory behavior can adversely affect the reliability of the Stehfest approximations [Stehfest, 1970]. For functions with unknown smoothness characteristics, Stehfest suggests varying N and comparing results to determine the optimum value. Since this model's Laplace domain equations are difficult to characterize in terms of smoothness, the model was run at various N values to quantitatively gauge Stehfest precision. The results suggest that all models converge on a unique limit at $N = 18$. At higher N values, rounding errors resulted and produced inconsistent model calculations. According to Stehfest, more accuracy should be achieved the greater the N value but numerical errors can be expected if N becomes too large [Stehfest, 1970:48].

Gauss-Quadrature Integration. In addition to numerical techniques to invert the Laplace solutions, the model needed a numerical integration technique to solve key integral expressions (Equations (3.66) and (3.105)). These integral expressions contained both exponential and exponentially-behaved functions. Having a characteristic sharp rise near one end-point, these expressions are sensitive to integration point

selection. Therefore, a numerical integration method that optimized point selection was needed.

The Gauss-Quadrature integration technique offers optimum integration accuracy for a given number of integration points. Although it is sensitive to function smoothness, it does provide greater or equivalent accuracy with approximately one-half the points of other methods. Logically then, Gauss-Quadrature was selected as the model's numerical integration technique [Press and others, 1992:140].

Cubic-Spline Interpolation. Since Gauss-Quadrature requires the flexibility to select its own integration points, a problem developed by incorporating arbitrary initial conditions into the model. Input as discrete points, the initial conditions are included in several integral expressions. To satisfy Gauss-Quadrature requirements, these points must emulate a function. Therefore, an interpolation routine was required.

Recalling that the Stehfest and Gauss-Quadrature algorithms are sensitive to function smoothness, interpolation smoothness was deemed necessary. Cubic-spline interpolation was selected because it offers smoothness in the first derivative and continuity in the second derivative. With cubic-spline interpolation, numerical errors due to Gauss-Quadrature integration and Laplace inversion routines are not aggravated.

Numerical Difficulties. Underflow and overflow errors initially posed a significant barrier to evaluating model solutions. The Bessel functions in the analytic solutions are

very sensitive to the argument size due to their exponential nature. Using exponentially scaled IMSL Bessel function routines, Equations (3.66) and (3.105) were rearranged to protect against underflow and overflow.

Another difficulty or limitation associated with the model is the long run-time. Currently, the time to evaluate aquifer solute concentrations at ten radial locations out from the well, ten time steps, six immobile region locations, and two pump on and off cycles, exceeds 24 hours on a 486DX personal computer. However, the run-time does fall to six or seven hours on a DEC VAX mainframe. These long run-times are due in part to the high-order requirements of integrating certain integrand expressions.

As previously discussed, certain integrand expressions, such as in Equation (3.99), have a shape heavily influenced by the modified Bessel function I_0 . When the Gauss-Quadrature routine is invoked to evaluate these integrals, high order must be used to insure that the significant area under the curve is adequately sampled. Figure 4.1 demonstrates that as the length of the integration interval rises, the function's exponential curve moves farther to the right. This characteristic reduces the number of Gauss-Quadrature sampling points under the significant region of the curve.

Model Simulations

As previously mentioned, the source code was designed to run pulsed pumping or continuous pumping simulations based on the

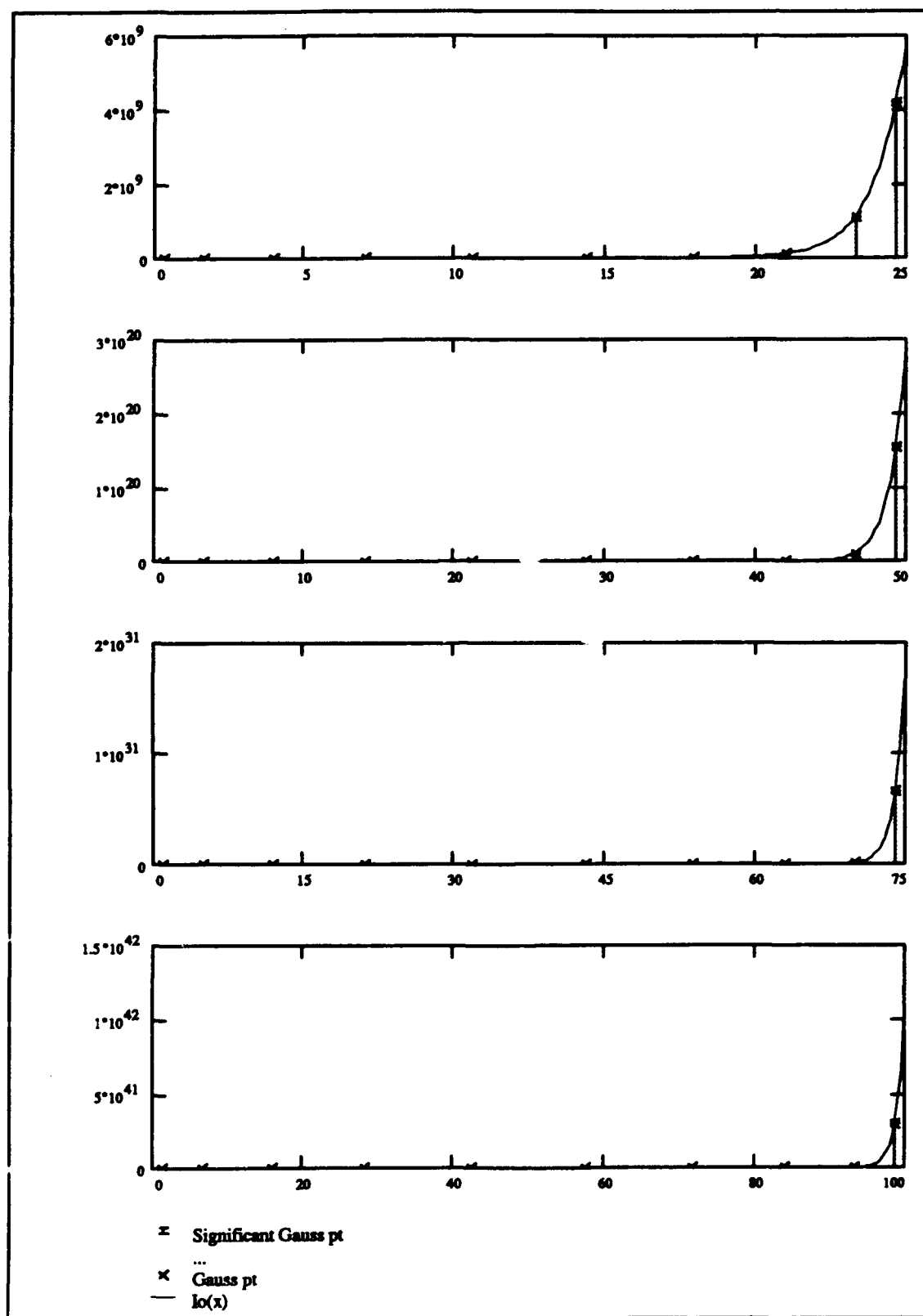


Figure 4.1 10-Point Gauss-Quadrature Sampling of $I_0(x)$

five assumptions presented in Chapter III and formulated in Appendix A. To demonstrate the capability of the code, two simulations were conducted. The first simulation was an internal comparison between pulsed pumping and continuous pumping remediation where sorption/desorption was controlled by diffusion within layered immobile water regions and the initial concentration distribution is constant throughout the aquifer. The second simulation was designed to track the migration of an arbitrary initial concentration profile under continuous pumping with the same sorption/desorption parameters as in the first simulation.

Pulsed versus Continuous Pumping. In this simulation, model comparisons were made between pulsed pumped and continuous pumped aquifers. The pulsed pump simulation consisted of cycling the pump on and off at 100 day intervals for a total duration of 400 days. The pumping rate was constant for both pulsed (when on) and continuous pumping, and the layered diffusion model was assumed. Other input parameters for this simulation are shown at Table 4.1.

Table 4.1

Input Parameters for the Layered Diffusion Simulation

Q_w (m ³ / d)	θ	ϕ	D_e (m ² / d)	b (m)	ρ (gm / cm ³)	f	a (m)	a_1 (m)	K_d (gm / cm ³)
1000.0	0.42	0.5	9.936E-6	10.0	1.81	0.4	0.05	0.5	1.48

The initial mobile and immobile contaminant concentration distributions were set at 1.0 (dimensionless) throughout the 56 meter diameter site of contamination and 0.0 for both mobile and immobile regions outside the site boundaries. In the case of the pulsed pumping simulation, the terminal conditions for both the mobile and immobile regions for the current interval became the initial conditions for each successive interval.

Figures 4.2 and 4.3 show the mobile effluent concentration profile at all radial locations for the pulsed pump and continuous pump simulations. However, for purposes of brevity, our analysis is restricted at the well. Table 4.2 shows the effluent concentration profile at the well for both the pulsed and continuous pumping simulations, and Figure 4.4 shows the graphical representation.

Table 4.2

Mobile Concentration Comparison at the Well

Day	Pulsed	Continuous	Day	Pulsed	Continuous
10	.9999	.9999	210	.1728	.0400
20	.9936	.9936	220	.1564	.0394
30	.6750	.6750	230	.0979	.0383
40	.2978	.2978	240	.0576	.0374
50	.1464	.1464	250	.0449	.0364
60	.1045	.1045	260	.0411	.0356
70	.0906	.0906	270	.0392	.0349
80	.0816	.0816	280	.0377	.0342
90	.0738	.0738	290	.0364	.0335
100	.0673	.0673	300	.0353	.0329
110	.0932	.0606	310	.0497	.0319
120	.1016	.0580	320	.0553	.0317
130	.1140	.0549	330	.0630	.0310
140	.1272	.0523	340	.0714	.0305
150	.1398	.0500	350	.0797	.0300
160	.1516	.0479	360	.0876	.0295
170	.1625	.0461	370	.0951	.0291
180	.1726	.0445	380	.1022	.0287
190	.1822	.0431	390	.1090	.0283
200	.1911	.0418	400	.1156	.0279

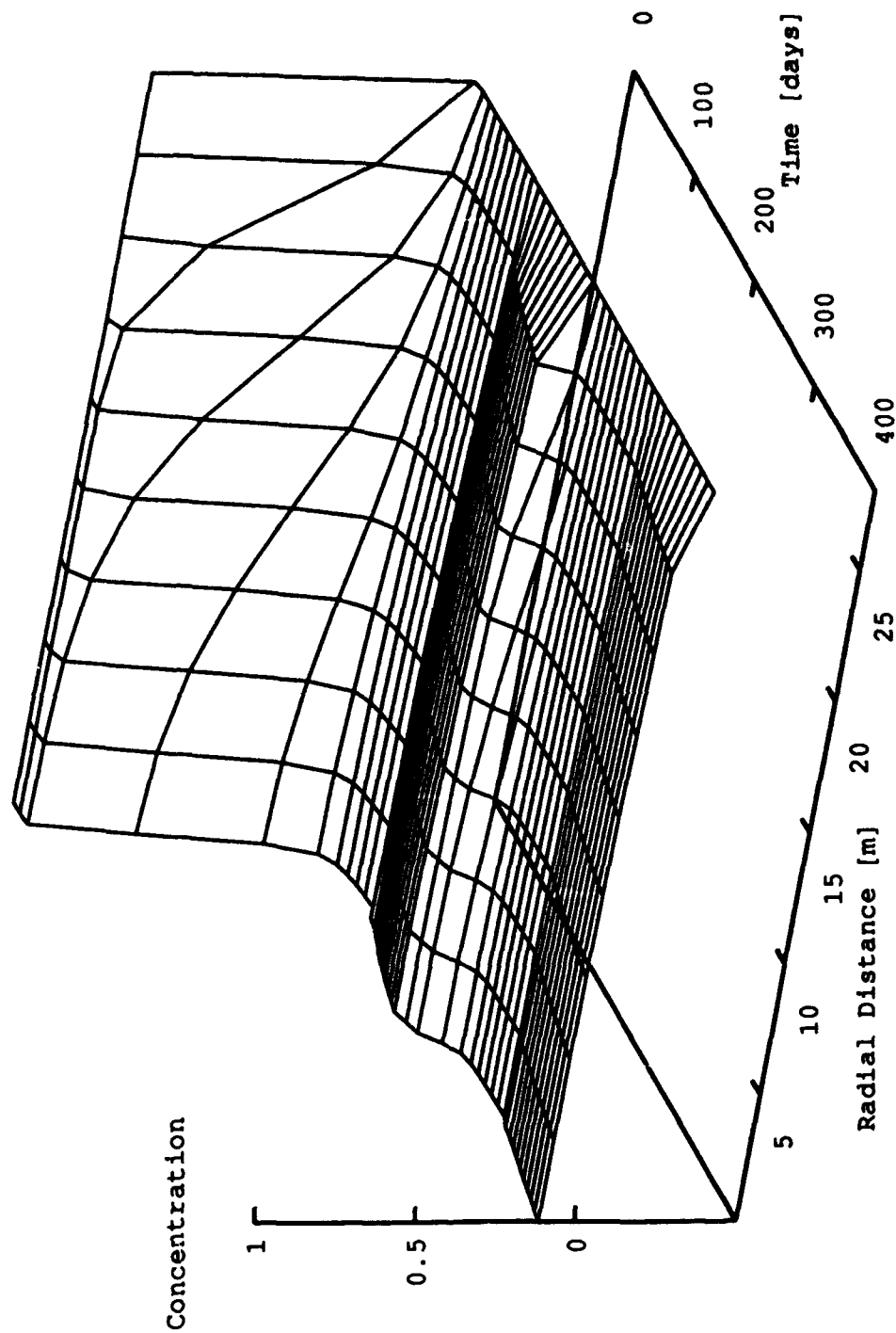


Figure 4.2. Pulsed Pumping Effluent Concentration Profile When Sorption/Desorption is Controlled by Diffusion Within Layers

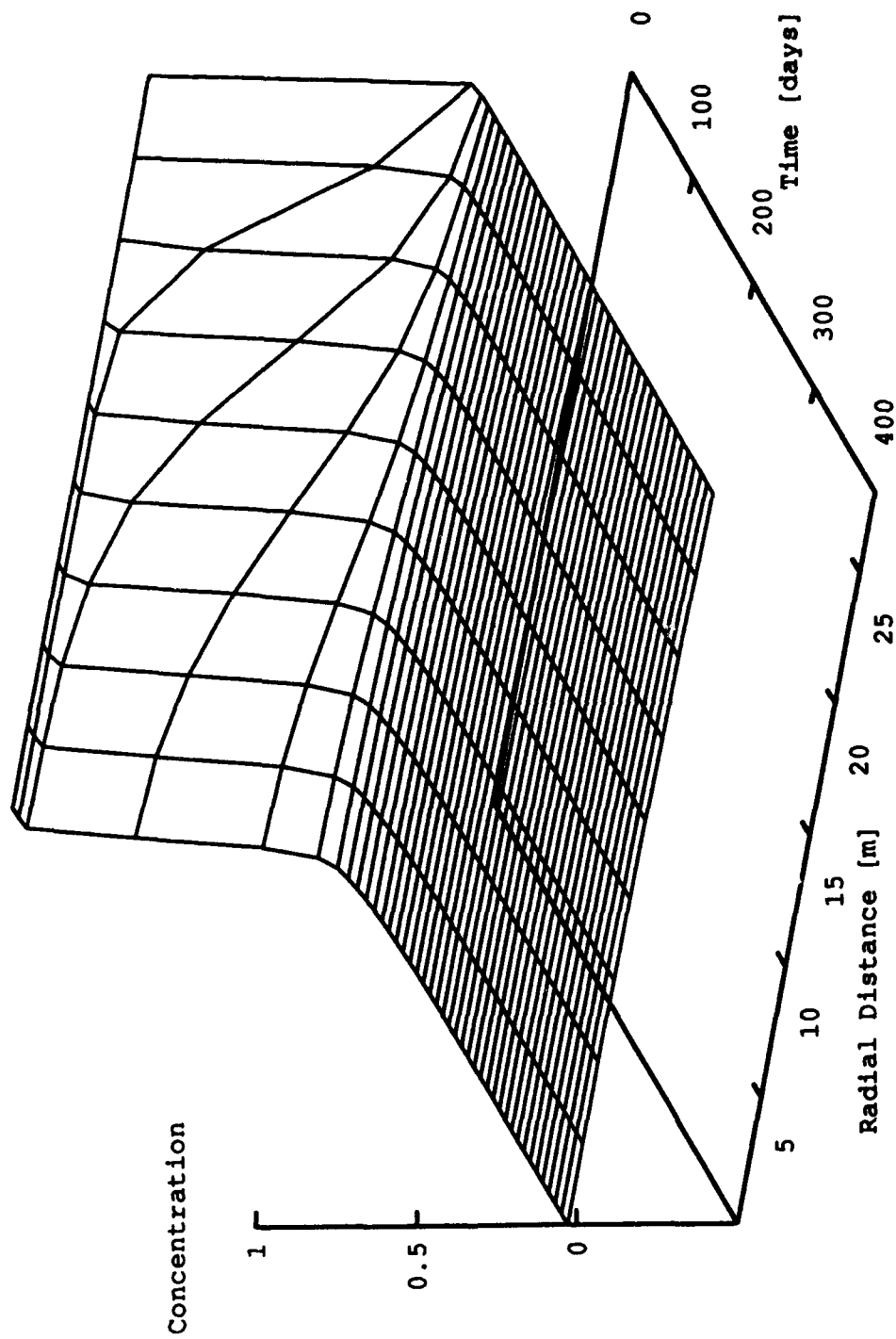


Figure 4.3. Continuous Pumping Effluent Concentration Profile When Sorption/Desorption is Controlled by Diffusion Within Layers

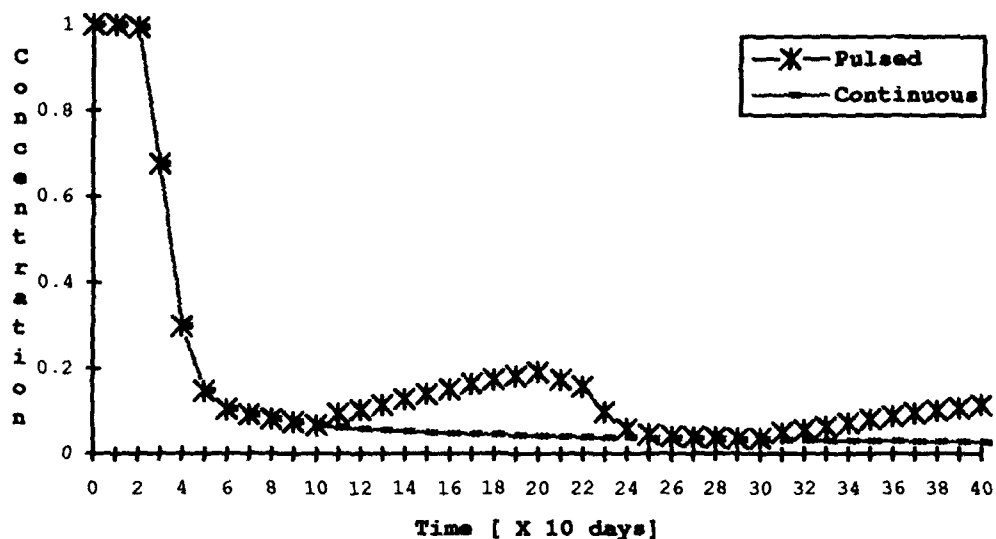


Figure 4.4. Effluent Concentration Profile for Pulsed Versus Continuous Pumping Comparison at the Well When Sorption/Desorption is Controlled by Diffusion Within Layers

As can be seen from Table 4.2 and Figure 4.4, the layered diffusion model initially shows a high removal of the contaminant in the mobile region, an early breakthrough after about 20 days, and eventually a tailing off to a concentration as low as 0.0673. During the second 100 day interval, a further decrease in the mobile concentration is seen for the continuous pump simulation

In the case of pulsed pumping, the pump is turned off during the second 100 day interval and, as can be seen from Figure 4.4, the solute concentration begins to rise or 'rebound'. This is not surprising since this phenomenon has already been observed by other researchers [Keely and others, 1987:91; Mackay and Cherry, 1989:633; Travis and Doty, 1990:1465].

To understand why this rebound phenomenon was occurring and to see if the model was simulating the physics of this phenomenon, the model tracked the immobile concentration profile. Tables 4.3 and 4.4 show the immobile region concentration profile at the well for both the pulsed and continuous pumping simulations at 100 days and 200 days, respectively. At the end of the first 100 day interval (pump on) the immobile region concentration profile showed that a significant amount of the contaminant remained in the immobile regions at all radial locations. Thus, when the pump is turned off, the contaminant slowly diffused from the immobile regions into the mobile region accounting for the rebound in concentration.

Table 4.3

Immobile Region Concentration Comparison
(Pulsed Versus Continuous Pumping at the well - at day 100)

Radial Distance	Pulsed	Continuous
0.0	.9998	.9998
0.2	.9987	.9987
0.4	.9858	.9858
0.6	.9055	.9055
0.8	.6212	.6212
1.0	.0673	.0673

Table 4.4

Immobile Region Concentration Comparison
(Pulsed Versus Continuous Pumping at the well - at day 200)

Radial Distance	Pulsed	Continuous
0.0	.9807	.9806
0.2	.9607	.9604
0.4	.8855	.8831
0.6	.7244	.7113
0.8	.4729	.4214
1.0	.1911	.0418

After 200 days, mobile (Table 4.2) and immobile (Table 4.4) region concentrations are lower in the continuous pumping case. This indicates that continuous pumping is more effective than pulsed pumping in removing the contaminant over time.

After 300 days, the immobile contaminant concentrations are not significantly different between the pulsed pumped and continuously pumped aquifers (Table 4.5). Continuous pumping has resulted in the lower residual contaminant level (.0329) but pulsed pumping yields only a slightly higher residual level (.0353). These results (Table 4.5) suggest that continuous pumping offers little tangible advantage over pulsed pumping when remediating an aquifer with rate-limited sorption characteristics.

In a broader sense, the model shows the insignificant effects of continuous pumping on immobile region contaminant release. As a result, the mobile concentration increases with time due to the rate-limited desorption of contaminant from the layered immobile water regions. This observation is further supported at day 400 in the pulsed pumping simulation (Table 4.6). The contaminant rebounds 327% from a level of .0353 to .1156.

Table 4.5

Immobile Region Concentration Comparison
(Pulsed Versus Continuous Pumping at the well - at day 300)

Radial Distance	Pulsed	Continuous
0.0	.9219	.9190
0.2	.8914	.8860
0.4	.7956	.7814
0.6	.6233	.5974
0.8	.3646	.3389
1.0	.0353	.0329

Table 4.6

Immobile Region Concentration Comparison
(Pulsed Versus Continuous Pumping at the well - at day 400)

Radial Distance	Pulsed	Continuous
0.0	.8476	.8391
0.2	.8136	.8032
0.4	.7106	.6956
0.6	.5422	.5201
0.8	.3290	.2898
1.0	.1156	.0279

Table 4.5 shows that at the end of 300 days, the mobile concentrations for the two simulations were 0.0329 (continuous) and 0.0353 (pulsed). Thus, the two concentration levels are not significantly different suggesting that both methods of remediation are capable of achieving similar levels of cleanup. Admittedly, this comparison is limited by the fact that pump off schedules were arbitrarily selected. It is possible that contaminant removal efficiencies may improve with longer 'pump off' times to allow more contaminant to desorb into the mobile water.

Overall, the model simulating continuous pumping is consistent with field observations - namely, that as pumping continues over time, large volumes of water are being extracted

and treated to remove only small quantities of contaminants [Goltz and Oxley, 1991:547; Olsen and Kavanaugh, 1993:44; Keely and others, 1987:91; Mackay and Cherry, 1989:630].

Efficiency Comparison. Model simulations, which show higher contaminant concentration removed at the well during pulsed pumping, suggest a pump on/pump off operation scheme may allow for more efficient contaminant removal in a groundwater remediation project. Efficiency is defined as the volume of contaminated water extracted for a fixed amount of contaminant mass. In order to quantify the comparison between pulsed and continuous pumping, a measurement of contaminant mass removed versus volume of water extracted was developed. Figure 4.4 shows the contaminant concentration within the extracted water at the well for both pulsed and continuous pumping. From this figure, a contaminant mass removal measurement can be easily derived on a mass per volume basis.

Separating the pulsed and continuous pumping curves, a contaminant mass measurement is obtained by numerically integrating each curve over its respective pump on interval (Figure 4.5). Since this simulation used a pump extraction rate of 1,000 cubic meters per day, time is converted to volume and plotted (Figure 4.6).

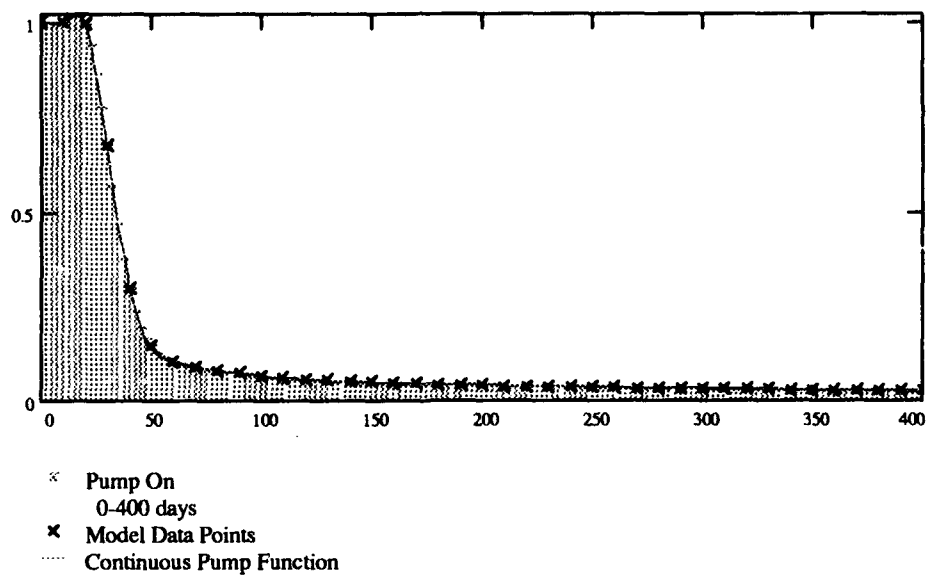
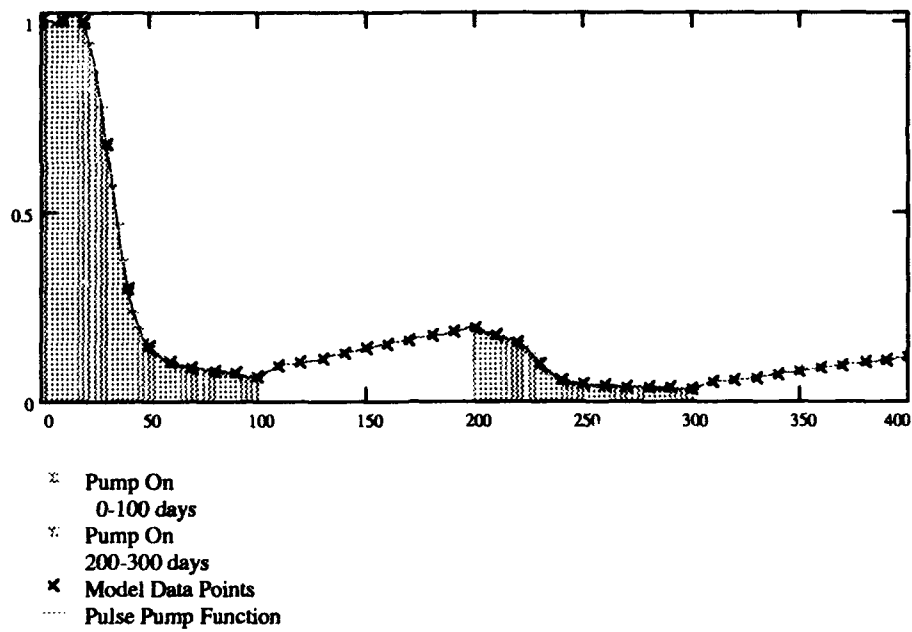


Figure 4.5. Efficiency Comparison: Pulsed Versus Continuous Pumping

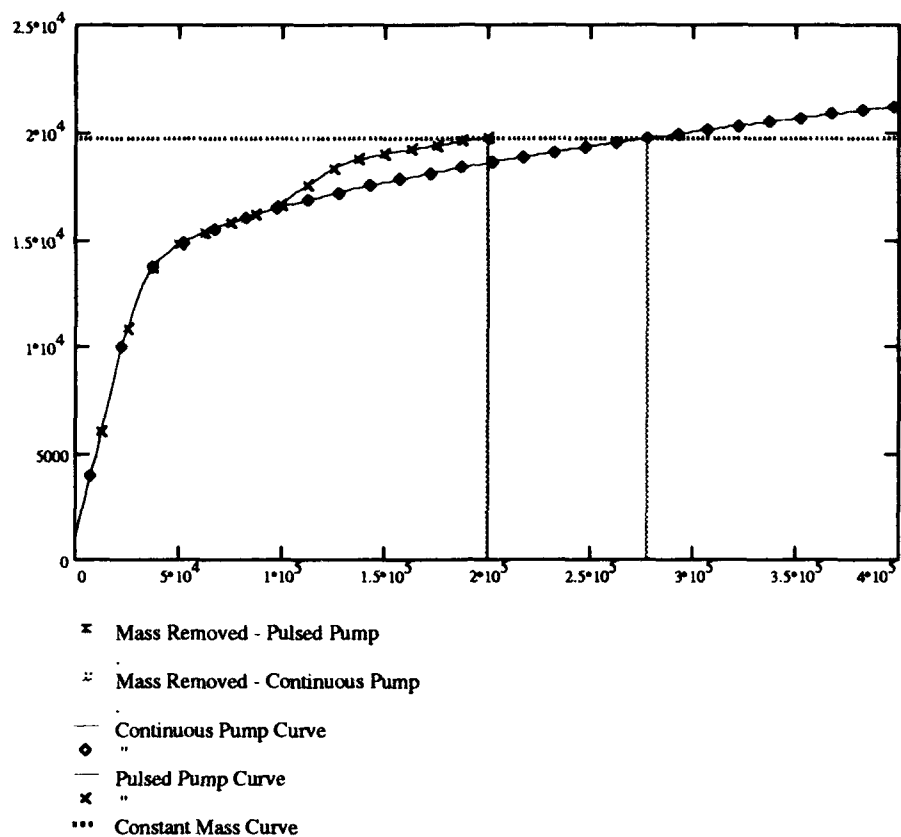


Figure 4.6. Mass Removed Versus Volume of Water Extracted: Pulsed Versus Continuous Pumping

Assuming an initial maximum concentration of 1 grams/cubic meter, operating in a pulsed pump mode removes 1,975 grams of contaminant in 200,000 cubic meters of water (Figure 4.6). To remove the equivalent mass of contaminant in a continuous pump mode, Figure 4.6 shows that approximately 277,500 cubic meters of water would have to be extracted. This represents an approximate 28 percent efficiency advantage of pulsed over continuous pumping given the uniform initial distribution and input parameters in Table 4.1.

The model demonstrates that operating in a pulsed pump mode provides time for the slow desorption process to release contaminant to the mobile water, thereby resulting in increased concentrations of contaminant in the extracted water, thus permitting higher removal of contaminant mass per volume of extracted water. By operating in a pulsed pump mode, advantages may include considerable savings in pumping and waste treatment costs along with minimizing excess groundwater removal. To an IRP program manager, this translates directly into dollars saved by providing the 'biggest bang for the buck'. However, if maximum contaminant mass removal is the IRP site remediation objective, then this simulation indicates that pulsed pumping will not remove more mass over time than continuous pumping, and it appears that pulsed pumping may extend the duration of the remediation efforts.

Continuous Pumping. In this simulation, we demonstrate the flexibility of the model by specifying arbitrary initial conditions, thus allowing simulations to more realistically depict an actual contaminated site remediation. During this simulation, the pump is left on continuously for a total duration of 100 days. The input aquifer parameters are the same as those used in the previous simulation (Table 4.1). The layered diffusion model is used, and the initial contaminant concentration distribution in the mobile region is entered as discrete points as shown at Figure 4.7.

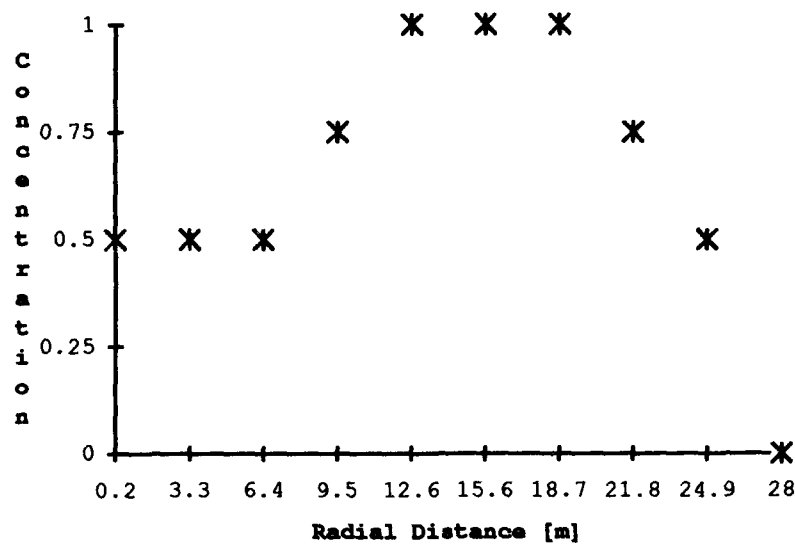


Figure 4.7. Initial Conditions for Continuous Pumping Simulation

The immobile region initial contaminant concentration distribution was set constant at 1.0 (dimensionless) radially throughout the aquifer (0.2-28.0 meters) and 0.0 at all other locations.

As can be seen from Figure 4.8, the layered diffusion model simulates the early breakthrough and long concentration tail at radial distances 12.6 meters, 15.6 meters, and 18.7 meters where the initial concentrations were 1.0 and at radial distances 21.8 meters and 24.9 meters where the initial concentrations were 0.75 and 0.5, respectively. Note that at radial distance less than 9.5 meters, there is a slight increase in the solute concentration with time. After this increase (which peaks at various times for the various radial distances), the breakthrough occurs and subsequently tailing at each of these locations.

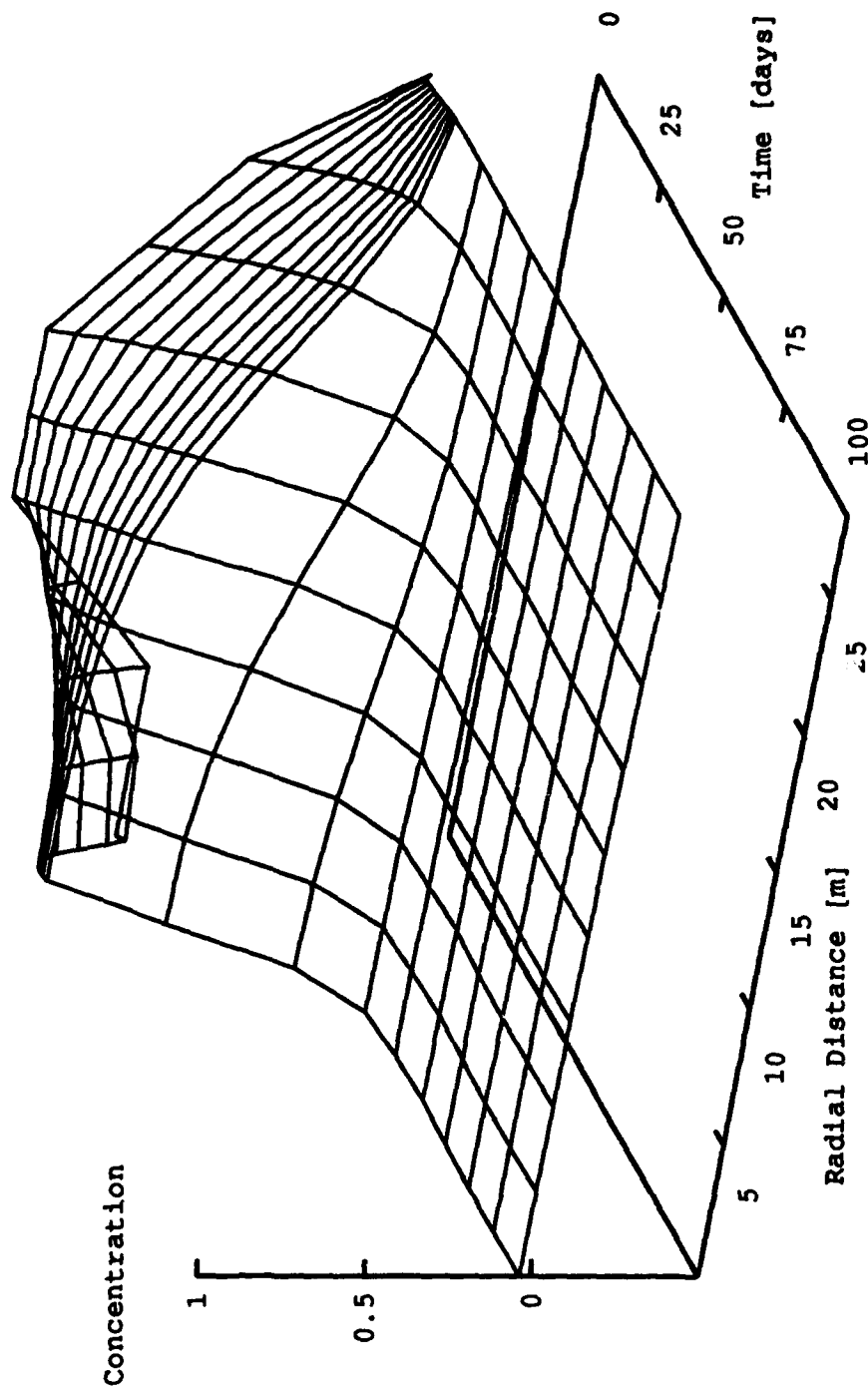


Figure 4.8. Continuous Pumping Effluent Concentration Profile Using Arbitrary Initial Conditions for the Layered Diffusion Model

In order to more clearly see this peaking during the early time period, we generated the effluent concentration profile for the first 10 days at all radial locations (Table 4.7) and the graphical representation (Figure 4.9).

Table 4.7

Mobile Concentration Profile for the First 10 Days

Day	Radial distance starting at the well [m]									
	0.2	3.3	6.4	9.5	12.6	15.6	18.7	21.8	24.9	28.0
0	.5000	.5000	.5000	.7500	1.000	1.000	1.000	.7500	.5000	.0000
1	.4794	.4955	.6063	.8344	.9710	.9742	.9220	.6862	.4158	.0236
2	.5421	.5786	.7068	.8685	.9430	.9366	.8489	.6192	.3461	.0246
3	.6351	.6700	.7715	.8741	.9131	.8912	.7788	.5526	.2871	.0211
4	.7084	.7342	.8027	.8639	.8799	.8407	.7112	.4884	.2369	.0173
5	.7509	.7677	.8103	.8443	.8427	.7870	.6458	.4277	.1944	.0139
6	.7678	.7781	.8027	.8183	.8016	.7316	.5828	.3715	.1587	.0111
7	.7824	.7882	.8011	.8032	.7730	.6897	.5336	.3271	.1297	.0074
8	.7878	.7906	.7949	.7860	.7432	.6485	.4873	.2872	.1043	.0051
9	.7865	.7870	.7844	.7656	.7114	.6072	.4433	.2509	.0828	.0036
10	.7802	.7788	.7703	.7427	.6783	.5665	.4019	.2180	.0654	.0027

Given the initial contaminant distribution (Figure 4.7), this peaking of highly contaminant water is transported inward toward the well the moment the well is turned on. Since we have assumed radial flow this sudden change generates this slight increase and surfaces as time progresses. This behavior appears to make physical sense and therefore is plausible that this simulation is depicting the physics that could be occurring in the aquifer.

Model Verification/Comparison

The basis for model verification was to compare this model with existing models formulated using the same

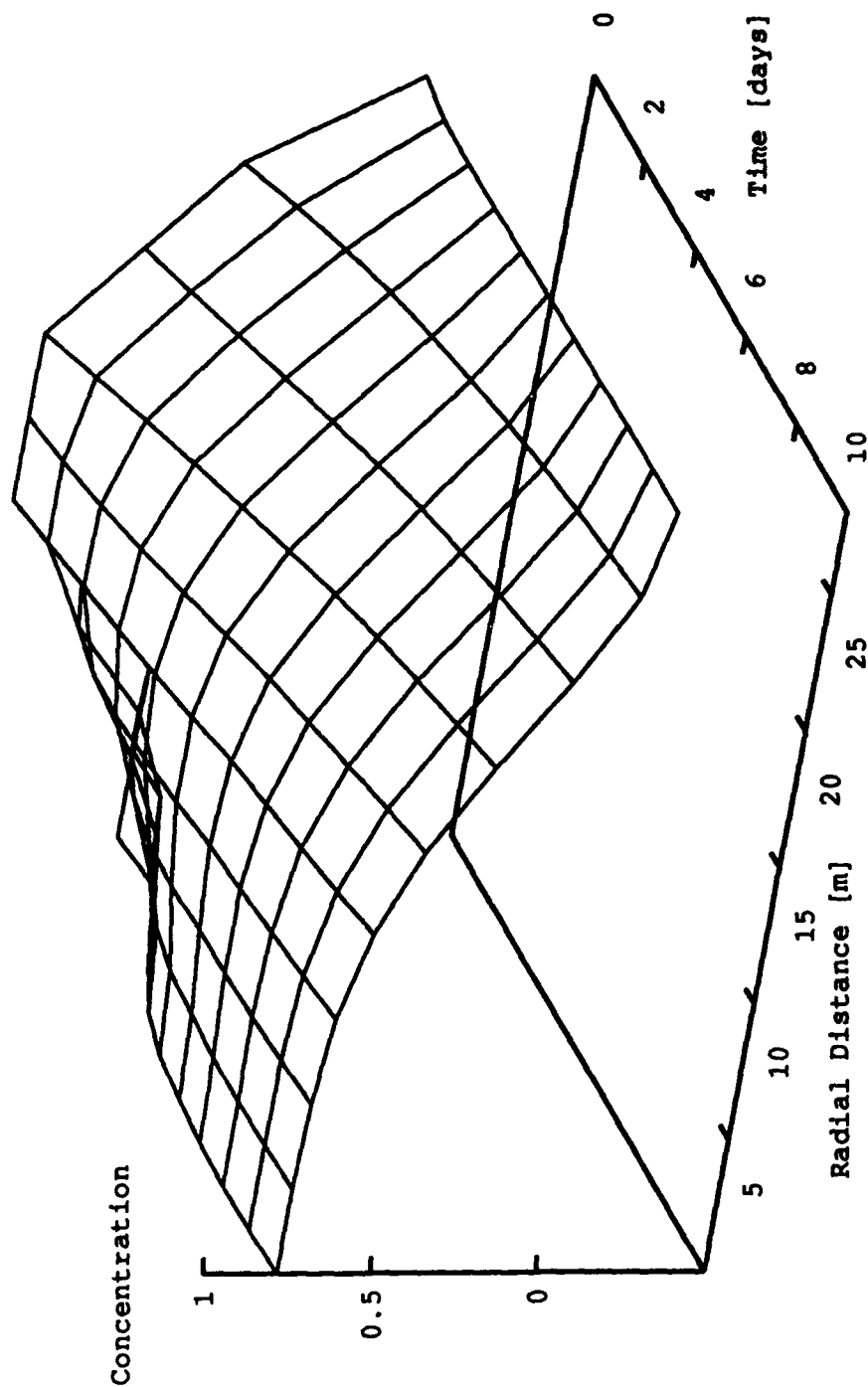


Figure 4.9. Continuous Pumping Effluent Concentration Profile Using Arbitrary Initial Conditions for the Layered Diffusion Model (first 10 days)

sorption/desorption assumptions. In Chapter II we reviewed the literature related to modeling sorbing solute transport. The review focused on analytical models describing converging radial transport and incorporating equilibrium or rate-limited sorption, with the rate-limitation described by either a first-order equation, or by Fickian diffusion in immobile regions of an aquifer. In addition, we searched for any independent modeling efforts in the area of pulsed pumping.

The literature search uncovered various researchers who have presented analytical models that met the above criteria. For purposes of comparison, the analytical model presented by Goltz and Oxley was used [Goltz and Oxley, 1991]. Their model solves the same sorption/desorption equation set for the pump on used in this research. However, their model does not allow for arbitrary initial conditions or pulsed pumping. Finding no analytical pulsed pumping models, the literature was searched for numerical models using the same criteria as above.

A numerical model by Huso was found that used the Finite Element Method and Finite Difference Method [Huso, 1989]. In this model, the pump on expression governing contaminant transport within the mobile region (Equation (3.1)) and Fick's second law of diffusion (Equation (3.14)) for spherical and layered immobile region geometry were incorporated. Huso's model allows for arbitrary initial conditions, multiple radial locations, and simulates pulsed pumping by using a small pumping rate. However, Huso's pulsed pumping simulation does not

explicitly include the governing contaminant transport equation when the pump is off (Equation (3.67)).

The test consisted of running the Goltz/Oxley model and Huso model and comparing simulations with simulations of the model presented in this research. The input parameters presented in Table 4.1 were used for all three models. With identical input data, all three models should produce similar results. However, some deviation will be expected since the analytical models solve for the mobile concentration for all time simultaneously, while the numerical model steps forward in time; thus, the numerical model is subject to compounding errors [Huso, 1989].

Simulation parameters consisted of cycling the pump on and off at 100 day intervals for a total duration of 400 days. The initial mobile and immobile contaminant concentration distribution was set constant at 1.0 throughout the aquifer (0.2 - 28.0 meters) and 0.0 outside the aquifer (beyond 28 meters).

Figure 4.2 shows the simulation at multiple radial locations for the model presented in this research operating in a pulsed pump mode. Because of data and design limitations with the other two models, the comparison test was conducted at the well only. Unfortunately, since the Goltz/Oxley model only permits pump on operation, data only exists for the first 100 days for that model. In addition, only selected data points in time were available for Huso's model. Table 4.8 shows the effluent

concentration profile comparison at the well, and Figure 4.10 shows the graphical representation.

Table 4.8

Layered Mobile Region Comparison Test

Day	Goltz	Huso	Model	Day	Goltz	Huso	Model
10	1.001	1.001	.9999	210	-	.18	.1728
20	.9937	.9937	.9936	220	-	.16	.1564
30	.6750	.6750	.6750	230	-	.12	.0979
40	.2978	.2978	.2978	240	-	.08	.0576
50	.1463	.1463	.1464	250	-	.04	.0449
60	.1045	.1045	.1045	260	-	.04	.0412
70	.0906	.0906	.0906	270	-	.04	.0392
80	.0816	.0816	.0816	280	-	.04	.0377
90	.0739	.0739	.0738	290	-	.04	.0364
100	.0673	.0673	.0673	300	-	.04	.0353
110	-	-	.0932	310	-	-	.0497
120	-	-	.1016	320	-	-	.0552
130	-	-	.1140	330	-	-	.0630
140	-	-	.1272	340	-	-	.0714
150	-	.14	.1398	350	-	.08	.0797
160	-	-	.1516	360	-	-	.0876
170	-	-	.1625	370	-	-	.0951
180	-	-	.1726	380	-	-	.1022
190	-	-	.1822	390	-	-	.1090
200	-	.20	.1911	400	-	.12	.1156

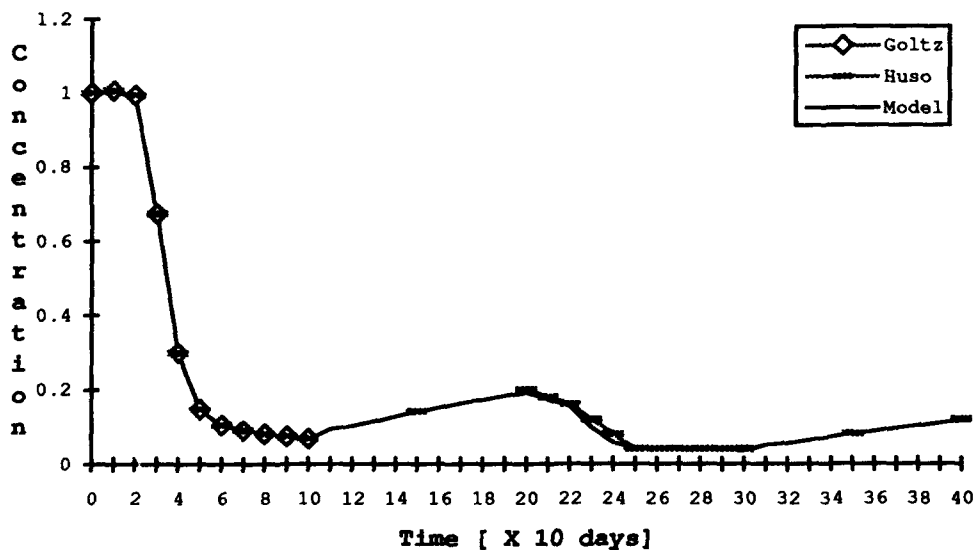


Figure 4.10. Effluent Concentration Profile Comparison at the Well When Sorption/Desorption is Controlled by Diffusion Within Layered Immobile Regions

As can be seen from Table 4.8 and Figure 4.10, the model presented in this thesis tracks very close to the Goltz/Oxley and Huso models. As Figure 4.10 demonstrates, all models initially show a high removal of contaminant until tailing appears around day 50. From this point to day 100, the tail appears and reaches a residual concentration. At day 100, the well is turned off and the mobile concentration rises, as contaminant in the immobile region slowly desorbs into the mobile region. At day 200, the well is turned on, and again the breakthrough and tailing is observed. At day 300, the well is turned off, and expectedly, the mobile concentration rebounds. At the end of the simulation (day 400), the levels in the immobile regions are still quite high (Table 4.6) which indicates only a portion of the total contaminant was removed during this 400 day simulation.

Although favorable comparison results with both models during the first 100 days, deviations are apparent with the Huso model at certain data points. As previously mentioned, one possible explanation for this deviation is that the numerical model steps forward in time; thus, the numerical model is subject to compounding errors. Another possible explanation for this deviation could be that Huso's simulations are based on a finite element and finite difference method which approximates the equation set. Still another possible explanation could be that the model presented in this thesis uses numerical

approximations, such as numerical integration, which could explain the difference in results.

V. Conclusions and Recommendations

This concluding chapter draws together the research presented in the previous chapters. It begins with an overview of the research effort. Next, it summarizes the findings of this study, and finally, it lists recommendations for model improvements and for follow-on research.

Overview

The focus of this research was to model the fate and transport of contaminated groundwater under certain simplifying assumptions. It was intended that our research would assist Installation Restoration Program (IRP) managers to estimate the level and type of aquifer cleanup effort. As such, the main thrust of the research was to analytically model contaminant transport and show how the rate-limited sorption process influences the fate of contaminants in porous media. With recent criticisms of pump and treat remediation, primarily due to its inability to account for rate-limited sorption and desorption, our research was tailored to account for this behavior. Specifically, it incorporated one method that has been proposed to enhance typical pump and treat remediation: pulsed pumping.

The literature review clearly revealed that research during the last few decades has contributed to a better understanding of the transfer of solute in porous media through the mechanisms

of rate-limited sorption and desorption. There appears to be an increase in mathematical models focused on contaminant transport and rate-limited sorption/desorption. However, there does not appear to be many computer-based analytical models that incorporate rate-limited sorption/desorption and none that include pulsed pumping.

In this research an analytical model was formulated based upon solutions governing the transport of a contaminant during aquifer remediation by pulsed pumping. Contaminant transport was assumed to be affected by radial advection, dispersion, and sorption/desorption. Sorption was modeled assuming equilibrium or rate-limited, with the rate-limitation described by either a first-order equation, or by Fickian diffusion of contaminant through layered, cylindrical, or spherical immobile water regions. The model equations were formulated using an arbitrary initial distribution of contaminant in both the mobile and immobile regions and were analytically solved in the Laplace domain. These analytical solutions were then numerically inverted and converted back to the time domain.

Summary of Findings

Simulations were used to demonstrate the capability of the model. In addition, a comparison of this model's simulations to other models was conducted with favorable results. Unfortunately, time constraints precluded a thorough evaluation

of the model. However, the model simulations that were conducted revealed the following:

(1) A pulsed pump operation may allow for more efficient contaminant removal in a groundwater remediation project. The model demonstrates that operating in a pulsed pump mode provides time for the slow desorption process to release contaminant to the mobile water and eventually allows the system to approach equilibrium.

(2) The pulsed pump simulation showed increased concentrations of contaminant in the extracted water indicating a higher removal of contaminant mass per volume of extracted water.

(3) The simulation indicates that pulsed pumping does not accelerate the cleanup time but can achieve approximately the same concentration levels of contaminant as continuous pumping. This may result in savings in pumping and waste treatment costs.

(4) The model was designed to provide flexibility by allowing arbitrary initial contaminant concentration distributions. Unfortunately, model simulations were limited and a thorough assessment of this aspect of the model still needs to be accomplished.

(5) A comparison test was conducted with existing models found in the literature. Goltz and Oxley presented an analytical model based upon the same sorption/desorption assumptions used in this research for a continuously operating

extraction well [Goltz and Oxley, 1991]. Huso presented a numerical model using the same sorption/desorption assumptions [Huso, 1989]. The model compares favorably with the Goltz/Oxley and Huso models.

Recommendations

As discussed in Chapter I, the development of an analytical model requires simplifying assumptions in formulating the equation sets. Therefore, the primary emphasis for future research is to relax or eliminate these assumptions. More specifically, emphasis should be focused in the following areas:

- (1) Include drawdown of the aquifer water table as part of the equation set formulation. This would reflect a more realistic scenario.

- (2) Eliminate the necessity for radial symmetry. That is, develop a mathematical model that is truly two dimensional or three dimensional.

- (3) Include an arbitrary groundwater velocity field or hydraulic gradient.

Other model applications could include:

- (1) The pumping schedule could be optimized so that a greater amount of contaminant can desorb from the immobile region. In this model, the pump off time was arbitrarily selected.

- (2) Extend the capability of the model by including multiple wells, including injection wells. Again, optimizing

the number of wells and cycling periods would provide a better simulation of a real contaminated site.

(3) Add the ability to estimate the contaminant mass remaining in the aquifer. Knowing this information will show the efficacy of an aquifer remediation effort.

Appendix A: A Green's Function Approach to
Analytical Modeling Aquifer Decontamination by Pulsed Pumping
With Arbitrary Initial Conditions

This appendix presents the theoretical development and detailed mathematical analysis of the equations and solutions that govern sorbing solute transport. The derivation uses arbitrary initial conditions and is developed based on the five expressions of sorption/desorption (equilibrium, two-region first-order rate, and Fickian diffusion of rectangular, cylindrical, and spherical immobile region geometry) for conditions when an extraction well is on and when an extraction well is off.

The mathematical representation of the advection and dispersion that govern dissolved transport of a single contaminant in saturated, homogeneous porous media with radial converging flow is

$$\frac{\partial C'_m(r, t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[r(D'_m(r) + D'_o) \frac{\partial C'_m(r, t)}{\partial r} \right] - V_m(r) \frac{\partial C'_m(r, t)}{\partial r} \quad (A.1)$$

where D'_m is the dispersivity [L] of the porous media and D'_o is the molecular diffusion coefficient [L^2 / T]. If we include a sink term to describe the transfer of contaminant from the aqueous phase to immobile water regions, and account for the distribution of contaminants between aquifer solids and the groundwater ($R_m = 1 + (\rho K_d) / \theta_m$), then Equation (A.1) becomes

$$\begin{aligned} \frac{\partial C'_m(r, t)}{\partial t} = & \frac{1}{R_m r} \frac{\partial}{\partial r} \left[r(D'_m(r) + D'_o) \frac{\partial C'_m(r, t)}{\partial r} \right] \\ & - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} - \frac{\theta_{im} R_{im}}{\theta_m R_m} \frac{\partial C'_{im}(r, t)}{\partial t} \end{aligned} \quad (A.2)$$

If we define

$$D'_m = a_1 V_m(r) \quad (A.3)$$

$$\beta = \frac{\theta_{im} R_{im}}{\theta_m R_m} \quad (A.4)$$

then Equation (A.2) becomes

$$\begin{aligned} \frac{\partial C'_m(r, t)}{\partial t} = & \frac{1}{R_m r} \frac{\partial}{\partial r} \left[(a_1 V_m(r) + r D'_o) \frac{\partial C'_m(r, t)}{\partial r} \right] \\ & - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} - \beta \frac{\partial C'_{im}(r, t)}{\partial t} \end{aligned} \quad (A.5)$$

or

$$\begin{aligned} \frac{\partial C'_m(r, t)}{\partial t} = & \frac{1}{R_m} \frac{\partial}{\partial r} \left[\left(\frac{a_1 V_m(r)}{r} + D'_o \right) \frac{\partial C'_m(r, t)}{\partial r} \right] \\ & - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} - \beta \frac{\partial C'_{im}(r, t)}{\partial t} \end{aligned} \quad (A.6)$$

If we substitute Equation (A.3) into Equation (A.6)

$$\begin{aligned} \frac{\partial C'_m(r, t)}{\partial t} = & \frac{1}{R_m} \frac{\partial}{\partial r} \left[(a_1 V_m(r) + D'_o) \frac{\partial C'_m(r, t)}{\partial r} \right] \\ & - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} - \beta \frac{\partial C'_{im}(r, t)}{\partial t} \end{aligned} \quad (A.7)$$

and define

$$D_m = a_1 |V_m(r)| \quad (A.8)$$

then Equation (A.7) becomes

$$\begin{aligned} \frac{\partial C'_m(r, t)}{\partial t} = \frac{1}{R_m} \frac{\partial}{\partial r} \left[(D_m + D'_o) \frac{\partial C'_m(r, t)}{\partial r} \right] \\ - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} - \beta \frac{\partial C'_{im}(r, t)}{\partial t} \end{aligned} \quad (A.9)$$

where D_m is the mobile region dispersion coefficient $[L^2 / T]$.

Equation (A.9) describes the transport of a single sorbing solute in saturated, homogeneous porous media. Mathematical modeling of this phenomena often incorporates simplifying assumptions, depending on whether an extraction well is on or off.

Model Formulation: Extraction Well On

In the case where we have an extraction well operating, it is often assumed that the mobile region dispersion coefficient, D_m , is much greater than the molecular diffusion coefficient, D'_o . Thus, D'_o is considered negligible sufficiently close to the well where the advective process due to the pump's influence overwhelms the molecular diffusive process [Valocchi, 1986:1694; Goltz and Oxley, 1991:548]. When this assumption is made, Equation (A.9) becomes

$$\frac{\partial C'_m(r, t)}{\partial t} = \frac{D_m}{R_m} \frac{\partial^2 C'_m(r, t)}{\partial r^2} - \frac{V_m(r)}{R_m} \frac{\partial C'_m(r, t)}{\partial r} - \beta \frac{\partial C'_{im}(r, t)}{\partial t} \quad (A.10)$$

which describes the transport of a single sorbing solute in a radially flowing aquifer in a porous medium with immobile water regions [Goltz and Oxley, 1991:548]. The dependent variable in this equation, C'_{im} , represents a volume-averaged solute concentration within the immobile region defined by [Goltz and Oxley, 1991:548]

$$C'_{im}(r, t) = \frac{v}{a^v} \int_0^a z^{v-1} C'_i(r, z, t) dz \quad (A.11)$$

If the depth or thickness of the aquifer region is b [L] and an extraction well is present pumping at a rate Q_w [L³ / T], with the mobile region dispersion coefficient, D_m , given by

$$D_m(r) = a_1 |V_m(r)| \quad (A.8)$$

then the radial velocity is

$$V_m(r) = \frac{-Q_w}{2\pi b \theta_m r} \quad (A.12)$$

We now seek a dimensionless form of Equation (A.10). Thus, we develop dimensionless variables. If we define

$$X = C_1 r \quad (A.13)$$

$$T = C_2 t \quad (A.14)$$

$$C_m(X, T) = \frac{C'_m(r, t)}{C'_o} \quad (A.15)$$

$$C_{im}(X, T) = \frac{C'_{im}(r, t)}{C'_0} \quad (A.16)$$

where X is the dimensionless radial distance, T is the dimensionless time, $C_m(X, T)$ is the dimensionless mobile region solute concentration, $C_{im}(X, T)$ is the dimensionless volume-averaged immobile region solute concentration, C_1 and C_2 are constants, and C'_0 is some initial maximum concentration of $C'_m(r, t = 0)$ and $C'_{im}(r, t = 0)$ between the well radius, r_w [L], and the radius of the initially contaminated zone, r [L]. Then

$$C'_m(r, t) = C'_m\left(\frac{X}{C_1}, \frac{T}{C_2}\right) = C_m(X, T) \quad (A.17)$$

$$C'_{im}(r, t) = C'_{im}\left(\frac{X}{C_1}, \frac{T}{C_2}\right) = C_{im}(X, T) \quad (A.18)$$

and

$$\frac{\partial C'_m(r, t)}{\partial t} = C'_0 \frac{\partial C_m(X, T)}{\partial T} \frac{dT}{dt} = C'_0 \frac{\partial C_m(X, T)}{\partial T} (C_2) \quad (A.19)$$

$$\frac{\partial C'_m(r, t)}{\partial r} = C'_0 \frac{\partial C_m(X, T)}{\partial X} \frac{dX}{dr} = C'_0 \frac{\partial C_m(X, T)}{\partial X} (C_1) \quad (A.20)$$

$$\frac{\partial^2 C'_m(r, t)}{\partial r^2} = \frac{\partial}{\partial X} \left[\frac{\partial C'_m(r, t)}{\partial r} \right] \frac{dX}{dr} = C'_0 \frac{\partial^2 C_m(X, T)}{\partial X^2} (C_1^2) \quad (A.21)$$

$$\frac{\partial C'_{im}(r, t)}{\partial t} = C'_0 \frac{\partial C_{im}(X, T)}{\partial T} \frac{dT}{dt} = C'_0 \frac{\partial C_{im}(X, T)}{\partial T} (C_2) \quad (A.22)$$

Substituting these expressions into Equation (A.10) gives us

$$\begin{aligned}
 C_2 C'_o \frac{\partial C_m(X, T)}{\partial T} &= \frac{D_m}{R_m} C_1^2 C'_o \frac{\partial^2 C_m(X, T)}{\partial X^2} - \frac{V_m(r)}{R_m} C_1 C'_o \frac{\partial C_m(X, T)}{\partial X} \\
 &\quad - \beta C_2 C'_o \frac{\partial C_{im}(X, T)}{\partial T}
 \end{aligned}
 \tag{A.23}$$

Dividing each term in this equation by C_2 and C'_o yields

$$\begin{aligned}
 \frac{\partial C_m(X, T)}{\partial T} &= \frac{D_m}{R_m} \frac{C_1^2}{C_2} \frac{\partial^2 C_m(X, T)}{\partial X^2} - \frac{V_m(r)}{R_m} \frac{C_1}{C_2} \frac{\partial C_m(X, T)}{\partial X} \\
 &\quad - \beta \frac{\partial C_{im}(X, T)}{\partial T}
 \end{aligned}
 \tag{A.24}$$

Recall that

$$D_m = a_l |V_m(r)| \tag{A.8}$$

$$V_m(r) = \frac{-Q_w}{2\pi b \theta_m r} \tag{A.12}$$

Substituting these expressions into Equation (A.24) produces

$$\begin{aligned}
 \frac{\partial C_m(X, T)}{\partial T} &= \frac{a_l Q_w C_1^3}{2\pi b \theta_m X R_m C_2} \frac{\partial^2 C_m(X, T)}{\partial X^2} + \frac{Q_w C_1^2}{2\pi b \theta_m X R_m C_2} \frac{\partial C_m(X, T)}{\partial X} \\
 &\quad - \beta \frac{\partial C_{im}(X, T)}{\partial T}
 \end{aligned}
 \tag{A.25}$$

In order to determine C_1 and C_2 uniquely, we seek a second equation. In Chapter 2, we discussed how the transfer of solute between mobile and immobile regions may be assumed to be

governed by Fickian diffusion of solute within immobile regions of specified geometry [Goltz and Oxley, 1991:548-549]. Mathematically, Fick's second law of diffusion describing contaminant transport within immobile regions is

$$R_{im} \frac{\partial C'_a(r, z, t)}{\partial t} = \frac{D'_e}{z^{v-1}} \frac{\partial}{\partial z} \left[z^{v-1} \frac{\partial C'_a(r, z, t)}{\partial z} \right] \quad 0 < z < a \quad (A.26)$$

If we define

$$Z = C_3 z \quad (A.27)$$

$$C_a(X, Z, T) = \frac{C'_a(r, z, t)}{C'_o} \quad (A.28)$$

where Z is the dimensionless immobile region variable, $C_a(X, Z, T)$ is the dimensionless concentration at points within the immobile region, and C_3 is a constant, then

$$C'_a(r, z, t) = C'_o \left(\frac{X}{C_1}, \frac{Z}{C_3}, \frac{T}{C_2} \right) = C_a(X, Z, T) \quad (A.29)$$

and

$$\frac{\partial C'_a(r, z, t)}{\partial t} = C'_o \frac{\partial C_a(X, Z, T)}{\partial T} \frac{dT}{dt} = C'_o \frac{\partial C_a(X, Z, T)}{\partial T} (C_2) \quad (A.30)$$

$$\frac{\partial C'_a(r, z, t)}{\partial z} = C'_o \frac{\partial C_a(X, Z, T)}{\partial Z} \frac{dZ}{dz} = C'_o \frac{\partial C_a(X, Z, T)}{\partial Z} (C_3) \quad (A.31)$$

Substituting these expressions into Equation (A.26) gives us

$$R_{im} C'_0 C_2 \frac{\partial C_a(X, Z, T)}{\partial T} = \frac{D'_e}{\left(\frac{Z}{C_3}\right)^{v-1}} \frac{\partial}{\partial Z} \left[\left(\frac{Z}{C_3}\right)^{v-1} C'_0 C_3 \frac{\partial C_a(X, Z, T)}{\partial Z} \right] \quad (A.32)$$

or

$$R_{im} C'_0 C_2 \frac{\partial C_a(X, Z, T)}{\partial T} = \frac{D'_e}{Z^{v-1}} C'_0 C_3^2 \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_a(X, Z, T)}{\partial Z} \right] \quad (A.33)$$

where Equations (A.32) and (A.33) are defined over the interval $0 < Z < a$. Dividing each term in this equation by R_{im} , C'_0 , and C_2 yields

$$\frac{\partial C_a(X, Z, T)}{\partial T} = \frac{D'_e}{R_{im}} \frac{C_3^2}{C_2} \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_a(X, Z, T)}{\partial Z} \right] \quad 0 < Z < a \quad (A.34)$$

We now seek the constants C_1 and C_2 in Equation (25) such that

$$\frac{a_1 Q_w C_1^3}{2 \pi b \theta_m R_m C_2} = 1 \quad (A.35)$$

and

$$\frac{Q_w C_1^2}{2 \pi b \theta_m R_m C_2} = 1 \quad (A.36)$$

Solving C_2 in terms of C_1 in Equation (A.36) yields

$$C_2 = \frac{Q_w C_1^2}{2 \pi b \theta_m R_m} \quad (A.37)$$

Substituting Equation (A.37) into Equation (A.35) gives us

$$\frac{a_1 Q_w C_1^3}{2 \pi b \theta_m R_m} \left(\frac{2 \pi b \theta_m R_m}{Q_w C_1^2} \right) = 1 \quad (A.38)$$

or

$$a_1 C_1 = 1 \quad (A.39)$$

Thus,

$$C_1 = \frac{1}{a_1} \quad (A.40)$$

Substituting Equation (A.40) into Equation (A.37) results in

$$C_2 = \frac{Q_w}{2 \pi b \theta_m R_m} \frac{1}{a_1^2} \quad (A.41)$$

Therefore, Equations (A.13) and (A.14) become

$$X = \frac{r}{a_1} \quad (A.42)$$

$$T = \frac{Q_w t}{2 \pi b \theta_m R_m a_1^2} \quad (A.43)$$

We now select C_3 so that when $z = 0, Z = 0$ and when $z = a, Z = 1$. That is, we want to normalize Z so that it

exists in the interval $0 < Z < 1$. Therefore, Equation (A.27) becomes

$$Z = \frac{z}{a} \quad (\text{A.44})$$

where

$$C_3 = \frac{1}{a} \quad (\text{A.45})$$

Using Equation (A.25) together with Equations (A.40) and (A.41) results in the dimensionless form of Equation (A.10):

$$\frac{\partial C_m(X, T)}{\partial T} = \frac{1}{X} \frac{\partial^2 C_m(X, T)}{\partial X^2} + \frac{1}{X} \frac{\partial C_m(X, T)}{\partial X} - \beta \frac{\partial C_{im}(X, T)}{\partial T} \quad (\text{A.46})$$

Taking the Laplace transformation of Equation (A.46) and suppressing the (X, s) notation where s is the Laplace transform variable results in

$$\mathcal{L}\left(\frac{\partial C_m}{\partial T}\right) = \mathcal{L}\left(\frac{1}{X} \frac{\partial^2 C_m}{\partial X^2}\right) + \mathcal{L}\left(\frac{1}{X} \frac{\partial C_m}{\partial X}\right) - \mathcal{L}\left(\beta \frac{\partial C_{im}}{\partial T}\right) \quad (\text{A.47})$$

or

$$\begin{aligned} s\bar{C}_m - C_m(X, T = 0) &= \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} \\ &\quad - \beta[s\bar{C}_{im} - C_{im}(X, T = 0)] \end{aligned} \quad (\text{A.48})$$

where $\bar{C}_m(X, s)$ is the Laplace domain dimensionless mobile region solute concentration, $\bar{C}_{im}(X, s)$ is the Laplace domain

dimensionless volume-averaged immobile region solute concentration, and s is the Laplace transform variable.

After describing remediation of a cylindrical contaminated area of extraction well radius r_w , radius of contamination r_c , and defining $X_w = r_w / a_1$ and $X_c = r_c / a_1$ as the nondimensionalized well radius and contaminated area radius, respectively, the following initial and boundary conditions can be formulated for the various models [Goltz and Oxley, 1991:549-550; Valocchi, 1986].

Initial Conditions:

$$C_m(X, T = 0) = F_m(X) \quad X_w < X < X_c \quad (A.49)$$

$$C_{im}(X, T = 0) = F_{im}(X) \quad X_w < X < X_c \quad (A.50)$$

$$C_m(X, T = 0) = C_{im}(X, T = 0) = 0 \quad X > X_c \quad (A.51)$$

where $F_m(X)$ and $F_{im}(X)$ are dimensionless arbitrary initial concentration conditions in the mobile region and immobile region, respectively. The diffusion models require the following additional initial conditions to describe transport within the immobile regions [Goltz and Oxley, 1991:549-550]:

$$C_i(X, Z, T = 0) = F_i(X, Z) \quad X_w < X < X_c \quad (A.52)$$

$$C_i(X, Z, T = 0) = 0 \quad X > X_c \quad (A.53)$$

where $F_i(X, Z)$ is the dimensionless arbitrary initial concentration condition in the immobile region of a certain geometry. Again, Equations (A.49), (A.50), (A.51), (A.52), and

(A.53) state the initial conditions, which assumes contamination of mobile and immobile regions at some arbitrary concentration within a cylindrical region of dimensionless radius $X_.$

Boundary Conditions:

$$C_m(X_., T) + \frac{\partial C_m}{\partial X}(X_., T) = 0 \quad (A.54)$$

$$\frac{\partial C_m}{\partial X}(X_w, T) = 0 \quad (A.55)$$

The diffusion models require additional boundary conditions to describe transport within the immobile regions of certain geometry.

$$\frac{\partial C_a}{\partial Z}(X, Z = 0, T) = 0 \quad X_w < X \quad (A.56)$$

$$C_a(X, Z = 1, T) = C_m(X, T) \quad X_w < X \quad (A.57)$$

Equation (A.54) states that the total mass flux inward at the outer boundary ($X = X_.$) must always be zero, since initially, there is no contaminant mass at $X > X_.$ Equation (A.55) states the boundary condition at the well radius and is based on the assumption that at any time, the concentration inside the well bore is equal to that entering the well from surrounding media [Goltz and Oxley, 1991:549]. This implies a zero concentration gradient at the interface between the well and its immediate adjacent aquifer. Equations (A.56) and (A.57) state that the concentration within an immobile region of certain geometry is

zero at the center and is equal to the mobile region concentration at its outer boundary.

Now that we have established the governing differential equation (Equation (A.46)) and the initial conditions and boundary conditions, we will now go through the mathematical formulation for each model.

Local Equilibrium Model (LEA). From Equation (A.46), if β is defined to be zero, and if we suppress the (X, T) notation, then Equation (A.46) becomes

$$\frac{\partial C_m}{\partial T} = \frac{1}{X} \frac{\partial^2 C_m}{\partial X^2} + \frac{1}{X} \frac{\partial C_m}{\partial X} \quad (A.58)$$

and Equation (A.48) becomes

$$s\bar{C}_m - C_m(X, T = 0) = \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} \quad (A.59)$$

Rearranging this expression and multiplying each term by X gives us

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - Xs\bar{C}_m = -XC_m(X, T = 0) \quad (A.60)$$

If we define

$$\gamma = s \quad (A.61)$$

and

$$\bar{F}(X, s) = -XC_m(X, T = 0) \quad (A.62)$$

together with the initial condition $C_m(X, T = 0) = F_m(X)$,
then Equation (A.60) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma \bar{C}_m = \bar{F}(X, s) \quad (A.63)$$

First-Order Rate Model. In Chapter II we introduced the first-order rate model. That is, the transfer of solute between the mobile and immobile region can be described using a first-order rate expression:

$$\frac{\partial C'_{im}(r, t)}{\partial t} = \frac{\alpha'}{\theta_{im} R_{im}} [C'_m(r, t) - C'_{im}(r, t)] \quad (A.64)$$

We seek a dimensionless form of Equation (A.64). Recall Equations (A.4), (A.15), (A.16) (A.42), and (A.43)

$$\beta = \frac{\theta_{im} R_{im}}{\theta_m R_m} \quad (A.4)$$

$$C_m(X, T) = \frac{C'_m(r, t)}{C'_o} \quad (A.15)$$

$$C_{im}(X, T) = \frac{C'_{im}(r, t)}{C'_o} \quad (A.16)$$

$$X = \frac{r}{a_1} \quad (A.42)$$

$$T = \frac{Q_w t}{2 \pi b \theta_m R_m a_1^2} \quad (A.43)$$

Rewriting Equation (A.64) into dimensionless form, term by term, yields

$$\frac{\partial C'_{im}(r, t)}{\partial t} = C'_o \frac{\partial C_{im}(X, T)}{\partial T} \frac{dT}{dt} = C'_o \frac{\partial C_{im}(X, T)}{\partial T} \frac{Q_w}{2 \pi b \theta_m a_1^2 R_m} \quad (A.65)$$

where

$$C'_m(r, t) = C'_o C_m(X, T) \quad (A.66)$$

$$C'_{im}(r, t) = C'_o C_{im}(X, T) \quad (A.67)$$

Substituting these expressions into Equation (A.64) gives us

$$C'_o \frac{\partial C_{im}(X, T)}{\partial T} \frac{Q_w}{2 \pi b \theta_m a_1^2 R_m} = \frac{\alpha'}{\theta_{im} R_{im}} C'_o [C_m(X, T) - C_{im}(X, T)] \quad (A.68)$$

or

$$\frac{\partial C_{im}(X, T)}{\partial T} = \left(\frac{2 \pi b \theta_m a_1^2 R_m}{Q_w C'_o} \right) \frac{\alpha'}{\theta_{im} R_{im}} C'_o [C_m(X, T) - C_{im}(X, T)] \quad (A.69)$$

Thus,

$$\frac{\partial C_{im}(X, T)}{\partial T} = \frac{\alpha' 2 \pi b a_1^2}{Q_w \beta} [C_m(X, T) - C_{im}(X, T)] \quad (A.70)$$

If we define the dimensionless first-order rate constant α as

$$\alpha = \frac{\alpha' 2 \pi b a_1^2}{Q_w \beta} \quad (A.71)$$

then Equation (A.70) becomes

$$\frac{\partial C_{im}(X, T)}{\partial T} = \alpha [C_m(X, T) - C_{im}(X, T)] \quad (A.72)$$

Taking the Laplace transform of Equation (A.72) and suppressing the (X, s) notation yields

$$\mathcal{L}\left(\frac{\partial C_{im}}{\partial T}\right) = \mathcal{L}(\alpha[C_m - C_{im}]) \quad (A.73)$$

$$s\bar{C}_{im} - C_{im}(X, T = 0) = \alpha(\bar{C}_m - \bar{C}_{im}) \quad (A.74)$$

and solving for $\bar{C}_{im}$ in terms of $\bar{C}_m$ gives us

$$\bar{C}_{im} = \frac{C_{im}(X, T = 0) + \alpha\bar{C}_m}{s + \alpha} \quad (A.75)$$

Inserting this expression into Equation (A.48) results in

$$\begin{aligned} s\bar{C}_m - C_m(X, T = 0) &= \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} + \beta C_{im}(X, T = 0) \\ &\quad - \beta s \left(\frac{C_{im}(X, T = 0)}{s + \alpha} + \frac{\alpha \bar{C}_m}{s + \alpha} \right) \end{aligned} \quad (A.76)$$

and rearranging, collecting similar terms, and multiply each term by X gives us

$$\begin{aligned} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\bar{C}_m \left(s + \frac{\alpha\beta s}{s + \alpha} \right) &= -XC_m(X, T = 0) \\ &\quad + XC_{im}(X, T = 0) \left(\frac{\beta s}{s + \alpha} - \beta \right) \end{aligned} \quad (A.77)$$

If we define

$$\gamma = s \left(1 + \frac{\beta\alpha}{s + \alpha} \right) \quad (A.78)$$

and

$$\bar{F}(X, s) = -X \left[C_m(X, T = 0) - C_{im}(X, T = 0) \left[\frac{\beta s - \beta(s + \alpha)}{s + \alpha} \right] \right] \quad (A.79)$$

or

$$\bar{F}(X, s) = -X \left[C_m(X, T = 0) + \frac{\beta \alpha C_{im}(X, T = 0)}{s + \alpha} \right] \quad (A.80)$$

together with the initial conditions $C_m(X, T = 0) = F_m(X)$ and $C_{im}(X, T = 0) = F_{im}(X)$ we get

$$\bar{F}(X, s) = -X \left(F_m(X) + \frac{\beta \alpha F_{im}(X)}{s + \alpha} \right) \quad (A.81)$$

So, Equation (A.77) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X \gamma \bar{C}_m = \bar{F}(X, s) \quad (A.82)$$

Diffusion Models. As previously discussed, the transfer of solute between the mobile and immobile regions may be assumed to be governed by Fickian (Fick's second law) diffusion within immobile regions of specified geometry [Goltz and Oxley, 1991:548-549]. Mathmatically, Fick's second law of diffusion describing contaminant transport within the immobile region is

$$R_{im} \frac{\partial C'_a(r, z, t)}{\partial t} = \frac{D'_e}{z^{v-1}} \frac{\partial}{\partial z} \left(z^{v-1} \frac{\partial C'_a(r, z, t)}{\partial z} \right) \quad 0 < z < a \quad (A.26)$$

Recall Equation (A.34) which is the dimensionless form of Equation (A.26):

$$\frac{\partial C_a(X, Z, T)}{\partial T} = \frac{D'_e}{R_{im}} \frac{C_3^2}{C_2} \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_a(X, Z, T)}{\partial Z} \right] \quad 0 < Z < a \quad (A.34)$$

If we substitute in Equations (A.41) and (A.45) then Equation (A.34) becomes

$$\frac{\partial C_s}{\partial T} = \frac{D'_e}{R_{im}} \frac{2 \pi b \theta_m R_m a_1^2}{Q_w a^2} \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s}{\partial Z} \right] \quad 0 < Z < 1 \quad (A.83)$$

If we define a dimensionless immobile region solute diffusion coefficient, D_e , as

$$D_e = \frac{D'_e a_1^2 2 \pi b \theta_m R_m}{a^2 Q_w R_{im}} \quad (A.84)$$

Then Equation (A.83) becomes

$$\frac{\partial C_s(X, Z, T)}{\partial T} = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (A.85)$$

and is valid for all the diffusion models. That is, $v = 1, 2$, and 3. Now we take the Laplace transform of Equation (A.85) using Equation (A.52) (initial condition) and Equations (A.56) and (A.57) (boundary conditions):

$$C_s(X, Z, T = 0) = F_s(X, Z) \quad X_w < X < X_s \quad (A.52)$$

$$\frac{\partial C_s(X, Z = 0, T)}{\partial Z} = 0 \quad X_w < X < X_s \quad (A.56)$$

$$C_s(X, Z = 1, T) = C_m(X, T) \quad X_w < X < X_s \quad (A.57)$$

So,

$$\mathcal{L} \left(\frac{\partial C_s}{\partial T} \right) = \mathcal{L} \left(\frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial C_s}{\partial Z} \right) \right) \quad (A.86)$$

$$s\bar{C}_i - C_i(X, Z, T = 0) = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_i}{\partial Z} \right) \quad (A.87)$$

$$s\bar{C}_i - F_i(X, Z) = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_i}{\partial Z} \right) \quad (A.88)$$

thus

$$\frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_i}{\partial Z} \right) - s\bar{C}_i = -F_i(X, Z) \quad (A.89)$$

where $\bar{C}_i(X, Z, s)$ is the Laplace domain dimensionless concentration at points within the immobile region. The boundary conditions associated with Equation (A.89) are derived by taking the Laplace transform of Equations (A.56) and (A.57). Thus,

$$\frac{\partial \bar{C}_i}{\partial Z}(X, Z = 0, s) = 0 \quad X_w < X < X_i \quad (A.90)$$

$$\bar{C}_i(X, Z = 1, s) = \bar{C}_m(X, s) \quad X_w < X < X_i \quad (A.91)$$

We seek the general solution to Equation (A.89) using the boundary conditions (A.90) and (A.91) for cases of $v = 1, 2, 3$ (layered, cylinder, and spherical geometry, respectively). That is, we seek

$$\bar{C}_i = \bar{C}_{i,c} + \bar{C}_{i,p} \quad (A.92)$$

where $\bar{C}_i$ is the general solution to the differential equation, $\bar{C}_{i,c}$ is the complementary solution to the homogeneous differential equation, and $\bar{C}_{i,p}$ is the particular solution to the

nonhomogeneous differential equation. Now we look at the case where $v = 1$.

Layered Diffusion. We first find the general solution to the homogeneous problem. So Equation (A.89) becomes

$$\frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_{a,c}}{\partial Z} \right) - s \bar{C}_{a,c} = 0 \quad 0 < Z < 1 \quad (\text{A.93})$$

If we define $u = \bar{C}_{a,c}$, then Equation (A.93) becomes

$$\frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial u}{\partial Z} \right) - su = 0 \quad 0 < Z < 1 \quad (\text{A.94})$$

When $v = 1$, Equation (A.94) transforms into a second order differential equation with constant coefficients:

$$D_e \frac{\partial^2 u}{\partial Z^2} - su = 0 \quad 0 < Z < 1 \quad (\text{A.95})$$

The general solution of this differential equation is of the form

$$u(Z) = c_1 u_1(Z) + c_2 u_2(Z) \quad (\text{A.96})$$

where c_1 and c_2 are constants and $u_i(Z)$ is of the form $u_i(Z) = e^{m_i Z}$ [Ritger and Rose, 1968:121, 129]. So,

$$D_e m^2 e^{mZ} - s e^{mZ} = 0 \quad (\text{A.97})$$

$$e^{mZ} (D_e m^2 - s) = 0 \quad (\text{A.98})$$

Since e^{mZ} is not equal to zero then the auxillary equation is

$$D_e m^2 - s = 0 \quad (\text{A.99})$$

So,

$$m^2 = \frac{s}{D_e} \quad \text{or} \quad m_1 = \sqrt{\frac{s}{D_e}} \quad m_2 = -\sqrt{\frac{s}{D_e}} \quad (\text{A.100})$$

Thus,

$$u(Z) = c_1 e^{\sqrt{\frac{s}{D_e}} Z} + c_2 e^{-\sqrt{\frac{s}{D_e}} Z} \quad (\text{A.101})$$

If we define

$$\omega = \sqrt{\frac{s}{D_e}} \quad (\text{A.102})$$

then

$$u(Z) = c_1 e^{\omega Z} + c_2 e^{-\omega Z} \quad (\text{A.103})$$

We now check this solution for linear independence to determine if Equation (A.103) is the general solution to Equation (A.95). Thus, we use the Wronskian, $W[u_1, u_2]$. That is, if $W[u_1, u_2] \neq 0$ then the two solutions, u_1 and u_2 , are linearly independent and $u(Z)$ is the general solution. Using Equation (A.103) with $u_1 = e^{\omega Z}$ and $u_2 = e^{-\omega Z}$ we get

$$W[u_1, u_2] = \begin{vmatrix} u_1 & u_2 \\ u_1' & u_2' \end{vmatrix} = \begin{vmatrix} e^{\omega Z} & e^{-\omega Z} \\ \omega e^{\omega Z} & -\omega e^{-\omega Z} \end{vmatrix} \quad (\text{A.104})$$

$$= -\omega e^{-\omega Z} e^{\omega Z} - \omega e^{\omega Z} e^{-\omega Z} = -\omega - \omega = -2\omega \neq 0 \quad (\text{A.105})$$

Thus, u_1 and u_2 are linearly independent so $u(Z) = c_1 e^{\omega Z} + c_2 e^{-\omega Z}$ is the general solution.

Now we seek the particular solution using a Green's function. If we define $U = \bar{C}_s$, then from Equation (A.89), we have the following nonhomogeneous differential equation:

$$D_e \frac{\partial^2 U}{\partial Z^2} - sU = -F_s(X, Z) \quad (A.106)$$

with boundary conditions

$$\frac{\partial U}{\partial Z}(Z = 0) = 0 \quad (A.107)$$

$$U(Z = 1) = 0 \quad (A.108)$$

Rewriting Equation (A.106) gives us

$$\frac{\partial^2 U}{\partial Z^2} - \frac{s}{D_e} U = -\frac{1}{D_e} F_s(X, Z) \quad (A.109)$$

or

$$\frac{\partial^2 U}{\partial Z^2} - \omega^2 U = -\frac{1}{D_e} F_s(X, Z) \quad (A.110)$$

where $\omega^2 = s / D_e$ (Equation (A.102)). We know the general solution of this equation is of the form

$$U(Z) = AU_1(Z) + BU_2(Z) + U_p \quad (A.111)$$

where A and B are constants and U_p (or $\bar{C}_{s,p}$) is the particular solution [Ritger and Ross, 1968:438]. Based on the homogeneous solution, we know that $U_1(Z) = c_1 e^{\omega Z} + c_2 e^{-\omega Z}$ satisfies the boundary condition $\partial U_1(Z = 0) / \partial Z = 0$. That is, $\omega c_1 e^{\omega(0)} - \omega c_2 e^{-\omega(0)} = 0$, which implies $c_1 = c_2$. So,

$$U_1(Z) = c_1 e^{\omega Z} + c_1 e^{-\omega Z} \quad (\text{A.112})$$

If we choose $c_1 = 1/2$ (without loss of generality), then

$$U_1(Z) = \frac{e^{\omega Z} + e^{-\omega Z}}{2} = \cosh \omega Z \quad (\text{A.113})$$

We also know that $U_2(Z) = c_3 e^{\omega Z} + c_4 e^{-\omega Z}$ satisfies the other boundary condition $U_2(Z=1) = 0$. Thus,

$$U_2(Z=1) = 0 = c_3 e^{\omega(1)} + c_4 e^{-\omega(1)} \quad (\text{A.114})$$

so

$$c_4 = -c_3 e^{2\omega} \quad (\text{A.115})$$

Therefore,

$$U_2(Z) = c_3 e^{\omega Z} - c_3 e^{2\omega} e^{-\omega Z} \quad (\text{A.116})$$

$$= c_3 e^{\omega} [e^{\omega Z} e^{-\omega} - e^{\omega} e^{-\omega Z}] \quad (\text{A.117})$$

$$= c_3 e^{\omega} [e^{\omega(Z-1)} - e^{-\omega(Z-1)}] \quad (\text{A.118})$$

or

$$U_2(Z) = c_3 e^{\omega} [-e^{\omega(1-Z)} + e^{-\omega(1-Z)}] \quad (\text{A.119})$$

Since $c_3 e^{\omega}$ is a constant, let's choose it to equal $-1/2$ (without loss of generality). This gives us

$$U_2(Z) = \frac{e^{\omega(1-Z)} - e^{-\omega(1-Z)}}{2} = \sinh \omega(1-Z) \quad (\text{A.120})$$

We now check to see if we have a trivial or non-trivial solution using the zero boundary conditions for the homogeneous case:

$$\frac{\partial u}{\partial Z}(Z = 0) = 0 \quad (\text{A.121})$$

$$u(Z = 1) = 0 \quad (\text{A.122})$$

This will determine the form of the Green's function for the particular solution. We know Equation (A.110) with the above boundary conditions has a unique solution if and only if the homogeneous problem (Equation (A.95)) has only the trivial solution for the same zero boundary conditions [Ritger and Ross, 1968:439]. Recall, $u(Z) = c_1 e^{\omega Z} + c_2 e^{-\omega Z}$ (Equation (A.103)), so

$$\frac{\partial u}{\partial Z}(Z = 0) = 0 = \omega c_1 e^{\omega(0)} - \omega c_2 e^{-\omega(0)} = \omega(c_1 - c_2) \quad (\text{A.123})$$

thus,

$$c_1 = c_2 \quad (\text{A.124})$$

At the other boundary condition, $u(Z = 1) = 0$, we get

$$u(Z = 1) = 0 = c_1 e^{\omega(1)} + c_2 e^{-\omega(1)} \quad (\text{A.125})$$

$$c_2 e^{-\omega} = -c_1 e^{\omega} \quad (\text{A.126})$$

$$c_2 = -c_1 e^{2\omega} \quad (\text{A.127})$$

thus,

$$c_1 = c_2 = -c_1 e^{2\omega} \quad \text{or} \quad c_1 = 0 \quad (\text{A.128})$$

so, $u(Z) = 0$ is the trivial solution.

Since we have a trivial solution we now construct the particular solution using a Green's function which is of the form [Ritger and Ross, 1968:440]

$$g(Z, \zeta) = \begin{cases} \frac{U_1(Z)U_2(\zeta)}{p(\zeta)W[U_1, U_2](\zeta)} & Z < \zeta < 1 \\ \frac{U_1(\zeta)U_2(Z)}{p(\zeta)W[U_1, U_2](\zeta)} & 0 < \zeta < Z \end{cases} \quad (\text{A.129})$$

where $W[U_1, U_2](\zeta)$ is the Wronskian of U_1 and U_2 , and $p(\zeta)$ is the coefficient of the first term in Equation (A.110). From Equation (A.110), we see that $p(\zeta) = 1$. Now we determine the Wronskian:

$$W[U_1, U_2] = \begin{vmatrix} U_1 & U_2 \\ U_1' & U_2' \end{vmatrix} = \begin{vmatrix} \cosh \omega Z & \sinh \omega(1-Z) \\ \omega \sinh \omega Z & -\omega \cosh \omega(1-Z) \end{vmatrix} \quad (\text{A.130})$$

$$= -\omega \cosh \omega(1-Z) \cosh \omega Z - \omega \sinh \omega Z \sinh \omega(1-Z) \quad (\text{A.131})$$

$$= -\omega [\cosh \omega Z \cosh \omega(1-Z) + \sinh \omega Z \sinh \omega(1-Z)] \quad (\text{A.132})$$

$$= -\omega \cosh(\omega Z + \omega(1-Z)) \quad (\text{A.133})$$

$$= -\omega \cosh \omega \neq 0 \quad (\text{A.134})$$

So,

$$g(Z, \zeta) = \begin{cases} \frac{\cosh \omega Z \sinh \omega(1 - \zeta)}{-\omega \cosh \omega} & Z < \zeta < 1 \\ \frac{\cosh \omega \zeta \sinh \omega(1 - Z)}{-\omega \cosh \omega} & 0 < \zeta < Z \end{cases} \quad (\text{A.135})$$

Therefore,

$$U_p = \bar{C}_{a_p}(X, Z, s) = - \int_0^1 g(Z, \zeta) \left[\frac{F_a(X, \zeta)}{D_e} \right] d\zeta \quad (\text{A.136})$$

Thus, Equation (A.92) is

$$\begin{aligned} \bar{C}_a &= \bar{C}_{a_c} + \bar{C}_{a_p} = A \cosh \omega Z + B \sinh \omega(1 - Z) \\ &\quad - \frac{1}{D_e} \int_0^1 g(Z, \zeta) F_a(X, \zeta) d\zeta \end{aligned} \quad (\text{A.137})$$

or

$$\begin{aligned} \bar{C}_a &= A \cosh \omega Z + B \sinh \omega(1 - Z) + \frac{\cosh \omega Z}{\omega D_e \cosh \omega} \int_Z^1 \sinh \omega(1 - \zeta) F_a(X, \zeta) d\zeta \\ &\quad + \frac{\sinh \omega(1 - Z)}{\omega D_e \cosh \omega} \int_0^Z \cosh(\omega \zeta) F_a(X, \zeta) d\zeta \end{aligned} \quad (\text{A.138})$$

Now we apply the nonzero boundary conditions (Equations (A.90) and (A.91)) to find the constants A and B.

$$\begin{aligned}
\frac{\partial \bar{C}_s}{\partial Z}(X, Z = 0, s) = 0 = & \omega A \sinh \omega(0) - \omega B \cosh \omega(1 - 0) \\
& + \frac{\omega \sinh \omega(0)}{\omega D_e \cosh \omega} \int_0^1 \sinh \omega(1 - \zeta) F_s(X, \zeta) d\zeta \\
& - \frac{\cosh \omega(0)}{\omega D_e \cosh \omega} \sinh \omega(1 - Z) F_s(X, Z) \Big|_{Z=0} \\
& - \frac{\omega \cosh \omega(1 - 0)}{\omega D_e \cosh \omega} \int_0^0 \cosh(\omega \zeta) F_s(X, \zeta) d\zeta \\
& + \frac{\sinh \omega(1 - 0)}{\omega D_e \cosh \omega} \cosh(\omega Z) F_s(X, Z) \Big|_{Z=0}
\end{aligned} \tag{A.139}$$

or

$$0 = -\omega B \cosh \omega \tag{A.140}$$

So, $B = 0$. Now we apply the second boundary condition

$$\bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s).$$

$$\begin{aligned}
\bar{C}_m(X, s) = A \cosh \omega(1) + \frac{\cosh \omega(1)}{\omega D_e \cosh \omega} \int_1^1 \sinh \omega(1 - \zeta) F_s(X, \zeta) d\zeta \\
+ \frac{\sinh \omega(1 - 1)}{\omega D_e \cosh \omega} \int_0^1 \cosh(\omega \zeta) F_s(X, \zeta) d\zeta
\end{aligned} \tag{A.141}$$

So, $A = \frac{\bar{C}_m(X, s)}{\cosh \omega}$. Thus, Equation (A.138) becomes

$$\bar{C}_s(X, Z, s) = \frac{\bar{C}_m(X, s)}{\cosh \omega} \cosh \omega Z - \frac{1}{D_e} \int_0^1 g(Z, \zeta) F_s(X, \zeta) d\zeta \tag{A.142}$$

Combining Equations (A.48), (A.49), and (A.50) we get

$$s\bar{C}_m - F_m(X) = \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \beta[s\bar{C}_m - F_m(X)] \quad (A.143)$$

Now we need an expression for $\bar{C}_m$. Recall Equation (A.11):

$$C'_{im}(r, t) = \frac{v}{a^v} \int_0^a z^{v-1} C'_i(r, z, t) dz \quad (A.11)$$

Normalizing and converting this equation to dimensionless form, where $C_{im}(X, T) = C'_{im}(r, t) / C'_0$ (Equation (A.16)) and $Z = z / a$ (Equation (A.44)) we get

$$C'_0 C_{im}(X, T) = \frac{v}{(1)^v} \int_0^1 (Z(1))^{v-1} C'_0 C_i dZ = v C'_0 \int_0^1 Z^{v-1} C_i dZ \quad (A.144)$$

So,

$$C_{im}(X, T) = v \int_0^1 Z^{v-1} C_i(X, Z, T) dZ \quad (A.145)$$

Taking the Laplace transform of Equation (A.145) with $v = 1$, we get

$$\bar{C}_{im}(X, s) = \int_0^1 \bar{C}_i(X, Z, s) dZ \quad (A.146)$$

Substituting in Equation (A.142) into Equation (A.146) we get

$$\bar{C}_{im}(X, s) = \int_0^1 \frac{\bar{C}_m(X, s) \cosh \omega Z}{\cosh \omega} dZ - \frac{1}{D_e} \int_0^1 \int_0^1 g(Z, \zeta) F_s(X, \zeta) d\zeta dZ \quad (A.147)$$

$$= \frac{\bar{C}_m(X, s)}{\cosh \omega} \int_0^1 \cosh \omega Z dZ - \frac{1}{D_e} \int_0^1 \left[\int_0^1 g(Z, \zeta) dZ \right] F_s(X, \zeta) d\zeta \quad (A.148)$$

$$= \frac{\bar{C}_m(X, s)}{\cosh \omega} \left[\frac{\sinh \omega Z}{\omega} \right]_0^1 - \frac{1}{D_e} \int_0^1 \left[\int_0^1 g(Z, \zeta) dZ \right] F_s(X, \zeta) d\zeta \quad (A.149)$$

$$= \frac{\bar{C}_m(X, s) \sinh \omega}{\omega \cosh \omega} - \frac{1}{D_e} \int_0^1 \left[\int_0^1 g(Z, \zeta) dZ \right] F_s(X, \zeta) d\zeta \quad (A.150)$$

Now we determine $\int_0^1 g(Z, \zeta) dZ$ where $g(Z, \zeta)$ is defined by Equation (A.135).

$$\int_0^1 g(Z, \zeta) dZ = \int_0^\zeta \left[\frac{\cosh \omega Z \sinh \omega(1 - \zeta)}{-\omega \cosh \omega} \right] dZ \quad (\text{A.151})$$

$$+ \int_\zeta^1 \left[\frac{\cosh \omega \zeta \sinh \omega(1 - Z)}{-\omega \cosh \omega} \right] dZ$$

$$= \frac{\sinh \omega Z \sinh \omega(1 - \zeta)}{-\omega^2 \cosh \omega} \Big|_0^\zeta + \frac{\cosh \omega \zeta \cosh \omega(1 - Z)}{-\omega \cosh \omega(-\omega)} \Big|_\zeta^1 \quad (\text{A.152})$$

$$= \frac{\sinh \omega \zeta \sinh \omega(1 - \zeta)}{-\omega^2 \cosh \omega} + \frac{\cosh \omega \zeta}{\omega^2 \cosh \omega} \quad (\text{A.153})$$

$$- \frac{\cosh \omega \zeta \cosh \omega(1 - \zeta)}{\omega^2 \cosh \omega}$$

$$= - \frac{1}{\omega^2 \cosh \omega} [\sinh \omega \zeta \sinh \omega(1 - \zeta) + \cosh \omega \zeta \cosh \omega(1 - \zeta)] \quad (\text{A.154})$$

$$+ \frac{\cosh \omega \zeta}{\omega^2 \cosh \omega}$$

$$= - \frac{1}{\omega^2 \cosh \omega} [\cosh(\omega \zeta + \omega(1 - \zeta))] + \frac{\cosh \omega \zeta}{\omega^2 \cosh \omega} \quad (\text{A.155})$$

So,

$$\int_0^1 g(Z, \zeta) dZ = \frac{1}{\omega^2} \left[-1 + \frac{\cosh \omega \zeta}{\cosh \omega} \right] \quad (\text{A.156})$$

Inserting this equation back into $\bar{C}_{im}(X, s)$ (Equation (A.150)) gives us

$$\bar{C}_{im}(X, s) = \frac{\bar{C}_m(X, s) \sinh \omega}{\omega \cosh \omega} - \frac{1}{\omega^2 D_e} \int_0^1 \left[-1 + \frac{\cosh \omega \zeta}{\cosh \omega} \right] F_i(X, \zeta) d\zeta \quad (\text{A.157})$$

Now we have an expression for $\bar{C}_m(X, s)$. Using this equation let's substitute it back into Equation (A.143):

$$s\bar{C}_m - F_m(X) = \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \beta [s\bar{C}_m - F_m(X)] \quad (A.143)$$

Thus,

$$\begin{aligned} s\bar{C}_m - F_m(X) &= \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} \\ &\quad - \beta \left[s \left\{ \frac{\bar{C}_m \sinh \omega}{\omega \cosh \omega} - \frac{1}{\omega^2 D_e} \int_0^1 \left[-1 + \frac{\cosh \omega \zeta}{\cosh \omega} \right] F_1(X, \zeta) d\zeta \right\} - F_m(X) \right] \end{aligned} \quad (A.158)$$

Rearranging this equation and multiplying each term by X gives us the following

$$\begin{aligned} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - Xs\bar{C}_m \left(1 + \frac{\beta \sinh \omega}{\omega \cosh \omega} \right) &= -X[F_m(X) + \beta F_m(X) \\ &\quad + \frac{\beta s}{\omega^2 D_e} \int_0^1 \left[-1 + \frac{\cosh \omega \zeta}{\cosh \omega} \right] F_1(X, \zeta) d\zeta] \end{aligned} \quad (A.159)$$

If we define

$$\gamma = s \left(1 + \frac{\beta \sinh \omega}{\omega \cosh \omega} \right) \quad (A.160)$$

and recall that $s = \omega^2 D_e$ (Equation (A.102)), then we get

$$\begin{aligned} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma\bar{C}_m &= -X[F_m(X) + \beta F_m(X) \\ &\quad + \beta \int_0^1 \left[\frac{\cosh \omega \zeta}{\cosh \omega} - 1 \right] F_1(X, \zeta) d\zeta] \end{aligned} \quad (A.161)$$

The right-hand side of this equation can be further simplified using the initial conditions $C_m(X, T = 0) = F_m(X)$ (Equation (A.50)), $C_i(X, Z, T = 0) = F_i(X, Z)$ (Equation (A.52)), and the dimensionless expression for the volume-average immobile region solute concentration, $C_m(X, T) = v \int_0^1 Z^{v-1} C_i(X, Z, T) dZ$ where $v = 1$ (Equation (A.145)). Therefore, at time $T = 0$

$$F_m(X) = C_m(X, T = 0) = \int_0^1 C_i(X, Z, T = 0) dZ = \int_0^1 F_i(X, Z) dZ \quad (A.162)$$

Putting this expression for $F_m(X)$ into the right-hand side of Equation (A.161) gives us

$$-X[F_m(X) + \beta \int_0^1 F_i(X, Z) dZ + \beta \int_0^1 \left[\frac{\cosh \omega \zeta}{\cosh \omega} - 1 \right] F_i(X, \zeta) d\zeta] \quad (A.163)$$

or

$$-X[F_m(X) + \beta \int_0^1 F_i(X, \zeta) d\zeta + \beta \int_0^1 \left(\frac{\cosh \omega \zeta}{\cosh \omega} \right) F_i(X, \zeta) d\zeta - \beta \int_0^1 F_i(X, \zeta) d\zeta] \quad (A.164)$$

Thus, Equation (A.164) becomes

$$-X[F_m(X) + \frac{\beta}{\cosh \omega} \int_0^1 \cosh(\omega \zeta) F_i(X, \zeta) d\zeta] \quad (A.165)$$

So, if we define

$$\bar{F}(X, s) = -X \left[F_m(X) + \frac{\beta}{\cosh \omega} \int_0^1 \cosh(\omega \zeta) F_i(X, \zeta) d\zeta \right] \quad (A.166)$$

then Equation (A.161) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma \bar{C}_m = \bar{F}(X, s) \quad (A.167)$$

Using similar techniques as in the above derivation when $v = 1$, we now seek the solution when $v = 2$.

Cylindrical Diffusion. From Equation (A.85) we have

$$\frac{\partial C_s(X, Z, T)}{\partial T} = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (\text{A.85})$$

which is valid for all the diffusion models. As previously derived, we now take the Laplace transform of Equation (A.85) using Equation (A.52) (initial condition) and Equations (A.56) and (A.57) (boundary conditions):

$$C_s(X, Z, T = 0) = F_s(X, Z) \quad X_w < X < X_s \quad (\text{A.52})$$

$$\frac{\partial C_s(X, Z = 0, T)}{\partial Z} = 0 \quad X_w < X < X_s \quad (\text{A.56})$$

$$C_s(X, Z = 1, T) = C_m(X, T) \quad X_w < X < X_s \quad (\text{A.57})$$

So,

$$\mathcal{L} \left(\frac{\partial C_s}{\partial T} \right) = \mathcal{L} \left(\frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial C_s}{\partial Z} \right) \right) \quad (\text{A.86})$$

$$s\bar{C}_s - C_s(X, Z, T = 0) = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z} \right) \quad (\text{A.87})$$

$$s\bar{C}_s - F_s(X, Z) = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z} \right) \quad (\text{A.88})$$

Thus,

$$\frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z} \right) - s\bar{C}_s = -F_s(X, Z) \quad (\text{A.89})$$

with the following boundary conditions:

$$\frac{\partial \bar{C}_s}{\partial Z}(X, Z = 0, s) = 0 \quad X_w < X < X_s \quad (A.90)$$

$$\bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s) \quad X_w < X < X_s \quad (A.91)$$

We seek the general solution to Equation (A.89) using the boundary conditions (A.90) and (A.91) for case of $v = 2$. That is,

$$\bar{C}_s = \bar{C}_{s,c} + \bar{C}_{s,p} \quad (A.92)$$

where $\bar{C}_s$ is the general solution to the differential equation, $\bar{C}_{s,c}$ is the complementary solution to the homogeneous differential equation, and $\bar{C}_{s,p}$ is the particular solution to the nonhomogeneous differential equation. So for the case of $v = 2$, Equation (A.89) becomes

$$\frac{D_e}{Z} \frac{\partial}{\partial Z} \left(Z \frac{\partial \bar{C}_s}{\partial Z} \right) - s \bar{C}_s = -F_s(X, Z) \quad (A.168)$$

Multiply Equation (A.168) by $1 / D_e$ and differentiating the first term gives us

$$\frac{1}{Z} \frac{\partial}{\partial Z} \left(Z \frac{\partial \bar{C}_s}{\partial Z} \right) - \frac{s}{D_e} \bar{C}_s = -\frac{F_s(X, Z)}{D_e} \quad (A.169)$$

or

$$\frac{1}{Z} \left[Z \frac{\partial^2 \bar{C}_s}{\partial Z^2} + \frac{\partial \bar{C}_s}{\partial Z} \right] - \frac{s}{D_e} \bar{C}_s = -\frac{F_s(X, Z)}{D_e} \quad (A.170)$$

Thus,

$$\frac{\partial^2 \bar{C}_s}{\partial Z^2} + \frac{1}{Z} \frac{\partial \bar{C}_s}{\partial Z} - \frac{s}{D_e} \bar{C}_s = -\frac{F_s(X, Z)}{D_e} \quad (A.171)$$

If we define

$$\hat{z} = \omega Z \quad (\text{A.172})$$

$$W(\hat{z}) = \bar{C}_s(Z) = \bar{C}_s\left(\frac{\hat{z}}{\omega}\right) \quad (\text{A.173})$$

where $\omega^2 = s / D_e$ (Equation (A.102)), then

$$\frac{\partial \bar{C}_s}{\partial Z} = \frac{\partial W}{\partial \hat{z}} \frac{d\hat{z}}{dZ} = \omega \frac{\partial W}{\partial \hat{z}} \quad (\text{A.174})$$

$$\frac{\partial^2 \bar{C}_s}{\partial Z^2} = \frac{\partial}{\partial Z} \left(\frac{\partial \bar{C}_s}{\partial Z} \right) = \frac{\partial}{\partial \hat{z}} \left(\omega \frac{\partial W}{\partial \hat{z}} \right) \frac{d\hat{z}}{dZ} = \omega^2 \frac{\partial^2 W}{\partial \hat{z}^2} \quad (\text{A.175})$$

Substituting these equations into Equation (A.171) gives us

$$\omega^2 \frac{\partial^2 W}{\partial \hat{z}^2} + \frac{\omega^2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - \omega^2 W = - \frac{F_s(X, \frac{\hat{z}}{\omega})}{D_e} \equiv - \frac{\hat{F}_s(X, \hat{z})}{D_e} \quad (\text{A.176})$$

Multiplying through by $1 / \omega^2$ yields

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{1}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = - \frac{\hat{F}_s(X, \hat{z})}{\omega^2 D_e} \quad (\text{A.177})$$

We now seek the complementary solution to Equation (A.177).

That is,

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{1}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = 0 \quad (\text{A.178})$$

which we know to be a modified Bessel function of order zero [Abramowitz and Stegun, 1970]. Therefore, the general solution to this homogeneous differential equation is

$$W(\hat{z}) = C_1 W_1(\hat{z}) + C_2 W_2(\hat{z}) \quad (\text{A.179})$$

where $W_1(\hat{z})$ and $W_2(\hat{z})$ are of the form

$$W_1(\hat{z}) = A I_0(\hat{z}) + B K_0(\hat{z}) \quad (\text{A.180})$$

$$W_2(\hat{z}) = C I_0(\hat{z}) + D K_0(\hat{z}) \quad (\text{A.181})$$

where C_1, C_2, A, B, C , and D are constants and $I_0(\hat{z})$ and $K_0(\hat{z})$ are modified Bessel functions of the first kind, order zero and third kind, order zero, respectively, and are of the form

$$I_0(\hat{z}) = \sum_{k=0}^{\infty} \frac{\left(\frac{\hat{z}}{2}\right)^{2k}}{(k!)^2} \quad (\text{A.182})$$

$$K_0(\hat{z}) = -\frac{1}{2} I_0(\hat{z}) \ln \hat{z} + \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{(k!)^2} \left(1 + \frac{1}{2} + \dots + \frac{1}{k}\right) \left(\frac{\hat{z}}{2}\right)^{2k} \quad (\text{A.183})$$

To find the first solution, $W_1(\hat{z})$, we apply the zero flux boundary condition to $W_1(\hat{z})$ since $Z = 0$ implies $\hat{z} = 0$ (Equation (A.90), thus

$$\frac{\partial W_1(\hat{z} = 0)}{\partial \hat{z}} = 0 \quad (\text{A.184})$$

So,

$$\frac{\partial W_1}{\partial \hat{z}} = 0 = A I'_0(\hat{z} = 0) + B K'_0(\hat{z} = 0) \quad (\text{A.185})$$

$$= B K'_0(\hat{z} = 0) \quad (\text{A.186})$$

since $K'_0(\hat{z} = 0)$ is not equal to zero, we take B equal to zero.

Therefore,

$$W_1(\hat{z}) = A I_0(\hat{z}) \quad (\text{A.187})$$

Without loss of generality, let's take $A = 1$, so

$$W_1(\hat{z}) = I_0(\hat{z}) \quad (\text{A.188})$$

We also know the second solution, $W_2(\hat{z})$, to be of the form

$$W_2(\hat{z}) = C I_0(\hat{z}) + D K_0(\hat{z}) \quad (\text{A.189})$$

and satisfies the 'zero' boundary condition (Equation (A.91))

where $Z = 1$ implies $\hat{z} = \omega$:

$$\bar{C}_s(X, Z = 1, s) = 0 = W_2(\hat{z} = \omega) \quad (\text{A.190})$$

So,

$$0 = C I_0(\omega) + D K_0(\omega) \quad (\text{A.191})$$

or

$$D = -\frac{C I_0(\omega)}{K_0(\omega)} \quad (\text{A.192})$$

So,

$$W_2(\hat{z}) = C I_0(\hat{z}) - \frac{C I_0(\omega)}{K_0(\omega)} K_0(\hat{z}) \quad (\text{A.193})$$

Without loss of generality, let's take $C = K_0(\omega)$. Thus,

$$W_2(\hat{z}) = K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z}) \quad (\text{A.194})$$

Now we seek the particular solution ($\bar{C}_{s,p}$) to the following nonhomogeneous differential equation using a Green's function:

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{1}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = - \frac{\hat{F}_s(X, \hat{z})}{\omega^2 D_e} \quad (\text{A.177})$$

First, we construct the Green's function which is of the form

$$g(\hat{z}, \zeta) = \begin{cases} \frac{W_1(\hat{z}) W_2(\zeta)}{p(\zeta) W[W_1, W_2](\zeta)} & \hat{z} < \zeta < \omega \\ \frac{W_1(\zeta) W_2(\hat{z})}{p(\zeta) W[W_1, W_2](\zeta)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.195})$$

where $W[W_1, W_2](\zeta)$ is the Wronskian of W_1 and W_2 , and $p(\zeta)$ is the coefficient of the first term in Equation (A.177). From Equation (A.177), we see that $p(\zeta) = 1$. Next we determine the Wronskian, $W[W_1, W_2]$:

$$W[W_1, W_2] = \begin{vmatrix} I_0(\hat{z}) & K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z}) \\ I'_0(\hat{z}) & K_0(\omega) I'_0(\hat{z}) - I_0(\omega) K'_0(\hat{z}) \end{vmatrix} \quad (\text{A.196})$$

$$= K_0(\omega) I_0(\hat{z}) I'_0(\hat{z}) - I_0(\omega) I_0(\hat{z}) K'_0(\hat{z}) \quad (\text{A.197})$$

$$- K_0(\omega) I_0(\hat{z}) I'_0(\hat{z}) + I_0(\omega) I'_0(\hat{z}) K_0(\hat{z})$$

$$= I_0(\omega) [I'_0(\hat{z}) K_0(\hat{z}) - I_0(\hat{z}) K'_0(\hat{z})] \quad (\text{A.198})$$

$$= I_0(\omega) W[K_0(\hat{z}), I_0(\hat{z})] \quad (\text{A.199})$$

We know that $W[K_0(\hat{z}), I_0(\hat{z})] = 1 / \hat{z}$ [Abramowitz and Stegun, 1970]. So,

$$W[W_1, W_2] = I_0(\omega) \frac{1}{\hat{z}} \quad (\text{A.200})$$

Therefore, the Green's function is

$$g(\hat{z}, \zeta) = \begin{cases} \frac{\zeta W_1(\hat{z}) W_2(\zeta)}{I_0(\omega)} & \hat{z} < \zeta < \omega \\ \frac{\zeta W_1(\zeta) W_2(\hat{z})}{I_0(\omega)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.201})$$

$$= \begin{cases} \frac{\zeta I_0(\hat{z}) [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} & \hat{z} < \zeta < \omega \\ \frac{\zeta I_0(\zeta) [K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})]}{I_0(\omega)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.202})$$

and

$$\bar{C}_s(\hat{z}) = - \int_0^\omega g(\hat{z}, \zeta) \left[\frac{\hat{F}_s(X, \zeta)}{\omega^2 D_e} \right] d\zeta \quad (\text{A.203})$$

So, the general solution is

$$W(\hat{z}) = \bar{C}_s(\hat{z}) = A W_1(\hat{z}) + B W_2(\hat{z}) - \int_0^\omega g(\hat{z}, \zeta) \left[\frac{\hat{F}_s(X, \zeta)}{\omega^2 D_e} \right] d\zeta \quad (\text{A.204})$$

$$\begin{aligned} &= A I_0(\hat{z}) + B [K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})] \\ &\quad - \frac{I_0(\hat{z})}{\omega^2 D_e} \int_{\hat{z}}^\omega \left[\frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} \right] \hat{F}_s(X, \zeta) d\zeta \quad (\text{A.205}) \\ &\quad - \frac{[K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})]}{\omega^2 D_e I_0(\omega)} \int_0^{\hat{z}} \zeta I_0(\zeta) \hat{F}_s(X, \zeta) d\zeta \end{aligned}$$

To find the constants A and B we use the 'nonzero' boundary conditions (Equations (A.90) and (A.91) where $W(\hat{z}) = \bar{C}_s(Z)$).

Therefore, applying the boundary condition

$$\frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 \quad (\text{A.206})$$

we get

$$\begin{aligned}
\frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 &= A I_0'(0) + B [K_0(\omega) I_0'(0) - I_0(\omega) K_0'(0)] \\
&- \frac{I_0'(0)}{\omega^2 D_e I_0(\omega)} \int_0^\infty \zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \\
&+ \frac{I_0(0)}{\omega^2 D_e I_0(\omega)} \left\{ (0) [K_0(\omega) I_0(0) - I_0(\omega) K_0(0)] \hat{F}_s(X, 0) \right\} \\
&- \frac{[K_0(\omega) I_0'(0) - I_0(\omega) K_0'(0)]}{\omega^2 D_e I_0(\omega)} \int_0^\infty \zeta I_0(\zeta) \hat{F}_s(X, \zeta) d\zeta \\
&- \frac{[K_0(\omega) I_0(0) - I_0(\omega) K_0(0)]}{\omega^2 D_e I_0(\omega)} [(0) I_0(0) \hat{F}_s(X, 0)]
\end{aligned}
\tag{A.207}$$

Since $I_0'(0) = 0$ [Abramowitz and Stegun, 1970] then

$$0 = B [-I_0(\omega) K_0'(0)] \tag{A.208}$$

Since $[-I_0(\omega) K_0'(0)]$ does not equal zero, we take $B = 0$.

Applying the second boundary condition (Equation (A.91))

$$W(\omega) = \bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s) \tag{A.209}$$

we get

$$\begin{aligned}
\bar{C}_m(X, s) &= A I_0(\omega) - \frac{I_0(\omega)}{\omega^2 D_e I_0(\omega)} \int_0^\infty \zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \\
&- \frac{[K_0(\omega) I_0(\omega) - I_0(\omega) K_0(\omega)]}{\omega^2 D_e I_0(\omega)} \int_0^\infty \zeta I_0(\zeta) \hat{F}_s(X, \zeta) d\zeta
\end{aligned}
\tag{A.210}$$

Thus,

$$A = \frac{\bar{C}_m(X, s)}{I_0(\omega)} \quad (A.211)$$

So, Equation (A.204) becomes

$$W(\hat{z}) = \frac{\bar{C}_m(X, s)}{I_0(\omega)} I_0(\hat{z}) - \frac{1}{\omega^2 D_e} \int_0^\omega g(\hat{z}, \zeta) \hat{F}_s(X, \zeta) d\zeta \quad (A.212)$$

$$\begin{aligned} &= \frac{\bar{C}_m(X, s)}{I_0(\omega)} I_0(\hat{z}) \\ &\quad - \frac{I_0(\hat{z})}{\omega^2 D_e I_0(\omega)} \int_z^\omega \zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \quad (A.213) \\ &\quad - \frac{[K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})]}{\omega^2 D_e I_0(\omega)} \int_0^{\hat{z}} \zeta I_0(\zeta) \hat{F}_s(X, \zeta) d\zeta \end{aligned}$$

Recall, Equation (A.145)

$$C_{im}(X, T) = v \int_0^1 Z^{v-1} C_s(X, Z, T) dZ \quad (A.145)$$

and $W(\hat{z}) = \bar{C}_s(\hat{z} / \omega) = \bar{C}_s(Z)$ where $\hat{z} = \omega Z$. Taking the Laplace transform of Equation (A.145) with $v = 2$, we get

$$\bar{C}_{im}(X, s) = 2 \int_0^1 Z \bar{C}_s(X, Z, s) dZ = \frac{2}{\omega^2} \int_0^\omega \hat{z} W(\hat{z}) d\hat{z} \quad (A.214)$$

Substituting the general solution, $W(\hat{z})$ (Equation (A.212)), into this expression gives us

$$\bar{C}_{im}(X, s) = \frac{2 \bar{C}_m(X, s)}{\omega^2 I_0(\omega)} \int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} - \frac{2}{\omega^4 D_e} \int_0^\omega \int_0^\omega \hat{z} g(\hat{z}, \zeta) \hat{F}_s(X, \zeta) d\zeta d\hat{z} \quad (A.215)$$

To determine the first integral, we use the following homogeneous differential equation:

$$\hat{z}^2 \frac{d^2 I_0(\hat{z})}{d\hat{z}^2} + \hat{z} \frac{dI_0(\hat{z})}{d\hat{z}} - \hat{z}^2 I_0(\hat{z}) = 0 \quad (\text{A.216})$$

Multiplying each term by $1/\hat{z}$ produces

$$\hat{z} \frac{d^2 I_0(\hat{z})}{d\hat{z}^2} + \frac{dI_0(\hat{z})}{d\hat{z}} - \hat{z} I_0(\hat{z}) = 0 \quad (\text{A.217})$$

So,

$$\hat{z} I_0(\hat{z}) = \hat{z} \frac{d^2 I_0(\hat{z})}{d\hat{z}^2} + \frac{dI_0(\hat{z})}{d\hat{z}} \quad (\text{A.218})$$

Integrating both sides of this equation gives us

$$\int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} = \int_0^\omega \hat{z} \frac{d^2 I_0(\hat{z})}{d\hat{z}^2} d\hat{z} + \int_0^\omega \frac{dI_0(\hat{z})}{d\hat{z}} d\hat{z} \quad (\text{A.219})$$

Now, using integration by parts on the right-hand side of this equation yields

$$\int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} = \hat{z} \frac{dI_0(\hat{z})}{d\hat{z}} \Big|_0^\omega - \int_0^\omega \frac{dI_0(\hat{z})}{d\hat{z}} d\hat{z} + I_0(\hat{z}) \Big|_0^\omega \quad (\text{A.220})$$

$$\int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} = \hat{z} \frac{dI_0(\hat{z})}{d\hat{z}} \Big|_0^\omega - I_0(\hat{z}) \Big|_0^\omega + I_0(\hat{z}) \Big|_0^\omega = \hat{z} \frac{dI_0(\hat{z})}{d\hat{z}} \Big|_0^\omega \quad (\text{A.221})$$

or

$$\int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} = \hat{z} I_0'(\hat{z}) \Big|_0^\omega = \omega I_0'(\omega) \quad (\text{A.222})$$

Thus, Equation (A.215) becomes

$$\bar{C}_m(X, s) = \frac{2\bar{C}_m(X, s)}{\omega^2 I_0(\omega)} [\omega I'_0(\omega)] - \frac{2}{\omega^4 D_e} \int_0^\infty \int_0^\infty \hat{z} g(\hat{z}, \zeta) \hat{F}_1(X, \zeta) d\zeta d\hat{z} \quad (A.223)$$

$$= \frac{2\bar{C}_m(X, s) I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^4 D_e} \int_0^\infty \left(\int_0^\infty \hat{z} g(\hat{z}, \zeta) d\hat{z} \right) \hat{F}_1(X, \zeta) d\zeta \quad (A.224)$$

Now we solve

$$\int_0^\infty \hat{z} g(\hat{z}, \zeta) d\hat{z} = \int_0^\zeta \hat{z} g(\hat{z}, \zeta) d\hat{z} + \int_\zeta^\infty \hat{z} g(\hat{z}, \zeta) d\hat{z} \quad (A.225)$$

$$= \frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} \int_0^\zeta \hat{z} I_0(\hat{z}) d\hat{z} \quad (A.226)$$

$$+ \frac{\zeta I_0(\zeta)}{I_0(\omega)} \int_\zeta^\infty \hat{z} [K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})] d\hat{z}$$

$$= \frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} \int_0^\zeta \hat{z} I_0(\hat{z}) d\hat{z}$$

$$+ \frac{\zeta I_0(\zeta) K_0(\omega)}{I_0(\omega)} \int_\zeta^\infty \hat{z} I_0(\hat{z}) d\hat{z} - \frac{\zeta I_0(\zeta) I_0(\omega)}{I_0(\omega)} \int_\zeta^\infty \hat{z} K_0(\hat{z}) d\hat{z} \quad (A.227)$$

From Equation (A.222), we know these integrals (similar derivation for $K_0(\hat{z})$). Thus, Equation (A.225) is

$$\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} = \frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} \left[\hat{z} I'_0(\hat{z}) \right] \Big|_0^\zeta$$

$$+ \frac{\zeta I_0(\zeta) K_0(\omega)}{I_0(\omega)} \left[\hat{z} I'_0(\hat{z}) \right] \Big|_\zeta^\omega$$

$$- \frac{\zeta I_0(\zeta) I_0(\omega)}{I_0(\omega)} \left[\hat{z} K'_0(\hat{z}) \right] \Big|_\zeta^\omega$$
(A.228)

$$= \frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} [\zeta I'_0(\zeta)]$$

$$+ \frac{\zeta I_0(\zeta) K_0(\omega)}{I_0(\omega)} [\omega I'_0(\omega) - \zeta I'_0(\zeta)]$$

$$- \frac{\zeta I_0(\zeta) I_0(\omega)}{I_0(\omega)} [\omega K'_0(\omega) - \zeta K'_0(\zeta)]$$
(A.229)

Collecting terms and simplifying,

$$\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} = -\zeta^2 I'_0(\zeta) K_0(\zeta) + \frac{\zeta \omega I_0(\zeta) K_0(\omega) I'_0(\omega)}{I_0(\omega)}$$

$$- \frac{\zeta \omega I_0(\zeta) I_0(\omega) K'_0(\omega)}{I_0(\omega)} + \zeta^2 I_0(\zeta) K'_0(\zeta)$$
(A.230)

$$= \zeta^2 [I_0(\zeta) K'_0(\zeta) - I'_0(\zeta) K_0(\zeta)]$$
(A.231)

$$+ \frac{\zeta \omega I_0(\zeta)}{I_0(\omega)} [K_0(\omega) I'_0(\omega) - I_0(\omega) K'_0(\omega)]$$

$$= \zeta^2 (-W[K_0, I_0](\zeta)) + \frac{\zeta \omega I_0(\zeta)}{I_0(\omega)} (W[K_0, I_0](\omega))$$
(A.232)

$$= \zeta^2 \left(-\frac{1}{\zeta} \right) + \frac{\zeta \omega I_0(\zeta)}{I_0(\omega)} \left(\frac{1}{\omega} \right)$$
(A.233)

So, Equation (A.225) becomes

$$\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} = \zeta \left[\frac{I_0(\zeta)}{I_0(\omega)} - 1 \right]$$
(A.234)

Returning to Equation (A.224)

$$\bar{C}_{im}(X, s) = \frac{2\bar{C}_m(X, s)I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^4 D_e} \int_0^\omega \left(\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} \right) \hat{F}_i(X, \zeta) d\zeta \quad (A.224)$$

and substituting in Equation (A.234) we get

$$\bar{C}_{im}(X, s) = \frac{2\bar{C}_m(X, s)I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^4 D_e} \int_0^\omega \left(\zeta \left[\frac{I_0(\zeta)}{I_0(\omega)} - 1 \right] \right) \hat{F}_i(X, \zeta) d\zeta \quad (A.235)$$

If we let $\zeta = \omega\xi$, then when $\zeta = 0$, $\xi = 0$ and when $\zeta = \omega$, $\xi = 1$. So,

$$\bar{C}_{im}(X, s) = \frac{2\bar{C}_m(X, s)I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^4 D_e} \int_0^1 \left(\omega\xi \left[\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right] \right) F_i(X, \xi) \omega d\xi \quad (A.236)$$

or

$$\bar{C}_{im}(X, s) = \frac{2\bar{C}_m(X, s)I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^2 D_e} \int_0^1 \xi \left[\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right] F_i(X, \xi) d\xi \quad (A.237)$$

Using Equation (A.143)

$$s\bar{C}_m - F_m(X) = \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \beta [s\bar{C}_{im} - F_{im}(X)] \quad (A.143)$$

we substitute in Equation (A.237):

$$s\bar{C}_m - F_m(X) = \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} + \beta F_m(X) \quad (A.238)$$

$$- \beta s \left\{ \frac{2\bar{C}_m}{I_0(\omega)} \frac{I'_0(\omega)}{\omega} - \frac{2}{\omega^2 D_e} \int_0^1 \xi \left[\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right] F_i(X, \xi) d\xi \right\}$$

Rearranging and multiplying each term by X gives us

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - Xs\bar{C}_m \left[\frac{2\beta I'_0(\omega)}{\omega I_0(\omega)} + 1 \right] = -X[F_m(X) + \beta F_m(X)$$

$$+ \frac{2\beta s}{\omega^2 D_e} \int_0^1 \xi \left(\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right) F_i(X, \xi) d\xi]$$

(A.239)

If we define

$$\gamma = s \left[1 + \frac{2\beta I_1(\omega)}{\omega I_0(\omega)} \right] \quad (A.240)$$

where $I'_0(\omega) = I_1(\omega)$, the modified Bessel function of order one [Abramowitz and Stegun, 1970], and recall that $s \approx \omega^2 D_e$ (Equation (A.102)), then

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma\bar{C}_m = -X[F_m(X) + \beta F_m(X)$$

$$+ 2\beta \int_0^1 \xi \left(\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right) F_i(X, \xi) d\xi]$$

(A.241)

The right-hand side of this equation can be further simplified using the initial conditions $C_m(X, T = 0) = F_m(X)$ (Equation (A.50)), $C_i(X, Z, T = 0) = F_i(X, Z)$ (Equation (A.52)), and the

dimensionless expression for the volume-average immobile region solute concentration, $C_m(X, T) = v \int_0^1 Z^{v-1} C_s(X, Z, T) dZ$ where

$v = 2$ (Equation (A.145)). Therefore, at time $T = 0$

$$F_m(X) = C_m(X, T = 0) = 2 \int_0^1 Z C_s(X, Z, T = 0) dZ = 2 \int_0^1 Z F_s(X, Z) dZ \quad (A.242)$$

Putting this expression for $F_m(X)$ into the right-hand side of Equation (A.241) gives us

$$\begin{aligned} & -X[F_m(X) + 2\beta \int_0^1 \xi F_s(X, \xi) d\xi + \frac{2\beta}{I_0(\omega)} \int_0^1 \xi I_0(\omega\xi) F_s(X, \xi) d\xi] \\ & -2\beta \int_0^1 \xi F_s(X, \xi) d\xi \end{aligned} \quad (A.243)$$

So, if we define

$$\bar{F}(X, s) = -X[F_s(X) + \frac{2\beta}{I_0(\omega)} \int_0^1 \xi I_0(\omega\xi) F_s(X, \xi) d\xi] \quad (A.244)$$

then Equation (A.241) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma \bar{C}_m = \bar{F}(X, s) \quad (A.245)$$

Spherical Diffusion. Using the above derivation when $v = 2$, we now seek the solution when $v = 3$. From Equation (A.85) we have

$$\frac{\partial C_s(X, Z, T)}{\partial T} = \frac{D_s}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (A.85)$$

which is valid for all the diffusion models. As previously derived, we now take the Laplace transform of Equation (A.85)

using Equation (A.52) (initial condition) and Equations (A.56) and (A.57) (boundary conditions):

$$C_s(X, Z, T = 0) = F_s(X, Z) \quad X_w < X < X_s \quad (A.52)$$

$$\frac{\partial C_s(X, Z = 0, T)}{\partial Z} = 0 \quad X_w < X < X_s \quad (A.56)$$

$$C_s(X, Z = 1, T) = C_m(X, T) \quad X_w < X < X_s \quad (A.57)$$

So,

$$L\left(\frac{\partial C_s}{\partial T}\right) = L\left(\frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial C_s}{\partial Z}\right)\right) \quad (A.86)$$

$$s\bar{C}_s - C_s(X, Z, T = 0) = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) \quad (A.87)$$

$$s\bar{C}_s - F_s(X, Z) = \frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) \quad (A.88)$$

Thus,

$$\frac{D_e}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) - s\bar{C}_s = -F_s(X, Z) \quad (A.89)$$

with the following boundary conditions

$$\frac{\partial \bar{C}_s}{\partial Z}(X, Z = 0, s) = 0 \quad X_w < X < X_s \quad (A.90)$$

$$\bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s) \quad X_w < X < X_s \quad (A.91)$$

We seek the general solution to Equation (A.89) using the boundary conditions (A.90) and (A.91) for case of $v = 3$.

That is,

$$\bar{C}_s = \bar{C}_{s,c} + \bar{C}_{s,p} \quad (\text{A.92})$$

where $\bar{C}_s$ is the general solution to the differential equation, $\bar{C}_{s,c}$ is the complementary solution to the homogeneous differential equation, and $\bar{C}_{s,p}$ is the particular solution to the nonhomogeneous differential equation. So for the case of $\nu = 3$, Equation (A.89) becomes

$$\frac{D_e}{Z^2} \frac{\partial}{\partial Z} \left(Z^2 \frac{\partial \bar{C}_s}{\partial Z} \right) - s \bar{C}_s = -F_s(X, Z) \quad (\text{A.246})$$

Multiplying Equation (A.246) by $1/D_e$ and differentiating the first term gives us

$$\frac{1}{Z^2} \frac{\partial}{\partial Z} \left(Z^2 \frac{\partial \bar{C}_s}{\partial Z} \right) - \frac{s}{D_e} \bar{C}_s = -\frac{F_s(X, Z)}{D_e} \quad (\text{A.247})$$

or

$$\frac{1}{Z^2} \left[Z^2 \frac{\partial^2 \bar{C}_s}{\partial Z^2} + 2Z \frac{\partial \bar{C}_s}{\partial Z} \right] - \frac{s}{D_e} \bar{C}_s = -\frac{F_s(X, Z)}{D_e} \quad (\text{A.248})$$

Thus,

$$\frac{\partial^2 \bar{C}_s}{\partial Z^2} + \frac{2}{Z} \frac{\partial \bar{C}_s}{\partial Z} - \frac{s}{D_e} \bar{C}_s = -\frac{F_s(X, Z)}{D_e} \quad (\text{A.249})$$

Using the previously defined variables

$$\hat{z} = \omega Z \quad (\text{A.172})$$

$$W(\hat{z}) = \bar{C}_s(Z) = \bar{C}_s\left(\frac{\hat{z}}{\omega}\right) \quad (\text{A.173})$$

where $\omega^2 = s / D_0$ (Equation (A.102)), then

$$\frac{\partial \bar{C}_s}{\partial Z} = \frac{\partial W}{\partial \hat{z}} \frac{d\hat{z}}{dZ} = \omega \frac{\partial W}{\partial \hat{z}} \quad (\text{A.174})$$

$$\frac{\partial^2 \bar{C}_s}{\partial Z^2} = \frac{\partial}{\partial Z} \left(\frac{\partial \bar{C}_s}{\partial Z} \right) = \frac{\partial}{\partial \hat{z}} \left(\omega \frac{\partial W}{\partial \hat{z}} \right) \frac{d\hat{z}}{dZ} = \frac{\partial}{\partial \hat{z}} \left(\omega \frac{\partial W}{\partial \hat{z}} \right) \omega = \omega^2 \frac{\partial^2 W}{\partial \hat{z}^2} \quad (\text{A.175})$$

Substituting these equations into Equation (A.249) gives us

$$\omega^2 \frac{\partial^2 W}{\partial \hat{z}^2} + \frac{2\omega^2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - \omega^2 W = - \frac{F_s(X, \frac{\hat{z}}{\omega})}{D_0} \equiv - \frac{\hat{F}_s(X, \hat{z})}{D_0} \quad (\text{A.250})$$

Multiplying through by $1 / \omega^2$ yields

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = - \frac{\hat{F}_s(X, \hat{z})}{\omega^2 D_0} \quad (\text{A.251})$$

We now seek the complementary solution to Equation (A.251).

That is,

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = 0 \quad (\text{A.252})$$

which we know to be a modified spherical Bessel function of order zero [Abramowitz and Stegun, 1970]. Therefore, the general solution to this homogeneous differential equation is

$$W(\hat{z}) = C_1 W_1(\hat{z}) + C_2 W_2(\hat{z}) \quad (\text{A.253})$$

where $W_1(\hat{z})$ and $W_2(\hat{z})$ are of the form

$$W_1(\hat{z}) = A i_0(\hat{z}) + B k_0(\hat{z}) \quad (\text{A.254})$$

$$W_2(\hat{z}) = C i_0(\hat{z}) + D k_0(\hat{z}) \quad (\text{A.255})$$

where C_1, C_2, A, B, C , and D are constants and $i_0(\hat{z})$ and $k_0(\hat{z})$ are modified spherical Bessel functions of the first kind, order zero and third kind, order zero, respectively, and are of the form

$$i_0(\hat{z}) = \sqrt{\frac{\pi}{2}} \hat{z}^{-\frac{1}{2}} I_{\frac{1}{2}}(\hat{z}) = \frac{\sinh \hat{z}}{\hat{z}} \quad (\text{A.256})$$

$$k_0(\hat{z}) = \sqrt{\frac{\pi}{2}} \hat{z}^{-\frac{1}{2}} K_{\frac{1}{2}}(\hat{z}) = \frac{\pi e^{-\hat{z}}}{2\hat{z}} \quad (\text{A.257})$$

To find the first solution, $W_1(\hat{z})$, we apply the boundary condition (Equation (A.90)) where $\bar{C}_1(Z=0) = W(\hat{z}=0)$.

Thus,

$$\frac{\partial W(\hat{z}=0)}{\partial \hat{z}} = 0 \quad (\text{A.258})$$

So,

$$\frac{\partial W}{\partial \hat{z}} = 0 = A i'_0(\hat{z}=0) + B k'_0(\hat{z}=0) \quad (\text{A.259})$$

since $k'_0(\hat{z}=0)$ is undefined [Abramowitz and Stegun, 1970], we take B equal to zero. Therefore,

$$W_1(\hat{z}) = A i_0(\hat{z}) \quad (\text{A.260})$$

Without loss of generality, let's take $A = 1$, so

$$W_1(\hat{z}) = i_0(\hat{z}) \quad (\text{A.261})$$

We also know the second solution, $W_2(\hat{z})$, to be of the form

$$W_2(\hat{z}) = C i_0(\hat{z}) + D k_0(\hat{z}) \quad (\text{A.262})$$

and satisfies the 'zero' boundary condition (Equation (A.91)) where $\bar{C}_s(Z = 1) = W(\hat{z} = \omega) :$

$$\bar{C}_s(X, Z = 1, s) = 0 = W(\hat{z} = \omega) \quad (\text{A.263})$$

Thus,

$$0 = C i_0(\omega) + D k_0(\omega) \quad (\text{A.264})$$

or

$$D = - \frac{C i_0(\omega)}{k_0(\omega)} \quad (\text{A.265})$$

So,

$$W_2(\hat{z}) = C i_0(\hat{z}) - \frac{C i_0(\omega)}{k_0(\omega)} k_0(\hat{z}) \quad (\text{A.266})$$

Without loss of generality, let's take $C = k_0(\omega)$. Thus,

$$W_2(\hat{z}) = k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z}) \quad (\text{A.267})$$

Now we seek the particular solution ($\bar{C}_s$) to the following nonhomogeneous differential equation using a Green's function:

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = - \frac{\hat{F}_s(X, \hat{z})}{\omega^2 D_e} \quad (\text{A.251})$$

First, we construct the Green's function which is of the form

$$g(\hat{z}, \zeta) = \begin{cases} \frac{W_1(\hat{z})W_2(\zeta)}{p(\zeta)W[W_1, W_2](\zeta)} & \hat{z} < \zeta < \omega \\ \frac{W_1(\zeta)W_2(\hat{z})}{p(\zeta)W[W_1, W_2](\zeta)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.268})$$

where $W[W_1, W_2](\zeta)$ is the Wronskian of W_1 and W_2 , and $p(\zeta)$ is the coefficient of the first term in Equation (A.251). From Equation (A.251), we see that $p(\zeta) = 1$. Next we determine the Wronskian, $W[W_1, W_2]$:

$$W[W_1, W_2] = \begin{vmatrix} i_0(\hat{z}) & k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z}) \\ i'_0(\hat{z}) & k_0(\omega) i'_0(\hat{z}) - i_0(\omega) k'_0(\hat{z}) \end{vmatrix} \quad (\text{A.269})$$

$$= k_0(\omega) i_0(\hat{z}) i'_0(\hat{z}) - i_0(\omega) i_0(\hat{z}) k'_0(\hat{z}) \quad (\text{A.270})$$

$$- k_0(\omega) i_0(\hat{z}) i'_0(\hat{z}) + i_0(\omega) i'_0(\hat{z}) k_0(\hat{z})$$

$$= i_0(\omega) [i'_0(\hat{z}) k_0(\hat{z}) - i_0(\hat{z}) k'_0(\hat{z})] \quad (\text{A.271})$$

$$= i_0(\omega) W[k_0(\hat{z}), i_0(\hat{z})] \quad (\text{A.272})$$

We know that $W[k_0(\hat{z}), i_0(\hat{z})] = \pi / (2\hat{z}^2)$ [Abramowitz and Stegun, 1970]. So,

$$W[W_1, W_2] = \frac{\pi i_0(\omega)}{2\hat{z}^2} \quad (\text{A.273})$$

Therefore, the Green's function is

$$g(\hat{z}, \zeta) = \begin{cases} \frac{2\zeta^2 W_1(\hat{z}) W_2(\zeta)}{\pi i_0(\omega)} & \hat{z} < \zeta < \omega \\ \frac{2\zeta^2 W_1(\zeta) W_2(\hat{z})}{\pi i_0(\omega)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.274})$$

$$= \begin{cases} \frac{2\zeta^2 i_0(\hat{z}) [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{\pi i_0(\omega)} & \hat{z} < \zeta < \omega \\ \frac{2\zeta^2 i_0(\zeta) [k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})]}{\pi i_0(\omega)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.275})$$

and

$$\bar{C}_s(\hat{z}) = - \int_0^\omega g(\hat{z}, \zeta) \left[\frac{\hat{F}_s(X, \zeta)}{\omega^2 D_e} \right] d\zeta \quad (\text{A.276})$$

So, the general solution is

$$W(\hat{z}) = \bar{C}_s(\hat{z}) = A W_1(\hat{z}) + B W_2(\hat{z}) - \int_0^\omega g(\hat{z}, \zeta) \left[\frac{\hat{F}_s(X, \zeta)}{\omega^2 D_e} \right] d\zeta \quad (\text{A.277})$$

$$\begin{aligned} &= A i_0(\hat{z}) + B [k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})] \\ &\quad - \frac{2i_0(\hat{z})}{\pi\omega^2 D_e} \int_{\hat{z}}^\omega \left[\frac{\zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{i_0(\omega)} \right] \hat{F}_s(X, \zeta) d\zeta \quad (\text{A.278}) \\ &\quad - \frac{2[k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})]}{\pi\omega^2 D_e i_0(\omega)} \int_0^{\hat{z}} \zeta^2 i_0(\zeta) \hat{F}_s(X, \zeta) d\zeta \end{aligned}$$

To find the constants A and B, we use the 'nonzero' boundary conditions (Equations (A.90) and (A.91) where $W(\hat{z}) = \bar{C}_s(Z)$).

Therefore, applying the boundary condition

$$\frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 \quad (\text{A.279})$$

we get

$$\begin{aligned}
\frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 = & A i'_0(0) + B [k_0(\omega) i'_0(0) - i_0(\omega) k'_0(0)] \\
& - \frac{2 i'_0(0)}{\pi \omega^2 D_e i_0(\omega)} \int_0^\infty \zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)] \hat{F}_1(X, \zeta) d\zeta \\
& + \frac{2 i_0(0)}{\pi \omega^2 D_e i_0(\omega)} \{ (0) [k_0(\omega) i_0(0) - i_0(\omega) k_0(0)] \hat{F}_1(X, 0) \} \\
& - \frac{2 [k_0(\omega) i'_0(0) - i_0(\omega) k'_0(0)]}{\pi \omega^2 D_e i_0(\omega)} \int_0^\infty \zeta^2 i_0(\zeta) \hat{F}_1(X, \zeta) d\zeta \\
& - \frac{2 [k_0(\omega) i_0(0) - i_0(\omega) k_0(0)]}{\pi \omega^2 D_e i_0(\omega)} [(0) i_0(0) \hat{F}_1(X, 0)]
\end{aligned}
\tag{A.280}$$

Since $i'_0(0) = 0$ [Abramowitz and Stegun, 1970] then

$$0 = B [-i_0(\omega) k'_0(0)] \tag{A.281}$$

Since $k'_0(0)$ is undefined [Abramowitz and Stegun, 1970], we take $B = 0$. Applying the second boundary condition (Equation (A.91))

$$W(\omega) = \bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s) \tag{A.282}$$

we get

$$\begin{aligned}\bar{C}_m(X, s) = & A i_0(\omega) - \frac{2i_0(\omega)}{\pi\omega^2 D_e i_0(\omega)} \int_0^\omega \zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \\ & - \frac{2[k_0(\omega) i_0(\omega) - i_0(\omega) k_0(\omega)]}{\pi\omega^2 D_e i_0(\omega)} \int_0^\omega \zeta^2 i_0(\zeta) \hat{F}_s(X, \zeta) d\zeta\end{aligned}\quad (A.283)$$

Thus,

$$A = \frac{\bar{C}_m(X, s)}{i_0(\omega)} \quad (A.284)$$

So, Equation (A.277) becomes

$$W(\hat{z}) = \frac{\bar{C}_m(X, s)}{i_0(\omega)} i_0(\hat{z}) - \frac{1}{\omega^2 D_e} \int_0^\omega g(\hat{z}, \zeta) \hat{F}_s(X, \zeta) d\zeta \quad (A.285)$$

$$\begin{aligned}&= \frac{\bar{C}_m(X, s)}{i_0(\omega)} i_0(\hat{z}) \\ &- \frac{2i_0(\hat{z})}{\pi\omega^2 D_e i_0(\omega)} \int_{\hat{z}}^\omega \zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \quad (A.286) \\ &- \frac{2[k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})]}{\pi\omega^2 D_e i_0(\omega)} \int_0^{\hat{z}} \zeta^2 i_0(\zeta) \hat{F}_s(X, \zeta) d\zeta\end{aligned}$$

Recall, Equation (A.145)

$$C_{im}(X, T) = v \int_0^1 Z^{v-1} C_s(X, Z, T) dZ \quad (A.145)$$

and $W(\hat{z}) = \bar{C}_s(\hat{z} / \omega) = \bar{C}_s(Z)$ where $\hat{z} = \omega Z$. Taking the Laplace transform of Equation (A.145) with $v = 3$, we get

$$\bar{C}_{im}(X, s) = 3 \int_0^1 Z^2 \bar{C}_s(X, Z, s) dZ = \frac{3}{\omega^3} \int_0^\omega \hat{z}^2 W(\hat{z}) d\hat{z} \quad (A.287)$$

Substituting the general solution, $W(\hat{z})$ (Equation (A.285)), into this expression gives us

$$\begin{aligned}\bar{C}_m(X, s) = & \frac{3\bar{C}_m(X, s)}{\omega^3 i_0(\omega)} \int_0^\omega \hat{z}^2 i_0(\hat{z}) d\hat{z} \\ & - \frac{3}{\omega^5 D_e} \int_0^\omega \int_0^\omega \hat{z}^2 g(\hat{z}, \zeta) \hat{F}_1(X, \zeta) d\zeta d\hat{z}\end{aligned}\quad (A.288)$$

To determine the first integral, we use the following homogeneous differential equation:

$$\hat{z}^2 \frac{d^2 i_0(\hat{z})}{d\hat{z}^2} + 2\hat{z} \frac{di_0(\hat{z})}{d\hat{z}} - \hat{z}^2 i_0(\hat{z}) = 0 \quad (A.289)$$

So,

$$\hat{z}^2 i_0(\hat{z}) = \hat{z}^2 \frac{d^2 i_0(\hat{z})}{d\hat{z}^2} + 2\hat{z} \frac{di_0(\hat{z})}{d\hat{z}} \quad (A.290)$$

Integrating both sides of this equation gives us

$$\int_0^\omega \hat{z}^2 i_0(\hat{z}) d\hat{z} = \int_0^\omega \hat{z}^2 \frac{d^2 i_0(\hat{z})}{d\hat{z}^2} d\hat{z} + 2 \int_0^\omega \hat{z} \frac{di_0(\hat{z})}{d\hat{z}} d\hat{z} \quad (A.291)$$

Now, using integration by parts on the right-hand side of this equation yields

$$\int_0^\omega \hat{z}^2 i_0(\hat{z}) d\hat{z} = \hat{z}^2 \frac{di_0(\hat{z})}{d\hat{z}} \Big|_0^\omega - 2 \int_0^\omega \hat{z} \frac{di_0(\hat{z})}{d\hat{z}} d\hat{z} + 2 \int_0^\omega \hat{z} \frac{di_0(\hat{z})}{d\hat{z}} d\hat{z} \quad (A.292)$$

$$\int \hat{z}^2 i_0(\hat{z}) d\hat{z} = \hat{z}^2 \frac{di_0(\hat{z})}{d\hat{z}} \Big|_0^\omega \quad (A.293)$$

or

$$\int \hat{z}^2 i_0(\hat{z}) d\hat{z} = \omega^2 i'_0(\omega) \quad (\text{A.294})$$

Thus, Equation (A.288) becomes

$$\bar{C}_m(X, s) = \frac{3\bar{C}_m(X, s)}{\omega^3 i_0(\omega)} [\omega^2 i'_0(\omega)] \quad (\text{A.295})$$

$$\begin{aligned} & - \frac{3}{\omega^5 D_e} \int_0^\infty \int_0^\infty \hat{z}^2 g(\hat{z}, \zeta) \hat{F}_*(X, \zeta) d\zeta d\hat{z} \\ & = \frac{3\bar{C}_m(X, s) i'_0(\omega)}{\omega i_0(\omega)} - \frac{3}{\omega^5 D_e} \int_0^\infty \left(\int_0^\infty \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} \right) \hat{F}_*(X, \zeta) d\zeta \quad (\text{A.296}) \end{aligned}$$

Now we solve

$$\int_0^\infty \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} = \int_0^\zeta \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} + \int_\zeta^\infty \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} \quad (\text{A.297})$$

$$= \frac{2\zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{\pi i_0(\omega)} \int_0^\zeta \hat{z}^2 i_0(\hat{z}) d\hat{z} \quad (\text{A.298})$$

$$\begin{aligned} & + \frac{2\zeta^2 i_0(\zeta)}{\pi i_0(\omega)} \int_\zeta^\infty \hat{z}^2 [k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})] d\hat{z} \\ & = \frac{2\zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{\pi i_0(\omega)} \int_0^\zeta \hat{z}^2 i_0(\hat{z}) d\hat{z} \\ & + \frac{2\zeta^2 i_0(\zeta) k_0(\omega)}{\pi i_0(\omega)} \int_\zeta^\infty \hat{z}^2 i_0(\hat{z}) d\hat{z} - \frac{2\zeta^2 i_0(\zeta) i_0(\omega)}{\pi i_0(\omega)} \int_\zeta^\infty \hat{z}^2 k_0(\hat{z}) d\hat{z} \quad (\text{A.299}) \end{aligned}$$

From Equation (A.294), we know these integrals (similar derivation for $k_0(\hat{z})$). Thus, Equation (A.297) is

$$\begin{aligned}
\int_0^\omega \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} &= \frac{2\zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{\pi i_0(\omega)} [\zeta^2 i'_0(\zeta)] \\
&+ \frac{2\zeta^2 i_0(\zeta) k_0(\omega)}{\pi i_0(\omega)} [\omega^2 i'_0(\omega) - \zeta^2 i'_0(\zeta)] \\
&- \frac{2\zeta^2 i_0(\zeta) i_0(\omega)}{\pi i_0(\omega)} [\omega^2 k'_0(\omega) - \zeta^2 k'_0(\zeta)]
\end{aligned} \tag{A.300}$$

Collecting terms and simplifying,

$$\begin{aligned}
\int_0^\omega \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} &= \frac{2\zeta^4 i'_0(\zeta) k_0(\omega) i_0(\zeta)}{\pi i_0(\omega)} - \frac{2\zeta^4 i'_0(\zeta) k_0(\zeta) i_0(\omega)}{\pi i_0(\omega)} \\
&+ \frac{2\zeta^2 \omega^2 i_0(\zeta) i'_0(\omega) k_0(\omega)}{\pi i_0(\omega)} - \frac{2\zeta^4 i_0(\zeta) k_0(\omega) i'_0(\zeta)}{\pi i_0(\omega)} \\
&- \frac{2\omega^2 \zeta^2 i_0(\zeta) i_0(\omega) k'_0(\omega)}{\pi i_0(\omega)} + \frac{2\zeta^4 i_0(\zeta) i_0(\omega) k'_0(\zeta)}{\pi i_0(\omega)}
\end{aligned} \tag{A.301}$$

or

$$\begin{aligned}
\int_0^\omega \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} &= \frac{2\zeta^4 i_0(\omega)}{\pi i_0(\omega)} [i_0(\zeta) k'_0(\zeta) - i'_0(\zeta) k_0(\zeta)] \\
&+ \frac{2\omega^2 \zeta^2 i_0(\zeta)}{\pi i_0(\omega)} [k_0(\omega) i'_0(\omega) - i_0(\omega) k'_0(\omega)]
\end{aligned} \tag{A.302}$$

Thus,

$$\int_0^\omega \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} = \frac{2\zeta^4 i_0(\omega)}{\pi i_0(\omega)} (W[i_0, k_0](\zeta)) + \frac{2\omega^2 \zeta^2 i_0(\zeta)}{\pi i_0(\omega)} (W[k_0, i_0](\omega)) \quad (\text{A.303})$$

$$= \frac{2\zeta^4 i_0(\omega)}{\pi i_0(\omega)} \left(-\frac{\pi}{2\zeta^2} \right) + \frac{2\omega^2 \zeta^2 i_0(\zeta)}{\pi i_0(\omega)} \left(\frac{\pi}{2\omega^2} \right) \quad (\text{A.304})$$

So, Equation (A.297) becomes

$$\int_0^\omega \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} = \zeta^2 \left[\frac{i_0(\zeta)}{i_0(\omega)} - 1 \right] \quad (\text{A.305})$$

Returning to Equation (A.296), with Equation (A.305) substituted in, gives us

$$\bar{C}_m(X, s) = \frac{3\bar{C}_m(X, s) i'_0(\omega)}{\omega i_0(\omega)} - \frac{3}{\omega^5 D_e} \int_0^\omega \zeta^2 \left[\frac{i_0(\zeta)}{i_0(\omega)} - 1 \right] \hat{F}_s(X, \zeta) d\zeta \quad (\text{A.306})$$

If we let $\zeta = \omega\xi$, then when $\zeta = 0$, $\xi = 0$ and when $\zeta = \omega$, $\xi = 1$. So,

$$\bar{C}_m(X, s) = \frac{3\bar{C}_m(X, s) i'_0(\omega)}{\omega i_0(\omega)} - \frac{3}{\omega^5 D_e} \int_0^1 \left(\omega^2 \xi^2 \left[\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right] \right) F_s(X, \xi) \omega d\xi \quad (\text{A.307})$$

or

$$\bar{C}_m(X, s) = \frac{3\bar{C}_m(X, s) i'_0(\omega)}{\omega i_0(\omega)} - \frac{3}{\omega^2 D_e} \int_0^1 \xi^2 \left[\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right] F_s(X, \xi) d\xi \quad (\text{A.308})$$

Using Equation (A.143)

$$s\bar{C}_m - F_m(X) = \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \beta[s\bar{C}_m - F_m(X)] \quad (A.143)$$

we substitute in Equation (A.308)

$$\begin{aligned} s\bar{C}_m - F_m(X) = & \frac{1}{X} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} + \beta F_m(X) \\ & - \beta s \left\{ \frac{3\bar{C}_m}{i_0(\omega)} \frac{i'_0(\omega)}{\omega} - \frac{3}{\omega^2 D_e} \int_0^1 \xi^2 \left[\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right] F_*(X, \xi) d\xi \right\} \end{aligned} \quad (A.309)$$

Rearranging and multiplying each term by X gives us

$$\begin{aligned} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X s \bar{C}_m \left[1 + \frac{3\beta i'_0(\omega)}{\omega i_0(\omega)} \right] = & -X[F_m(X) + \beta F_m(X) \\ & + \frac{3\beta s}{\omega^2 D_e} \int_0^1 \xi^2 \left(\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right) F_*(X, \xi) d\xi] \end{aligned} \quad (A.310)$$

If we define

$$\gamma = s \left[1 + \frac{3\beta i_1(\omega)}{\omega i_0(\omega)} \right] \quad (A.311)$$

where $i'_0(\omega) = i_1(\omega)$, a spherical Bessel function of the first kind, order one [Abramowitz and Stegun, 1970] and recall that $s = \omega^2 D_e$ (Equation (A.102)), then

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma \bar{C}_m = -X[F_m(X) + \beta F_m(X)] \quad (A.312)$$

$$+ 3\beta \int_0^1 \xi^2 \left(\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right) F_1(X, \xi) d\xi]$$

The right-hand side of this equation can be further simplified using the initial conditions $C_m(X, T = 0) = F_m(X)$ (Equation (A.50)), $C_1(X, Z, T = 0) = F_1(X, Z)$ (Equation (A.52)), and the dimensionless expression for the volume-average immobile region solute concentration, $C_m(X, T) = v \int_0^1 Z^{v-1} C_1(X, Z, T) dZ$ where $v = 3$ (Equation (A.145)). Therefore, at time $T = 0$

$$F_m(X) = C_m(X, T = 0) = 3 \int_0^1 Z^2 C_1(X, Z, T = 0) dZ = 3 \int_0^1 Z^2 F_1(X, Z) dZ \quad (A.313)$$

Putting this expression for $F_m(X)$ into the right-hand side of Equation (A.312) gives us

$$\begin{aligned} & -X[F_m(X) + 3\beta \int_0^1 \xi^2 F_1(X, \xi) d\xi + \frac{3\beta}{i_0(\omega)} \int_0^1 \xi^2 i_0(\omega\xi) F_1(X, \xi) d\xi \\ & - 3\beta \int_0^1 \xi^2 F_1(X, \xi) d\xi] \end{aligned} \quad (A.314)$$

So, if we define

$$\bar{F}(X, s) = -X[F_m(X) + \frac{3\beta}{i_0(\omega)} \int_0^1 \xi^2 i_0(\omega\xi) F_1(X, \xi) d\xi] \quad (A.315)$$

then Equation (A.312) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma \bar{C}_m = \bar{F}(X, s) \quad (A.316)$$

Green's Function. The Laplace transform of Equation (A.46) together with the appropriate conditions for the various models resulted in a common differential equation which is of the form

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma \bar{C}_m = \bar{F}(X, s) \quad (A.317)$$

where the overbar indicates the transformed function and γ and $\bar{F}(X, s)$ were developed in the previous sections. Now assume that Equation (A.317) has a solution of the form

$$\bar{C}_m(X, s) = \phi(X, s) e^{-\frac{1}{2}X} \quad (A.318)$$

Then, substituting this into Equation (A.317) yields

$$\frac{d^2(\phi e^{-\frac{1}{2}X})}{dX^2} + \frac{d(\phi e^{-\frac{1}{2}X})}{dX} - X\gamma \left[\phi e^{-\frac{1}{2}X} \right] = \bar{F}(X, s) \quad (A.319)$$

Evaluating the first term of Equation (A.319) gives us

$$\frac{d}{dX} \left(\frac{d\phi e^{-\frac{1}{2}X}}{dX} \right) = \frac{d}{dX} \left(\phi \frac{de^{-\frac{1}{2}X}}{dX} + e^{-\frac{1}{2}X} \frac{d\phi}{dX} \right) \quad (A.320)$$

$$= \frac{d}{dX} \left(-\frac{1}{2} \phi e^{-\frac{1}{2}X} + e^{-\frac{1}{2}X} \frac{d\phi}{dX} \right) \quad (A.321)$$

$$= -\frac{1}{2} \frac{d}{dX} \left(\phi e^{-\frac{1}{2}X} \right) + \frac{d}{dX} \left(e^{-\frac{1}{2}X} \frac{d\phi}{dX} \right) \quad (A.322)$$

$$= -\frac{1}{2} \left[\phi \frac{de^{-\frac{1}{2}X}}{dX} + e^{-\frac{1}{2}X} \frac{d\phi}{dX} \right] + e^{-\frac{1}{2}X} \frac{d^2\phi}{dX^2} + \frac{d\phi}{dX} \frac{de^{-\frac{1}{2}X}}{dX} \quad (A.323)$$

$$= \frac{1}{4} \phi e^{-\frac{1}{2}X} - \frac{1}{2} e^{-\frac{1}{2}X} \frac{d\phi}{dX} + e^{-\frac{1}{2}X} \frac{d^2\phi}{dX^2} - \frac{1}{2} e^{-\frac{1}{2}X} \frac{d\phi}{dX} \quad (A.324)$$

So,

$$\frac{d}{dX} \left(\frac{d\phi e^{-\frac{1}{2}X}}{dX} \right) = e^{-\frac{1}{2}X} \frac{d^2\phi}{dX^2} - e^{-\frac{1}{2}X} \frac{d\phi}{dX} + \frac{1}{4} \phi e^{-\frac{1}{2}X} \quad (\text{A.325})$$

Evaluating the second term in Equation (A.319) gives us

$$\frac{d}{dX} \left(\phi e^{-\frac{1}{2}X} \right) = \phi \frac{de^{-\frac{1}{2}X}}{dX} + e^{-\frac{1}{2}X} \frac{d\phi}{dX} = -\frac{1}{2} \phi \left(e^{-\frac{1}{2}X} \right) + e^{-\frac{1}{2}X} \frac{d\phi}{dX} \quad (\text{A.326})$$

Combining both terms, simplifying, and inserting these terms back into Equation (A.319) results in the following

$$e^{-\frac{1}{2}X} \frac{d^2\phi}{dX^2} - \frac{1}{4} \phi e^{-\frac{1}{2}X} - X \gamma \phi e^{-\frac{1}{2}X} = \bar{F}(X, s) \quad (\text{A.327})$$

Multiplying each term by $e^{\frac{1}{2}X}$ gives us

$$\frac{d^2\phi}{dX^2} - \frac{1}{4} \phi - X \gamma \phi = e^{\frac{1}{2}X} \bar{F}(X, s) \quad (\text{A.328})$$

or

$$\frac{d^2\phi}{dX^2} - \gamma \phi \left[X + \frac{1}{4\gamma} \right] = e^{\frac{1}{2}X} \bar{F}(X, s) \quad (\text{A.329})$$

We seek a simpler form of Equation (A.329), one where the left-hand side has no constants in it. Therefore, we define

$$y = C \left[X + \frac{1}{4\gamma} \right] \quad (\text{A.330})$$

where C is a constant. Thus, we rewrite Equation (A.329) in terms of y , and define $\Phi(y) = \phi(X)$. Therefore,

$$\frac{d\phi}{dX} = \frac{d\Phi}{dy} \frac{dy}{dX} = \frac{d\Phi}{dy} [C] = C \frac{d\Phi}{dy} \quad (\text{A.331})$$

$$\frac{d^2\phi}{dX^2} = \frac{d}{dX} \left(\frac{d\Phi}{dX} \right) = \frac{d}{dX} \left(C \frac{d\Phi}{dy} \right) = \frac{d}{dy} \left(C \frac{d\Phi}{dy} \right) \frac{dy}{dX} = C^2 \frac{d^2\Phi}{dy^2} \quad (\text{A.332})$$

Substituting this expression back into Equation (A.329) yields

$$C^2 \frac{d^2\Phi}{dy^2} - \gamma \Phi \left(\frac{y}{C} \right) = e^{\frac{1}{2} \left[\frac{y}{C} - \frac{1}{4\gamma} \right]} \bar{F} \left(\frac{y}{C} - \frac{1}{4\gamma}, s \right) \quad (\text{A.333})$$

Multiplying each term by $1 / C^2$ gives us

$$\frac{d^2\Phi}{dy^2} - \frac{\gamma \Phi y}{C^3} = \frac{1}{C^2} e^{\frac{1}{2} \left[\frac{y}{C} - \frac{1}{4\gamma} \right]} \bar{F} \left(\frac{y}{C} - \frac{1}{4\gamma}, s \right) \quad (\text{A.334})$$

We want $\gamma / C^3 = 1$, thus $C = \gamma^{1/3}$. Therefore, Equation (A.334) becomes

$$\frac{d^2\Phi}{dy^2} - y \Phi = \gamma^{-\frac{2}{3}} e^{\frac{1}{2} \left[\frac{y}{\gamma^{1/3}} - \frac{1}{4\gamma} \right]} \bar{F} \left(\frac{y}{\gamma^{1/3}} - \frac{1}{4\gamma}, s \right) \quad (\text{A.335})$$

where Φ is now a function of y and s .

We now look at the Laplace transformed boundary condition at the dimensionless well radius (Equation (A.55)) and convert it into terms of y_w . Equation (A.55) implies the following:

$$\frac{d\bar{C}_m}{dX} (X_w, s) = 0 \quad (\text{A.336})$$

where $\bar{C}_m(X_w, s)$ is the transformed function. Assuming a solution exists in the form of Equation (A.318) then, Equation (A.336) becomes

$$\frac{d}{dX} \left(\phi(X, s) e^{-\frac{1}{2}X} \right) = \frac{d\phi}{dX} e^{-\frac{1}{2}X} + \phi \frac{d}{dX} \left(e^{-\frac{1}{2}X} \right) \quad (\text{A.337})$$

$$= e^{-\frac{1}{2}X} \frac{d\phi}{dX} - \frac{1}{2} e^{-\frac{1}{2}X} \phi \quad (\text{A.338})$$

$$= e^{-\frac{1}{2}X} \left(\frac{d\phi}{dX} - \frac{1}{2} \phi \right) \quad (\text{A.339})$$

At X_w ,

$$\frac{d}{dX} \left(\phi(X_w, s) e^{-\frac{1}{2}X} \right) = 0 \quad (\text{A.340})$$

Suppressing the s dependency, Equation (A.339) is now

$$e^{-\frac{1}{2}X_w} \left(\frac{d\phi(X_w)}{dX} - \frac{1}{2} \phi(X_w) \right) = 0 \quad (\text{A.341})$$

We know that $e^{-\frac{1}{2}X_w}$ does not equal zero. Therefore,

$$-\frac{1}{2} \phi(X_w) + \frac{d\phi(X_w)}{dX} = 0 \quad (\text{A.342})$$

If we define $y_w = \gamma^{1/3} [X_w + 1 / (4\gamma)]$ and

$\Phi(y_w) = \phi(X_w) = \phi[y_w / (\gamma^{1/3}) - 1 / (4\gamma)]$ then the second term in

Equation (A.342) is

$$\frac{d\phi(X_w)}{dX} = \frac{d\Phi}{dy} \left(\frac{y_w}{\gamma^{1/3}} - \frac{1}{4\gamma} \right) \frac{dy}{dX} = \frac{d\Phi(y_w)}{dy} \left(\gamma^{1/3} \right) \quad (\text{A.343})$$

Thus, the boundary condition at the dimensionless well radius

(Equation (A.342)) becomes

$$-\frac{1}{2} \Phi(y_w) + \gamma^{\frac{1}{3}} \frac{d\Phi}{dy}(y_w) = 0 \quad (\text{A.344})$$

Now, we look at the boundary condition at a dimensionless radius of the initially contaminated zone ($X_.$). Recall the boundary condition at $X_.$, Equation (A.54), which implies

$$\bar{C}_m(X_., s) + \frac{d\bar{C}_m}{dX}(X_., s) = 0 \quad (\text{A.345})$$

where $\bar{C}_m$ is the transformed function. If we assume a solution of the form of Equation (A.318), then equation (A.345) becomes

$$\phi(X_., s) e^{-\frac{1}{2}X_..} + \frac{d}{dX} \left(\phi(X_., s) e^{-\frac{1}{2}X_..} \right) = 0 \quad (\text{A.346})$$

Again, suppressing the s dependency yields

$$e^{-\frac{1}{2}X_..} \phi(X_.) + e^{-\frac{1}{2}X_..} \frac{d\phi(X_.)}{dX} - \frac{1}{2} e^{-\frac{1}{2}X_..} \phi(X_.) = 0 \quad (\text{A.347})$$

$$\frac{1}{2} e^{-\frac{1}{2}X_..} \phi(X_.) + e^{-\frac{1}{2}X_..} \frac{d\phi(X_.)}{dX} = 0 \quad (\text{A.348})$$

$$e^{-\frac{1}{2}X_..} \left[\frac{1}{2} \phi(X_.) + \frac{d\phi(X_.)}{dX} \right] = 0 \quad (\text{A.349})$$

We know that $e^{-\frac{1}{2}X_..}$ does not equal zero. Therefore,

$$\frac{1}{2} \phi(X_.) + \frac{d\phi(X_.)}{dX} = 0 \quad (\text{A.350})$$

If we define $y_. = \gamma^{1/3} [X_. + 1 / (4\gamma)]$ and $\Phi(y_.) = \phi(X_.) = \phi[y_. / (\gamma^{1/3}) - 1 / (4\gamma)]$ then the second term in Equation (A.350) is

$$\frac{d\phi(X.)}{dX} = \frac{d\Phi}{dy} \left(\frac{y.}{\gamma^{\frac{1}{3}}} - \frac{1}{4\gamma} \right) \frac{dy}{dX} = \frac{d\Phi(y.)}{dy} \left(\gamma^{\frac{1}{3}} \right) \quad (A.351)$$

Thus, the boundary condition at a dimensionless radius of an initially contaminated zone (Equation (A.350)) becomes

$$\frac{1}{2} \Phi(y.) + \gamma^{\frac{1}{3}} \frac{d\Phi}{dy}(y.) = 0 \quad (A.352)$$

We now seek the solution to the following nonhomogeneous differential equation (Equation (A.335)):

$$\frac{d^2\Phi}{dy^2} - y \Phi = \gamma^{-\frac{2}{3}} e^{\frac{1}{2} \left[\frac{y}{\gamma^{\frac{1}{3}}} - \frac{1}{4\gamma} \right]} \bar{F} \left(\frac{y}{\gamma^{\frac{1}{3}}} - \frac{1}{4\gamma}, s \right) \quad y_w < y < y. \quad (A.335)$$

subject to the following boundary conditions

$$-\frac{1}{2} \Phi(y_w) + \gamma^{\frac{1}{3}} \frac{d\Phi(y_w)}{dy} = 0 \quad (A.344)$$

$$\frac{1}{2} \Phi(y.) + \gamma^{\frac{1}{3}} \frac{d\Phi(y.)}{dy} = 0 \quad (A.352)$$

Recall Equation (A.330) where $C = \gamma^{1/3}$. That is,

$$y = \gamma^{\frac{1}{3}} \left[X + \frac{1}{4\gamma} \right] \quad (A.353)$$

Also, recall

$$\Phi(y) = \phi(X) = \phi \left(\frac{y}{\gamma^{\frac{1}{3}}} - \frac{1}{4\gamma} \right) \quad (A.354)$$

Then Equation (A.335) becomes

$$\frac{d^2\Phi}{dy^2} - y\Phi = \gamma^{-\frac{2}{3}} e^{\frac{1}{2}\left[\frac{y}{\gamma^{\frac{1}{3}}} - \frac{1}{4\gamma}\right]} \bar{F}\left(\frac{y}{\gamma^{\frac{1}{3}}} - \frac{1}{4\gamma}, s\right) \equiv \mathcal{F}(y, s) \quad y_w < y < y. \quad (\text{A.355})$$

We know the general solution to Equation (A.355) is of the form

$$\Phi(y) = C_1 \Phi_1(y) + C_2 \Phi_2(y) + \Phi_p \quad (\text{A.356})$$

where C_1 and C_2 are constants, $\Phi_1(y)$ and $\Phi_2(y)$ are the complementary solutions, and Φ_p is the particular solution. We also know that $\Phi_1(y)$ and $\Phi_2(y)$ must satisfy the boundary conditions and are of the form

$$\Phi_1(y) = A \text{Ai}(y) + B \text{Bi}(y) \quad (\text{A.357})$$

$$\Phi_2(y) = C \text{Ai}(y) + D \text{Bi}(y) \quad (\text{A.358})$$

where A, B, C, D are constants and $\text{Ai}(y), \text{Bi}(y)$ are Airy and Bairy functions, respectively [Abramowitz and Stegun, 1970].

The approach we take to find the solutions to Equation (A.356) is a Green's function technique which is of the form

$$g(y, \eta) = \begin{cases} \frac{\Phi_1(y) \Phi_2(\eta)}{p(\eta) W[\Phi_1, \Phi_2](\eta)} & y \leq \eta \leq y. \\ \frac{\Phi_1(\eta) \Phi_2(y)}{p(\eta) W[\Phi_1, \Phi_2](\eta)} & y_w \leq \eta \leq y \end{cases} \quad (\text{A.359})$$

where $p(\eta)$ is the coefficient of the first term in Equation (A.355), which is equal to one, and $W[\Phi_1, \Phi_2](\eta)$ is the Wronskian of Φ_1 and Φ_2 .

To find one solution we apply the boundary condition at y_w . That is,

$$-\frac{1}{2} \Phi_1(y_w) + \gamma^{\frac{1}{3}} \frac{d\Phi_1}{dy}(y_w) = 0 \quad (\text{A.360})$$

$$-\frac{1}{2} [A \text{Ai}(y_w) + B \text{Bi}(y_w)] + \gamma^{\frac{1}{3}} \left[A \frac{d\text{Ai}}{dy}(y_w) + B \frac{d\text{Bi}}{dy}(y_w) \right] = 0 \quad (\text{A.361})$$

$$A \left[-\frac{1}{2} \text{Ai}(y_w) + \gamma^{\frac{1}{3}} \frac{d\text{Ai}}{dy}(y_w) \right] + B \left[-\frac{1}{2} \text{Bi}(y_w) + \gamma^{\frac{1}{3}} \frac{d\text{Bi}}{dy}(y_w) \right] = 0 \quad (\text{A.362})$$

Solving B in terms of A yields

$$B = \frac{-A \left[-\frac{1}{2} \text{Ai}(y_w) + \gamma^{\frac{1}{3}} \frac{d\text{Ai}}{dy}(y_w) \right]}{\left[-\frac{1}{2} \text{Bi}(y_w) + \gamma^{\frac{1}{3}} \frac{d\text{Bi}}{dy}(y_w) \right]} \quad (\text{A.363})$$

Therefore,

$$\Phi_1(y) = A \text{Ai}(y) - A \left[\frac{\left[-\frac{1}{2} \text{Ai}(y_w) + \gamma^{\frac{1}{3}} \frac{d\text{Ai}}{dy}(y_w) \right]}{\left[-\frac{1}{2} \text{Bi}(y_w) + \gamma^{\frac{1}{3}} \frac{d\text{Bi}}{dy}(y_w) \right]} \right] \text{Bi}(y) \quad (\text{A.364})$$

To find the second solution, we apply the boundary condition at y_0 . Thus, we have

$$\frac{1}{2} \Phi_2(y_0) + \gamma^{\frac{1}{3}} \frac{d\Phi_2}{dy}(y_0) = 0 \quad (\text{A.365})$$

$$\frac{1}{2} [C Ai(y_*) + D Bi(y_*)] + \gamma^{\frac{1}{3}} \left[C \frac{dAi}{dy}(y_*) + D \frac{dBi}{dy}(y_*) \right] = 0 \quad (A.366)$$

$$C \left[\frac{1}{2} Ai(y_*) + \gamma^{\frac{1}{3}} \frac{dAi}{dy}(y_*) \right] + D \left[\frac{1}{2} Bi(y_*) + \gamma^{\frac{1}{3}} \frac{dBi}{dy}(y_*) \right] = 0 \quad (A.367)$$

Solving D in terms of C yields

$$D = \frac{-C \left[\frac{1}{2} Ai(y_*) + \gamma^{\frac{1}{3}} \frac{dAi}{dy}(y_*) \right]}{\left[\frac{1}{2} Bi(y_*) + \gamma^{\frac{1}{3}} \frac{dBi}{dy}(y_*) \right]} \quad (A.368)$$

Therefore,

$$\Phi_2(y) = C Ai(y) - C \left[\frac{\left[\frac{1}{2} Ai(y_*) + \gamma^{\frac{1}{3}} \frac{dAi}{dy}(y_*) \right]}{\left[\frac{1}{2} Bi(y_*) + \gamma^{\frac{1}{3}} \frac{dBi}{dy}(y_*) \right]} \right] Bi(y) \quad (A.369)$$

If we define the following operators:

$$G[Ai](y_w) = -\frac{1}{2} Ai(y_w) + \gamma^{\frac{1}{3}} \frac{dAi}{dy}(y_w) \quad (A.370)$$

$$G[Bi](y_w) = -\frac{1}{2} Bi(y_w) + \gamma^{\frac{1}{3}} \frac{dBi}{dy}(y_w) \quad (A.371)$$

$$H[Ai](y_*) = \frac{1}{2} Ai(y_*) + \gamma^{\frac{1}{3}} \frac{dAi}{dy}(y_*) \quad (A.372)$$

$$H[Bi](y_*) = \frac{1}{2} Bi(y_*) + \gamma^{\frac{1}{3}} \frac{dBi}{dy}(y_*) \quad (A.373)$$

then Equations (A.364) and (A.369) become

$$\Phi_1(y) = A \left[Ai(y) - \frac{G[Ai](y_w)}{G[Bi](y_w)} Bi(y) \right] \quad (A.374)$$

$$\Phi_2(y) = C \left[A_i(y) - \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i(y) \right] \quad (A.375)$$

Now we seek the particular solution to Equation (A.355). That is, we construct the Green's function (Equation (A.359)). First determine the Wronskian:

$$W[\Phi_1, \Phi_2](y) = \begin{vmatrix} \Phi_1 & \Phi_2 \\ \Phi_1' & \Phi_2' \end{vmatrix} \quad (A.376)$$

or

$$W[\Phi_1, \Phi_2](y) = \begin{vmatrix} A \left[A_i(y) - \frac{G[A_i](y_w)}{G[B_i](y_w)} B_i(y) \right] & C \left[A_i(y) - \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i(y) \right] \\ A \left[A_i'(y) - \frac{G[A_i](y_w)}{G[B_i](y_w)} B_i'(y) \right] & C \left[A_i'(y) - \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i'(y) \right] \end{vmatrix} \quad (A.377)$$

So,

$$\begin{aligned} W[\Phi_1, \Phi_2](y) &= AC \left[A_i(y) - \frac{G[A_i](y_w)}{G[B_i](y_w)} B_i(y) \right] \left[A_i'(y) - \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i'(y) \right] \\ &\quad - AC \left[A_i'(y) - \frac{G[A_i](y_w)}{G[B_i](y_w)} B_i'(y) \right] \left[A_i(y) - \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i(y) \right] \end{aligned} \quad (A.378)$$

$$\begin{aligned} &= AC \left\{ A_i(y) A_i'(y) - A_i(y) \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i'(y) - A_i'(y) \frac{G[A_i](y_w)}{G[B_i](y_w)} B_i(y) \right. \\ &\quad + \frac{G[A_i](y_w)}{G[B_i](y_w)} \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i(y) B_i'(y) - A_i(y) A_i'(y) + A_i'(y) \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i(y) \\ &\quad \left. + A_i(y) \frac{G[A_i](y_w)}{G[B_i](y_w)} B_i'(y) - \frac{G[A_i](y_w)}{G[B_i](y_w)} \frac{H[A_i](y_*)}{H[B_i](y_*)} B_i(y) B_i'(y) \right\} \end{aligned} \quad (A.379)$$

Simplifying this expression gives us

$$W[\Phi_1, \Phi_2](y) = AC \left\{ A_i(y) B'_i(y) \left[\frac{G[A_i](y_w)}{G[B_i](y_w)} - \frac{H[A_i](y.)}{H[B_i](y.)} \right] - A'_i(y) B_i(y) \left[\frac{G[A_i](y_w)}{G[B_i](y_w)} - \frac{H[A_i](y.)}{H[B_i](y.)} \right] \right\} \quad (A.380)$$

$$= AC \left[\frac{G[A_i](y_w)}{G[B_i](y_w)} - \frac{H[A_i](y.)}{H[B_i](y.)} \right] W[A_i, B_i](y) \quad (A.381)$$

We know that $W[A_i, B_i](y) = 1 / \pi$ [Abramowitz and Stegun, 1970]. Therefore,

$$W[\Phi_1, \Phi_2](y) = AC \left[\frac{G[A_i](y_w)}{G[B_i](y_w)} - \frac{H[A_i](y.)}{H[B_i](y.)} \right] \frac{1}{\pi} \quad (A.382)$$

Thus, the Green's function (Equation (A.359)) is

$$g(y, \eta) = \begin{cases} \frac{\Phi_1(y) \Phi_2(\eta)}{p(\eta) W[\Phi_1, \Phi_2](\eta)} & y \leq \eta \leq y. \\ \frac{\Phi_1(\eta) \Phi_2(y)}{p(\eta) W[\Phi_1, \Phi_2](\eta)} & y_w \leq \eta \leq y \end{cases} \quad (A.383)$$

Thus,

$$g(y, \eta) = \begin{cases} \frac{A \left[Ai(y) - \frac{G[Ai](y_w)}{G[Bi](y_w)} Bi(y) \right] C \left[Ai(\eta) - \frac{H[Ai](y.)}{H[Bi](y.)} Bi(\eta) \right]}{AC \left[\frac{G[Ai](y_w)}{G[Bi](y_w)} - \frac{H[Ai](y.)}{H[Bi](y.)} \right] \frac{1}{\pi}} \\ \frac{A \left[Ai(\eta) - \frac{G[Ai](y_w)}{G[Bi](y_w)} Bi(\eta) \right] C \left[Ai(y) - \frac{H[Ai](y.)}{H[Bi](y.)} Bi(y) \right]}{AC \left[\frac{G[Ai](y_w)}{G[Bi](y_w)} - \frac{H[Ai](y.)}{H[Bi](y.)} \right] \frac{1}{\pi}} \end{cases} \quad (A.384)$$

Simplifying gives us

$$g(y, \eta) = \begin{cases} \frac{\pi [G[Bi](y_w) Ai(y) - G[Ai](y_w) Bi(y)] [H[Bi](y.) Ai(\eta) - H[Ai](y.) Bi(\eta)]}{G[Ai](y_w) H[Bi](y.) - G[Bi](y_w) H[Ai](y.)} \\ \frac{\pi [G[Bi](y_w) Ai(\eta) - G[Ai](y_w) Bi(\eta)] [H[Bi](y.) Ai(y) - H[Ai](y.) Bi(y)]}{G[Ai](y_w) H[Bi](y.) - G[Bi](y_w) H[Ai](y.)} \end{cases} \quad (A.385)$$

where the top expression is defined for the interval $y \leq \eta \leq y$,
and the bottom expression is defined for the interval
 $y_w \leq \eta \leq y$.

We now need to verify that the nonhomogeneous boundary-value problem (Equation (A.355)) together with the boundary conditions (Equations (A.344) and (A.352)) has a unique solution. We know that a unique solution exists if and only if the corresponding homogeneous problem together with the same (zero) boundary

conditions has only the trivial solution [Ritger and Rose, 1968:439]. In the case when the homogeneous problem has only the trivial solution, we shall obtain a Green's function of the form of Equation (A.359). That is, there will be no nonzero complementary solution. To determine if a trivial or nontrivial solution exists we will use the Maximum principle [Protter and Weinberger].

For the moment, let $\Phi(y)$ denote the solution to the homogeneous differential equation with zero boundary conditions. We claim $\Phi(y) \geq 0$ for all $y_w \leq y \leq y_.$. Suppose, for contradiction, that there exists some y_1 in the interval $[y_w, y.]$ such that $\Phi(y_1) < 0$. Without loss of generality, suppose that the minimum occurs at y_1 . We will consider cases. Case 1: Suppose $y_w < y_1 < y_.$, then having a minimum at y_1 implies $\Phi''(y_1) \geq 0$ by the Maximum Principle. Using Equation (A.355) (homogeneous case), $\Phi''(y_1) = y_1 \Phi(y_1) < 0$, we get $\Phi''(y_1) < 0$ and $\Phi''(y_1) \geq 0$ which is a contradiction. Therefore, $\Phi(y)$ does not have a negative minimum in $y_w < y < y_.$. Now suppose Case 2 $y_1 = y_w$. By the Maximum Principle, then $\Phi'(y_w) \geq 0$. Using the boundary condition (Equation (A.344)) $\Phi'(y_w) = (1/2)\Phi(y_w) < 0$, we get $\Phi'(y_w) \geq 0$ and $\Phi'(y_w) < 0$ which is a contradiction. Thus, $y_1 \neq y_w$ and $\Phi(y)$ does not have a negative minimum at y_w . Now suppose Case 3 $y_1 = y_.$. By the Maximum Principle $\Phi'(y_.) \leq 0$. Using the boundary condition (Equation (A.352)) $\Phi'(y_.) = (-1/2)\Phi(y_.) > 0$, we get $\Phi'(y_.) \leq 0$ and $\Phi'(y_.) > 0$

which is a contradiction. Therefore, the original assumption that there exists some y_1 in the interval $y_w \leq y \leq y_.$ subject to $\Phi(y_1) < 0$ is false. Hence, $\Phi(y) \geq 0$ for all y in the interval $y_w \leq y \leq y_.$

We claim $\Phi(y) \leq 0$ for all $y_w \leq y \leq y_.$ Suppose for contradiction that there exists some y_2 in the interval $[y_w, y_.]$ such that $\Phi(y_2) > 0$. Without loss of generality, suppose that the maximum occurs at y_2 . We will consider cases. Case 1: Suppose $y_w < y_2 < y_.$, then having a maximum at y_2 implies $\Phi''(y_2) \leq 0$ by the Maximum Principle. Using Equation (A.355) (homogeneous case), $\Phi''(y_2) = y_2 \Phi(y_2) > 0$, we get $\Phi''(y_2) \leq 0$ and $\Phi''(y_2) > 0$ which is a contradiction. Therefore, $\Phi(y)$ does not have a positive maximum in $y_w < y < y_.$ Now suppose Case 2 $y_2 = y_w$. By the Maximum Principle $\Phi'(y_w) \leq 0$. Using the boundary condition (Equation (A.344)) $\Phi'(y_w) = (1/2)\Phi(y_w) > 0$, we get $\Phi'(y_w) > 0$ and $\Phi'(y_w) \leq 0$ which is a contradiction. Thus, $y_2 \neq y_w$ and $\Phi(y)$ does not have a positive maximum at y_w . Now suppose Case 3 $y_2 = y_.$. By the Maximum Principle $\Phi'(y_.) \geq 0$. Using the boundary condition (Equation (A.352)) $\Phi'(y_.) = (-1/2)\Phi(y_.) < 0$, we get $\Phi'(y_.) \geq 0$ and $\Phi'(y_.) < 0$ which is a contradiction. Therefore, the original assumption that there exists some y_2 in the interval $y_w \leq y \leq y_.$ subject to $\Phi(y_2) > 0$ is false. Hence, $\Phi(y) \leq 0$ for all y in the interval $y_w \leq y \leq y_.$

Combining the two claims, we see that $\Phi(y) \leq 0$ and $\Phi(y) \geq 0$. This implies $\Phi(y) = 0$ for all y in the interval $y_w \leq y \leq y_*$ and in fact, this is true for all choices $0 < y_w < y_* < \infty$ of y_w and y_* . Thus, we have a unique solution and we now know the general solution to Equation (A.355) is of the form of Equation (A.356). However, Ritger and Rose have shown that in the case when the homogeneous problem has only the trivial solution there exists no complementary solution [Ritger and Rose, 1968:439-440]. Thus, the general solution to Equation (A.355) is of the form

$$\Phi(y) = \int_{y_w}^{y_*} g(y, \eta, s) f(\eta, s) d\eta \quad (\text{A.386})$$

Since

$$y = \gamma^{\frac{1}{3}} \left[X + \frac{1}{4\gamma} \right] \quad (\text{A.353})$$

$$\Phi(y) = \phi(X) \quad (\text{A.354})$$

then

$$\eta = \gamma^{\frac{1}{3}} \left[\xi + \frac{1}{4\gamma} \right]; d\eta = \gamma^{\frac{1}{3}} d\xi \quad (\text{A.387})$$

Thus, Equation (A.386), together with the right-hand side of Equation (A.355), becomes

$$\phi(X) = \int_{x_0}^{x_1} g\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right], \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \mathcal{F}\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \gamma^{\frac{1}{3}} d\xi \quad (\text{A.388})$$

$$= \int_{x_0}^{x_1} g\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right], \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \gamma^{-\frac{2}{3}} e^{\frac{1}{2}\xi} \bar{F}(\xi, s) \gamma^{\frac{1}{3}} d\xi \quad (\text{A.389})$$

$$= \int_{x_0}^{x_1} g\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right], \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \gamma^{-\frac{1}{3}} e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \quad (\text{A.390})$$

Since $\bar{C}_m(X, s) = \phi(X, s) e^{-\frac{1}{2}X}$ (Equation (A.318)), then

$$\bar{C}_m(X, s) = e^{-\frac{1}{2}X} \int_{x_0}^{x_1} g\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right], \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \gamma^{-\frac{1}{3}} e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \quad (\text{A.391})$$

If we define

$$b(X, \xi, s) = g\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right], \gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right], s\right) \quad (\text{A.392})$$

then

$$\bar{C}_m(X, s) = e^{-\frac{1}{2}X} \int_{x_0}^{x_1} b(X, \xi, s) \gamma^{-\frac{1}{3}} e^{\frac{1}{2}\xi} \bar{F}(\xi, s) d\xi \quad (\text{A.393})$$

Substituting in the constructed Green's function (Equation (A.385)) gives us

$$\bar{C}_m(X, s) = \left\{ \frac{\pi e^{-\frac{1}{2}X} \gamma^{-\frac{1}{3}}}{G[Ai](y_w)H[Bi](y_*) - G[Bi](y_w)H[Ai](y_*)} \right\} \cdot$$

$$\left\{ \begin{aligned} & G[Bi](y_w)H[Bi](y_*)Ai\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right]\right)\int_{x_w}^x Ai\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]\right)e^{\frac{1}{2}\xi}\bar{F}(\xi, s)d\xi \\ & - G[Bi](y_w)H[Ai](y_*)Bi\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right]\right)\int_{x_w}^x Ai\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]\right)e^{\frac{1}{2}\xi}\bar{F}(\xi, s)d\xi \\ & + G[Ai](y_w)H[Ai](y_*)Bi\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right]\right)\int_{x_w}^x Bi\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]\right)e^{\frac{1}{2}\xi}\bar{F}(\xi, s)d\xi \\ & - G[Ai](y_w)H[Bi](y_*)Ai\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right]\right)\int_{x_w}^x Bi\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]\right)e^{\frac{1}{2}\xi}\bar{F}(\xi, s)d\xi \\ & + G[Bi](y_w)H[Bi](y_*)Ai\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right]\right)\int_x^{x_*} Ai\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]\right)e^{\frac{1}{2}\xi}\bar{F}(\xi, s)d\xi \\ & - G[Ai](y_w)H[Bi](y_*)Bi\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right]\right)\int_x^{x_*} Ai\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]\right)e^{\frac{1}{2}\xi}\bar{F}(\xi, s)d\xi \\ & + G[Ai](y_w)H[Ai](y_*)Bi\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right]\right)\int_x^{x_*} Bi\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]\right)e^{\frac{1}{2}\xi}\bar{F}(\xi, s)d\xi \\ & - G[Bi](y_w)H[Ai](y_*)Ai\left(\gamma^{\frac{1}{3}}\left[X + \frac{1}{4\gamma}\right]\right)\int_x^{x_*} Bi\left(\gamma^{\frac{1}{3}}\left[\xi + \frac{1}{4\gamma}\right]\right)e^{\frac{1}{2}\xi}\bar{F}(\xi, s)d\xi \end{aligned} \right\}$$

(A.394)

Model Formulation: Extraction Well Off

If we now consider turning off the extraction well after a certain period of time, say $\hat{t}$, such that $Q_w = 0$, then the mobile region dispersion coefficient, $D_m = 0$ (Equation (A.8)), and the molecular diffusion coefficient, D'_o , becomes the

dominant transport mechanism. As a result, Equation (A.2) becomes

$$\frac{\partial C'_m(r, t)}{\partial t} = \frac{1}{R_m r} \frac{\partial}{\partial r} \left[(r D'_o) \frac{\partial C'_m(r, t)}{\partial r} \right] - \frac{\theta_{im} R_{im}}{\theta_m R_m} \frac{\partial C'_{im}(r, t)}{\partial t} \quad (A.395)$$

Recall that

$$\beta = \frac{\theta_{im} R_{im}}{\theta_m R_m} \quad (A.4)$$

Then, Equation (A.395) is

$$\frac{\partial C'_m(r, t)}{\partial t} = \frac{D'_o}{R_m} \frac{1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial C'_m(r, t)}{\partial r} \right] - \beta \frac{\partial C'_{im}(r, t)}{\partial t} \quad (A.396)$$

We seek a dimensionless form of Equation (A.396). Thus, as before, we develop dimensionless variables using similar techniques when the extraction well is on. Although the techniques and the resulting form of the expressions derived in this section are similar to the pump on case, notice the different meanings of the dimensionless variables defined. If we define

$$X = A r \quad (A.397)$$

$$T = B t \quad (A.398)$$

where A and B are constants, X and T have the same meaning as the variables defined in Equations (A.42) and (A.43), and recall

$$C_m(X, T) = \frac{C'_m(r, t)}{C'_o} \quad (A.15)$$

$$C_{im}(X, T) = \frac{C'_{im}(r, t)}{C'_o} \quad (A.16)$$

where C'_0 is some initial maximum of $C'_m(r, t = \hat{t})$ and $C'_{im}(r, t = \hat{t})$, where $\hat{t}$ is the time after the extraction well has been turned off, between $r_w \leq r \leq r_e$, then

$$C'_m(r, t) = C'_m\left(\frac{X}{A}, \frac{T}{B}\right) = C'_0 C_m(X, T) \quad (\text{A.399})$$

$$C'_{im}(r, t) = C'_{im}\left(\frac{X}{A}, \frac{T}{B}\right) = C'_0 C_{im}(X, T) \quad (\text{A.400})$$

and

$$\frac{\partial C'_m(r, t)}{\partial t} = C'_0 \frac{\partial C_m(X, T)}{\partial T} \frac{dT}{dt} = C'_0 \frac{\partial C_m(X, T)}{\partial T} (B) \quad (\text{A.401})$$

$$\frac{\partial C'_m(r, t)}{\partial r} = C'_0 \frac{\partial C_m(X, T)}{\partial X} \frac{dX}{dr} = C'_0 \frac{\partial C_m(X, T)}{\partial X} (A) \quad (\text{A.402})$$

$$r \frac{\partial C'_m(r, t)}{\partial r} = \frac{XC'_0}{A} \frac{\partial C_m(X, T)}{\partial X} \frac{dX}{dr} = C'_0 X \frac{\partial C_m(X, T)}{\partial X} \quad (\text{A.403})$$

$$\frac{\partial}{\partial r} \left(r \frac{\partial C'_m(r, t)}{\partial r} \right) = \frac{\partial}{\partial r} \left(C'_0 X \frac{\partial C_m(X, T)}{\partial X} \right) \quad (\text{A.404})$$

$$= C'_0 \frac{\partial}{\partial X} \left(X \frac{\partial C_m(X, T)}{\partial X} \right) \frac{dX}{dr} \quad (\text{A.405})$$

$$= C'_0 \frac{\partial}{\partial X} \left(X \frac{\partial C_m(X, T)}{\partial X} \right) (A) \quad (\text{A.406})$$

$$\frac{\partial C'_{im}(r, t)}{\partial t} = C'_0 \frac{\partial C_{im}(X, T)}{\partial T} \frac{dT}{dt} = C'_0 \frac{\partial C_{im}(X, T)}{\partial T} (B) \quad (\text{A.407})$$

Substituting these expressions into Equation (A.396) gives us

$$BC'_0 \frac{\partial C_m(X, T)}{\partial T} = \frac{D'_0}{R_m} \frac{A}{X} C'_0 \frac{\partial}{\partial X} \left(X \frac{\partial C_m(X, T)}{\partial X} \right) A - \beta B C'_0 \frac{\partial C_{im}(X, T)}{\partial T} \quad (A.408)$$

Dividing each term in this equation by B and C'_0 yields

$$\frac{\partial C_m(X, T)}{\partial T} = \frac{D'_0}{R_m} \frac{A^2}{B} \frac{1}{X} \frac{\partial}{\partial X} \left(X \frac{\partial C_m(X, T)}{\partial X} \right) - \beta \frac{\partial C_{im}(X, T)}{\partial T} \quad (A.409)$$

We want

$$\frac{D'_0}{R_m} \frac{A^2}{B} = 1 \quad (A.410)$$

So,

$$A = \sqrt{\frac{R_m B}{D'_0}} \quad (A.411)$$

In order to determine A and B uniquely, we seek a second equation. Recall Fick's second law of diffusion describing contaminant transport within immobile regions (Equation (A.26))

$$R_{im} \frac{\partial C'_i(r, z, t)}{\partial t} = \frac{D'_c}{z^{v-1}} \frac{\partial}{\partial z} \left[z^{v-1} \frac{\partial C'_i(r, z, t)}{\partial z} \right] \quad 0 < z < a \quad (A.26)$$

and Equations (A.28) and (A.44)

$$C_i(X, Z, T) = \frac{C'_i(r, z, t)}{C'_0} \quad (A.28)$$

$$Z = \frac{z}{a} \quad (A.44)$$

Then

$$C'_i(r, z, t) = C'_i \left(\frac{X}{A}, a Z, \frac{T}{B} \right) = C'_0 C_i(X, Z, T) \quad (A.412)$$

So,

$$\frac{\partial C'_s(r, z, t)}{\partial t} = C'_o \frac{\partial C_s(X, Z, T)}{\partial T} \frac{dT}{dt} = C'_o \frac{\partial C_s(X, Z, T)}{\partial T} (B) \quad (A.413)$$

$$\frac{\partial C'_s(r, z, t)}{\partial z} = C'_o \frac{\partial C_s(X, Z, T)}{\partial Z} \frac{dZ}{dz} = C'_o \frac{\partial C_s(X, Z, T)}{\partial Z} \left(\frac{1}{a} \right) \quad (A.414)$$

$$z^{v-1} = (aZ)^{v-1} = a^{v-1} Z^{v-1} \quad (A.415)$$

Substituting these expressions into Equation (A.26) gives us

$$R_{im} C'_o B \frac{\partial C_s(X, Z, T)}{\partial T} = \frac{D'_e}{a^{v-1} Z^{v-1}} \frac{\partial}{\partial Z} \left[a^{v-1} Z^{v-1} C'_o \frac{\partial C_s(X, Z, T)}{\partial Z} \frac{1}{a} \right] \frac{dZ}{dz} \quad (A.416)$$

$$= \frac{D'_e}{a^{v-1} Z^{v-1}} \frac{\partial}{\partial Z} \left[a^{v-1} Z^{v-1} C'_o \frac{\partial C_s(X, Z, T)}{\partial Z} \frac{1}{a} \right] \frac{1}{a} \quad (A.417)$$

or

$$R_{im} C'_o B \frac{\partial C_s(X, Z, T)}{\partial T} = \frac{D'_e}{a^2 Z^{v-1}} C'_o \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad (A.418)$$

where Equations (A.416), (A.417), and (A.418) are defined over the interval $0 < Z < 1$. Dividing each term in this equation by R_{im} , C'_o , and B yields

$$\frac{\partial C_s(X, Z, T)}{\partial T} = \frac{D'_e}{R_{im} B a^2} \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (A.419)$$

Again, we want

$$\frac{D'_e}{R_{im} B a^2} = 1 \quad (A.420)$$

So,

$$B = \frac{D'_e}{R_{im} a^2} \quad (A.421)$$

Substituting Equation (A.421) into Equation (A.411) produces

$$A = \sqrt{\frac{R_m B}{D'_o}} = \sqrt{\frac{R_m}{D'_o} \frac{D'_e}{R_{im} a^2}} \quad (A.422)$$

or

$$A = \frac{1}{a} \sqrt{\frac{R_m}{D'_o} \frac{D'_e}{R_{im}}} \quad (A.423)$$

Thus, Equation (A.397) becomes

$$X = \frac{r}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{im}}} \quad (A.424)$$

and Equation (A.398) is

$$T = \frac{D'_e t}{R_{im} a^2} \quad (A.425)$$

Using Equations (A.421) and (A.423) results in the dimensionless form of Equation (A.409):

$$\frac{\partial C_m(X, T)}{\partial T} = \frac{1}{X} \frac{\partial}{\partial X} \left[X \frac{\partial C_m(X, T)}{\partial X} \right] - \beta \frac{\partial C_{im}(X, T)}{\partial T} \quad (A.426)$$

$$= \frac{1}{X} \frac{\partial}{\partial X} \left[X \frac{\partial^2 C_m(X, T)}{\partial X^2} + \frac{\partial C_m(X, T)}{\partial X} \right] - \beta \frac{\partial C_{im}(X, T)}{\partial T} \quad (A.427)$$

or

$$\frac{\partial C_m(X, T)}{\partial T} = \frac{\partial^2 C_m(X, T)}{\partial X^2} + \frac{1}{X} \frac{\partial C_m(X, T)}{\partial X} - \beta \frac{\partial C_{im}(X, T)}{\partial T} \quad (A.428)$$

Similarly, if we substitute Equation (A.421) into Equation (A.419) we get a dimensionless form of Equation (A.26)

$$\frac{\partial C_s(X, Z, T)}{\partial T} = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (A.429)$$

Taking the Laplace transform of Equation (A.428), and suppressing the (X, T) notation, gives us

$$\mathcal{L} \left(\frac{\partial C_m}{\partial T} \right) = \mathcal{L} \left(\frac{\partial^2 C_m}{\partial X^2} \right) + \mathcal{L} \left(\frac{1}{X} \frac{\partial C_m}{\partial X} \right) - \mathcal{L} \left(\beta \frac{\partial C_{im}}{\partial T} \right) \quad (A.430)$$

or

$$\begin{aligned} s \bar{C}_m - C_m(X, T = \hat{T}) &= \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} \\ &- \beta [s \bar{C}_{im} - C_{im}(X, T = \hat{T})] \end{aligned} \quad (A.431)$$

To attain a form of the solution when the extraction well is off, we will assume that the arbitrary initial conditions are of the same form as the initial conditions when the well is on, except for two significant differences. First, the initial conditions are at some later time, $T = \hat{T}$, rather than at time $T = 0$. This time $(\hat{T})$ reflects the contaminant concentration in the mobile and immobile regions at the time the extraction well is turned off. Thus, the initial conditions at $\hat{T}$ are the terminal conditions for the pump on. Second, as

previously mentioned, the dimensionless variables, X , X_w , X_* , and T have a different form in comparison to when the extraction well is on but have the same meaning. From Equation (A.424) we have

$$X_w = \frac{r_w}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{im}}} \quad (A.432)$$

$$X_* = \frac{r_*}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{im}}} \quad (A.433)$$

Thus, the initial conditions are

$$C_m(X, T = \hat{T}) = F_m(X) \quad X_w < X < X_* \quad (A.434)$$

$$C_{im}(X, T = \hat{T}) = F_{im}(X) \quad X_w < X < X_* \quad (A.435)$$

$$C_m(X, T = \hat{T}) = C_{im}(X, T = \hat{T}) = 0 \quad X > X_* \quad (A.436)$$

where $F_m(X)$ and $F_{im}(X)$ are dimensionless arbitrary initial concentration conditions in the mobile region and immobile region, respectively at time $\hat{T}$. As before, the diffusion models require the following additional initial conditions to describe transport within the immobile regions:

$$C_s(X, Z, T = \hat{T}) = F_s(X, Z) \quad X_w < X < X_* \quad (A.437)$$

$$C_s(X, Z, T = \hat{T}) = 0 \quad X > X_* \quad (A.438)$$

where $F_s(X, Z)$ is the dimensionless arbitrary initial concentration condition in the immobile region of a certain geometry at time $\hat{T}$. Again, Equations (A.434), (A.435),

(A.436), (A.437), and (A.438) state the initial conditions, which assumes contamination of mobile and immobile regions at some arbitrary concentration within a cylindrical region of dimensionless radius X_1 at time $\hat{T}$.

The boundary condition at the well for the pump on case is still assumed to be applicable when the pump is off (Equation (A.55)). That is, we assume that the concentration inside the well bore is equal to that entering the well from the adjacent surrounding media. Thus,

$$\frac{\partial C_m}{\partial X}(X_w, T) = 0 \quad (A.439)$$

Similarly, the boundary conditions within the immobile regions of layered, cylindrical, and spherical geometry remain as stated in Equations (A.56) and (A.57). That is, these equations state that the concentration within an immobile region of certain geometry is zero at the center and is equal to the mobile region concentration at its outer boundary, respectively.

$$\frac{\partial C_i(X, Z = 0, T)}{\partial Z} = 0 \quad X_w < X \quad (A.440)$$

$$C_i(X, Z = 1, T) = C_m(X, T) \quad X_w < X \quad (A.441)$$

The outer boundary condition is modified to allow for leakage of the contaminant, since molecular diffusion is assumed to be the dominant mechanism responsible for transport. Thus, we assume that the total mass flux outward at the outer boundary

of the contamination area (r_*) is proportional to the amount of the contaminant mass present in the mobile region. Mathematically, this boundary condition is represented as

$$D'_o \frac{\partial C'_m}{\partial r}(r_*, \hat{t}) = k C'_m(r_*, \hat{t}) \quad (\text{A.442})$$

or

$$\frac{D'_o}{k} \frac{\partial C'_m}{\partial r}(r_*, \hat{t}) - C'_m(r_*, \hat{t}) = 0 \quad (\text{A.443})$$

where k is a proportionality constant. Recall Equations (A.15) and (A.424)

$$C_m(X, T) = \frac{C'_m(r, t)}{C'_o} \quad (\text{A.15})$$

$$X = \frac{r}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{im}}} \quad (\text{A.424})$$

If we nondimensionalize Equation (A.443), term by term, we get

$$C'_m(r_*, \hat{t}) = C'_o C_m(X_*, \hat{T}) \quad (\text{A.444})$$

$$\frac{\partial C'_m(r_*, \hat{t})}{\partial r} = C'_o \frac{\partial C_m(X_*, \hat{T})}{\partial X} \frac{dX}{dr} = C'_o \frac{\partial C_m(X_*, \hat{T})}{\partial X} \left[\frac{1}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{im}}} \right] \quad (\text{A.445})$$

Substituting these equations into Equation (A.443) gives us

$$\frac{D'_o}{k} \frac{C'_o}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{im}}} \frac{\partial C_m(X_*, \hat{T})}{\partial X} - C'_o C_m(X_*, \hat{T}) = 0 \quad (\text{A.446})$$

Dividing each term in this equation by C'_0 yields

$$\frac{D'_0}{k} \frac{1}{a} \sqrt{\frac{D'_e R_m}{D'_0 R_{im}}} \frac{\partial C_m(X., \hat{T})}{\partial X} - C_m(X., \hat{T}) = 0 \quad (A.447)$$

If we define

$$\epsilon = \frac{D'_0}{k} \frac{1}{a} \sqrt{\frac{D'_e R_m}{D'_0 R_{im}}} \quad (A.448)$$

where ϵ represents the coefficient of leakage of the contaminant through the outer boundary, then the outer boundary condition (Equation(A.447)) becomes

$$\epsilon \frac{\partial C_m}{\partial X}(X., \hat{T}) - C_m(X., \hat{T}) = 0 \quad (A.449)$$

Now that we have established the governing differential equation (Equation (A.428)) and the initial conditions and boundary conditions, we will now go through the mathematical formulation for each model.

Local Equilibrium Model (LEA). From Equation (A.428), if β is defined to be zero, and if we suppress the (X, T) notation, then Equation (A.428) becomes

$$\frac{\partial C_m}{\partial T} = \frac{\partial^2 C_m}{\partial X^2} + \frac{1}{X} \frac{\partial C_m}{\partial X} \quad (A.450)$$

Taking the Laplace transformation of this equation gives us

$$\mathcal{L}\left(\frac{\partial C_m}{\partial T}\right) = \mathcal{L}\left(\frac{\partial^2 C_m}{\partial X^2}\right) + \mathcal{L}\left(\frac{1}{X} \frac{\partial C_m}{\partial X}\right) \quad (A.451)$$

or

$$s\bar{C}_m - C_m(X, T = \hat{T}) = \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} \quad (A.452)$$

Rearranging this expression yields

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - s\bar{C}_m = -C_m(X, T = \hat{T}) \quad (A.453)$$

If we define

$$\gamma = s \quad (A.454)$$

and

$$\bar{F}(X, s) = -C_m(X, T = \hat{T}) \quad (A.455)$$

together with the initial condition $C_m(X, T = \hat{T}) = F_m(X)$, then Equation (A.453) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \gamma \bar{C}_m = \bar{F}(X, s) \quad (A.456)$$

First-Order Rate Model. Previously, we introduced the first-order rate model. That is, the transfer of solute between the mobile and immobile region can be described using a first-order rate expression:

$$\frac{\partial C'_{im}(r, t)}{\partial t} = \frac{\alpha'}{\theta_{im} R_{im}} [C'_m(r, t) - C'_{im}(r, t)] \quad (A.64)$$

We seek a dimensionless form of Equation (A.64). Recall Equations (A.15), (A.16), (A.424), and (A.425):

$$C_m(X, T) = \frac{C'_m(r, t)}{C'_o} \quad (A.15)$$

$$C_{im}(X, T) = \frac{C'_{im}(r, t)}{C'_o} \quad (A.16)$$

$$X = \frac{r}{a} \sqrt{\frac{D'_e R_m}{D'_o R_{im}}} \quad (A.424)$$

$$T = \frac{D'_e t}{R_{im} a^2} \quad (A.425)$$

Rewriting Equation (A.64) into dimensionless form yields

$$\frac{\partial C_{im}(X, T)}{\partial T} \frac{D'_e}{R_{im} a^2} = \frac{\alpha'}{\theta_{im} R_{im}} [C_m(X, T) - C_{im}(X, T)] \quad (A.457)$$

Rearranging this equation gives us

$$\frac{\partial C_{im}(X, T)}{\partial T} = \frac{\alpha' a^2}{\theta_{im} D'_e} [C_m(X, T) - C_{im}(X, T)] \quad (A.458)$$

If we define the dimensionless first-order rate constant α as

$$\alpha = \frac{\alpha' a^2}{\theta_{im} D'_e} \quad (A.459)$$

then Equation (A.458) is in the form as Equation (A.72):

$$\frac{\partial C_{im}(X, T)}{\partial T} = \alpha [C_m(X, T) - C_{im}(X, T)] \quad (A.72)$$

Recall the Laplace transform equations of Equation (A.72):

$$\mathcal{L}\left(\frac{\partial C_{im}}{\partial T}\right) = \mathcal{L}(\alpha [C_m - C_{im}]) \quad (A.73)$$

$$s \bar{C}_{im} - C_{im}(X, T = \hat{T}) = \alpha (\bar{C}_m - \bar{C}_{im}) \quad (A.74)$$

However, notice that these expressions are now at time $T = \hat{T}$ rather than $T = 0$. Solving for $\bar{C}_{im}$ in terms of $\bar{C}_m$ gives us

$$\bar{C}_{im} = \frac{C_{im}(X, T = \hat{T}) + \alpha \bar{C}_m}{s + \alpha} \quad (A.75)$$

Inserting this expression into Equation (A.431) and rearranging results in

$$\begin{aligned} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \bar{C}_m \left(s + \frac{\alpha \beta s}{s + \alpha} \right) = & -C_m(X, T = \hat{T}) \\ & + C_{im}(X, T = \hat{T}) \left(\frac{\beta s}{s + \alpha} - \beta \right) \end{aligned} \quad (A.460)$$

If we define

$$\gamma = s \left(1 + \frac{\beta \alpha}{s + \alpha} \right) \quad (A.461)$$

and

$$\bar{F}(X, s) = - \left[C_m(X, T = \hat{T}) + \frac{\beta \alpha C_{im}(X, T = \hat{T})}{s + \alpha} \right] \quad (A.462)$$

together with the initial conditions $C_m(X, T = \hat{T}) = F_m(X)$ and $C_{im}(X, T = \hat{T}) = F_{im}(X)$ we get

$$\bar{F}(X, s) = - \left(F_m(X) + \frac{\beta \alpha F_{im}(X)}{s + \alpha} \right) \quad (A.463)$$

So, Equation (A.460) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \gamma \bar{C}_m = \bar{F}(X, s) \quad (A.464)$$

Diffusion Models. As previously discussed, the transfer of solute between the mobile and immobile regions may be assumed to be governed by Fickian (Fick's second law) diffusion within immobile regions of specified geometry [Goltz and Oxley, 1991:548-549]. Mathmatically, Fick's second law of diffusion describing contaminant transport within the immobile region is

$$R_{im} \frac{\partial C'_i(r, z, t)}{\partial t} = \frac{D'_e}{z^{v-1}} \frac{\partial}{\partial z} \left(z^{v-1} \frac{\partial C'_i(r, z, t)}{\partial z} \right) \quad 0 < z < a \quad (A.26)$$

Recall Equation (A,429) which is the dimensionless form of Equation (A.26):

$$\frac{\partial C_i(X, Z, T)}{\partial T} = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_i(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (A.429)$$

which is valid for all the diffusion models. That is, $v = 1, 2$, and 3 . Now we take the Laplace transform of Equation (A.429) using Equation (A.437) (initial condition) and Equations (A.440) and (A.441) (boundary conditions):

$$C_i(X, Z, T = \hat{T}) = F_i(X, Z) \quad X_w < X < X. \quad (A.437)$$

$$\frac{\partial C_i(X, Z = 0, T)}{\partial Z} = 0 \quad X_w < X < X. \quad (A.440)$$

$$C_i(X, Z = 1, T) = C_m(X, T) \quad X_w < X < X. \quad (A.441)$$

So,

$$\mathcal{L} \left(\frac{\partial C_i}{\partial T} \right) = \mathcal{L} \left(\frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial C_i}{\partial Z} \right) \right) \quad (A.465)$$

$$s\bar{C}_s - C_s(X, Z, T = \hat{T}) = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z} \right) \quad (\text{A.466})$$

$$s\bar{C}_s - F_s(X, Z) = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z} \right) \quad (\text{A.467})$$

thus

$$\frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z} \right) - s\bar{C}_s = -F_s(X, Z) \quad (\text{A.468})$$

The boundary conditions associated with this equation are derived by taking the Laplace transform of Equations (A.440) and (A.441). Thus,

$$\frac{\partial \bar{C}_s}{\partial Z}(X, Z = 0, s) = 0 \quad X_w < X < X_s \quad (\text{A.469})$$

$$\bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s) \quad X_w < X < X_s \quad (\text{A.470})$$

We seek the general solution to Equation (A.468) using the boundary conditions (A.469) and (A.470) for cases of $v = 1, 2, 3$ (layered, cylinder, and spherical geometry, respectively). That is, we seek

$$\bar{C}_s = \bar{C}_{s,c} + \bar{C}_{s,p} \quad (\text{A.471})$$

where $\bar{C}_s$ is the general solution to the differential equation, $\bar{C}_{s,c}$ is the complementary solution to the homogeneous differential equation, and $\bar{C}_{s,p}$ is the particular solution to the nonhomogeneous differential equation. Now we look at the case where $v = 1$.

Layered Diffusion. We first find the general solution to the homogeneous problem. So Equation (A.468) becomes

$$\frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_{\bullet c}}{\partial Z} \right) - s \bar{C}_{\bullet c} = 0 \quad 0 < Z < 1 \quad (\text{A.472})$$

If we define $u = \bar{C}_{\bullet c}$, then Equation (A.472) becomes

$$\frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial u}{\partial Z} \right) - su = 0 \quad 0 < Z < 1 \quad (\text{A.473})$$

When $v = 1$, Equation (A.473) transforms into a second order differential equation with constant coefficients:

$$\frac{\partial^2 u}{\partial Z^2} - su = 0 \quad 0 < Z < 1 \quad (\text{A.474})$$

The general solution of this differential equation is of the form

$$u(Z) = c_1 u_1(Z) + c_2 u_2(Z) \quad (\text{A.475})$$

where c_1 and c_2 are constants and $u_i(Z)$ is of the form $u_i(Z) = e^{m_i Z}$ [Ritger and Rose, 1968:121, 129]. So,

$$m^2 e^{mZ} - s e^{mZ} = 0 \quad (\text{A.476})$$

$$e^{mZ} (m^2 - s) = 0 \quad (\text{A.477})$$

Since e^{mZ} is not equal to zero then the auxillary equation is

$$m^2 - s = 0 \quad (\text{A.478})$$

So,

$$m^2 = s \quad \text{or} \quad m_1 = \sqrt{s} \quad m_2 = -\sqrt{s} \quad (\text{A.479})$$

Thus,

$$u(Z) = c_1 e^{\sqrt{s} Z} + c_2 e^{-\sqrt{s} Z} \quad (\text{A.480})$$

If we define

$$\omega = \sqrt{s} \quad (\text{A.481})$$

then

$$u(Z) = c_1 e^{\omega Z} + c_2 e^{-\omega Z} \quad (\text{A.482})$$

We now check this solution for linear independence to determine if Equation (A.482) is the general solution to Equation (A.474). Thus, we use the Wronskian, $W[u_1, u_2]$. That is, if $W[u_1, u_2] \neq 0$ then the two solutions, u_1 and u_2 , are linearly independent and $u(Z)$ is the general solution. Using Equation (A.482) with $u_1 = e^{\omega Z}$ and $u_2 = e^{-\omega Z}$ we get

$$W[u_1, u_2] = \begin{vmatrix} u_1 & u_2 \\ u_1' & u_2' \end{vmatrix} = \begin{vmatrix} e^{\omega Z} & e^{-\omega Z} \\ \omega e^{\omega Z} & -\omega e^{-\omega Z} \end{vmatrix} \quad (\text{A.483})$$

$$= -\omega e^{-\omega Z} e^{\omega Z} - \omega e^{\omega Z} e^{-\omega Z} = -\omega - \omega = -2\omega \neq 0 \quad (\text{A.484})$$

Thus, u_1 and u_2 are linearly independent so $u(Z) = c_1 e^{\omega Z} + c_2 e^{-\omega Z}$ is the general solution.

Now we seek the particular solution using a Green's function. If we define $U = \bar{C}_1$, then from Equation (A.468), we have the following nonhomogeneous differential equation

$$\frac{\partial^2 U}{\partial Z^2} - sU = -F_1(X, Z) \quad (\text{A.485})$$

with boundary conditions

$$\frac{\partial U}{\partial Z}(Z = 0) = 0 \quad (\text{A.486})$$

$$U(Z = 1) = 0 \quad (\text{A.487})$$

Rewriting Equation (A.485) gives us

$$\frac{\partial^2 U}{\partial Z^2} - \omega^2 U = -F_1(X, Z) \quad (\text{A.488})$$

where $\omega^2 = s$ (Equation (A.481)). We know the general solution of this equation is of the form

$$U(Z) = AU_1(Z) + BU_2(Z) + U_p \quad (\text{A.489})$$

where A and B are constants and U_p (or $\bar{C}_{1p}$) is the particular solution [Ritger and Ross, 1968:438]. Based on the homogeneous solution, we know that $U_1(Z) = c_1 e^{\omega Z} + c_2 e^{-\omega Z}$ satisfies the boundary condition $\partial U_1(Z = 0) / \partial Z = 0$. That is, $\omega c_1 e^{\omega(0)} - \omega c_2 e^{-\omega(0)} = 0$, which implies $c_1 = c_2$. So,

$$U_1(Z) = c_1 e^{\omega Z} + c_1 e^{-\omega Z} \quad (\text{A.490})$$

If we choose $c_1 = 1/2$ (without loss of generality), then

$$U_1(Z) = \frac{e^{\omega Z} + e^{-\omega Z}}{2} = \cosh \omega Z \quad (\text{A.491})$$

We also know that $U_2(Z) = c_3 e^{\omega Z} + c_4 e^{-\omega Z}$ satisfies the other boundary condition $U_2(Z = 1) = 0$. Thus,

$$U_2(Z = 1) = 0 = c_3 e^{\omega(1)} + c_4 e^{-\omega(1)} \quad (\text{A.492})$$

so

$$c_4 = -c_3 e^{2\omega} \quad (\text{A.493})$$

Therefore,

$$U_2(Z) = c_3 e^{\omega Z} - c_3 e^{2\omega} e^{-\omega Z} \quad (\text{A.494})$$

$$= c_3 e^{\omega} [e^{\omega Z} e^{-\omega} - e^{\omega} e^{-\omega Z}] \quad (\text{A.495})$$

$$= c_3 e^{\omega} [e^{\omega(Z-1)} - e^{-\omega(Z-1)}] \quad (\text{A.496})$$

or

$$U_2(Z) = c_3 e^{\omega} [-e^{\omega(1-Z)} + e^{-\omega(1-Z)}] \quad (\text{A.497})$$

Since $c_3 e^{\omega}$ is a constant, let's choose it to equal $-1/2$ (without loss of generality). This gives us

$$U_2(Z) = \frac{e^{\omega(1-Z)} - e^{-\omega(1-Z)}}{2} = \sinh \omega(1-Z) \quad (\text{A.498})$$

We now check to see if we have a trivial or non-trivial solution using the zero boundary conditions for the homogeneous case:

$$\frac{\partial u}{\partial Z}(Z = 0) = 0 \quad (\text{A.499})$$

$$u(Z = 1) = 0 \quad (\text{A.500})$$

This will determine the form of the Green's function for the particular solution. We know Equation (A.488) with the above

boundary conditions has a unique solution if and only if the homogeneous problem (Equation (A.474)) has only the trivial solution for the same zero boundary conditions [Ritger and Ross, 1968:439]. Recall, $u(Z) = c_1 e^{\omega Z} + c_2 e^{-\omega Z}$ (Equation (A.482)), so

$$\frac{\partial u}{\partial Z}(Z = 0) = 0 = \omega c_1 e^{\omega(0)} - \omega c_2 e^{-\omega(0)} = \omega(c_1 - c_2) \quad (\text{A.501})$$

thus,

$$c_1 = c_2 \quad (\text{A.502})$$

At the other boundary condition, $u(Z = 1) = 0$, we get

$$u(Z = 1) = 0 = c_1 e^{\omega(1)} + c_2 e^{-\omega(1)} \quad (\text{A.503})$$

$$c_2 e^{-\omega} = -c_1 e^{\omega} \quad (\text{A.504})$$

$$c_2 = -c_1 e^{2\omega} \quad (\text{A.505})$$

thus,

$$c_1 = c_2 = -c_1 e^{2\omega} \quad \text{or} \quad c_1 = 0 \quad (\text{A.506})$$

so, $u(Z) = 0$ is the trivial solution.

Since we have a trivial solution we now construct the particular solution using a Green's function which is of the form [Ritger and Ross, 1968:440]

$$g(Z, \zeta) = \begin{cases} \frac{U_1(Z)U_2(\zeta)}{p(\zeta)W[U_1, U_2](\zeta)} & Z < \zeta < 1 \\ \frac{U_1(\zeta)U_2(Z)}{p(\zeta)W[U_1, U_2](\zeta)} & 0 < \zeta < Z \end{cases} \quad (\text{A.507})$$

where $W[U_1, U_2](\zeta)$ is the Wronskian of U_1 and U_2 , and $p(\zeta)$ is the coefficient of the first term in Equation (A.488). From Equation (A.488), we see that $p(\zeta) = 1$. Now we determine the Wronskian:

$$W[U_1, U_2] = \begin{vmatrix} U_1 & U_2 \\ U_1' & U_2' \end{vmatrix} = \begin{vmatrix} \cosh \omega Z & \sinh \omega(1-Z) \\ \omega \sinh \omega Z & -\omega \cosh \omega(1-Z) \end{vmatrix} \quad (\text{A.508})$$

$$= -\omega \cosh \omega(1-Z) \cosh \omega Z - \omega \sinh \omega Z \sinh \omega(1-Z) \quad (\text{A.509})$$

$$= -\omega [\cosh \omega Z \cosh \omega(1-Z) + \sinh \omega Z \sinh \omega(1-Z)] \quad (\text{A.510})$$

$$= -\omega \cosh(\omega Z + \omega(1-Z)) \quad (\text{A.511})$$

$$= -\omega \cosh \omega \neq 0 \quad (\text{A.512})$$

So,

$$g(Z, \zeta) = \begin{cases} \frac{\cosh \omega Z \sinh \omega(1-\zeta)}{-\omega \cosh \omega} & Z < \zeta < 1 \\ \frac{\cosh \omega \zeta \sinh \omega(1-Z)}{-\omega \cosh \omega} & 0 < \zeta < Z \end{cases} \quad (\text{A.513})$$

Therefore,

$$U_p = \bar{C}_{\alpha_r}(X, Z, s) = -\int_0^1 g(Z, \zeta) F_s(X, \zeta) d\zeta \quad (\text{A.514})$$

Thus, Equation (A.471) is

$$\bar{C}_s = \bar{C}_{s_c} + \bar{C}_{s_r} = A \cosh \omega Z + B \sinh \omega(1 - Z) \quad (A.515)$$

$$- \int_0^1 g(Z, \zeta) F_s(X, \zeta) d\zeta$$

or

$$\begin{aligned} \bar{C}_s = & A \cosh \omega Z + B \sinh \omega(1 - Z) + \frac{\cosh \omega Z}{\omega \cosh \omega} \int_Z^1 \sinh \omega(1 - \zeta) F_s(X, \zeta) d\zeta \\ & + \frac{\sinh \omega(1 - Z)}{\omega \cosh \omega} \int_0^Z \cosh(\omega \zeta) F_s(X, \zeta) d\zeta \end{aligned} \quad (A.516)$$

Now we apply the nonzero boundary conditions (Equations (A.440) and (A.441)) to find the constants A and B.

$$\begin{aligned} \frac{\partial \bar{C}_s}{\partial Z}(X, Z = 0, s) = 0 = & \omega A \sinh \omega(0) - \omega B \cosh \omega(1 - 0) \\ & + \frac{\omega \sinh \omega(0)}{\omega \cosh \omega} \int_0^1 \sinh \omega(1 - \zeta) F_s(X, \zeta) d\zeta \\ & - \frac{\cosh \omega(0)}{\omega \cosh \omega} \sinh \omega(1 - Z) F_s(X, Z) \Big|_{Z=0} \\ & - \frac{\omega \cosh \omega(1 - 0)}{\omega \cosh \omega} \int_0^0 \cosh(\omega \zeta) F_s(X, \zeta) d\zeta \\ & + \frac{\sinh \omega(1 - 0)}{\omega \cosh \omega} \cosh(\omega Z) F_s(X, Z) \Big|_{Z=0} \end{aligned} \quad (A.517)$$

or

$$0 = -\omega B \cosh \omega \quad (\text{A.518})$$

So, $B = 0$. Now we apply the second boundary condition

$$\bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s)$$

$$\begin{aligned} \bar{C}_m(X, s) = & A \cosh \omega(1) + \frac{\cosh \omega(1)}{\omega \cosh \omega} \int_1^1 \sinh \omega(1 - \zeta) F_s(X, \zeta) d\zeta \\ & + \frac{\sinh \omega(1 - 1)}{\omega D_s \cosh \omega} \int_0^1 \cosh(\omega \zeta) F_s(X, \zeta) d\zeta \end{aligned} \quad (\text{A.519})$$

So, $A = \frac{\bar{C}_m(X, s)}{\cosh \omega}$. Thus, Equation (A.515) becomes

$$\bar{C}_s(X, Z, s) = \frac{\bar{C}_m(X, s)}{\cosh \omega} \cosh \omega Z - \int_0^1 g(Z, \zeta) F_s(X, \zeta) d\zeta \quad (\text{A.520})$$

Combining Equations (A.431), (A.434), and (A.435) we get

$$s\bar{C}_m - F_m(X) = \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \beta[s\bar{C}_m - F_m(X)] \quad (\text{A.521})$$

Now we need an expression for $\bar{C}_{im}$. Recall Equation (A.146):

$$\bar{C}_{im}(X, s) = \int_0^1 \bar{C}_s(X, Z, s) dZ \quad (\text{A.146})$$

Substituting Equation (A.520) into Equation (A.146) we get

$$\bar{C}_{im}(X, s) = \int_0^1 \frac{\bar{C}_m(X, s) \cosh \omega Z}{\cosh \omega} dZ - \int_0^1 \int_0^1 g(Z, \zeta) F_*(X, \zeta) d\zeta dZ \quad (A.522)$$

$$= \frac{\bar{C}_m(X, s)}{\cosh \omega} \int_0^1 \cosh \omega Z dZ - \int_0^1 \left[\int_0^1 g(Z, \zeta) dZ \right] F_*(X, \zeta) d\zeta \quad (A.523)$$

$$= \frac{\bar{C}_m(X, s)}{\cosh \omega} \left[\frac{\sinh \omega Z}{\omega} \right]_0^1 - \int_0^1 \left[\int_0^1 g(Z, \zeta) dZ \right] F_*(X, \zeta) d\zeta \quad (A.524)$$

$$= \frac{\bar{C}_m(X, s) \sinh \omega}{\omega \cosh \omega} - \int_0^1 \left[\int_0^1 g(Z, \zeta) dZ \right] F_*(X, \zeta) d\zeta \quad (A.525)$$

Now we determine $\int_0^1 g(Z, \zeta) dZ$:

$$\int_0^1 g(Z, \zeta) dZ = \int_0^\zeta \left[\frac{\cosh \omega Z \sinh \omega(1 - \zeta)}{-\omega \cosh \omega} \right] dZ \quad (A.526)$$

$$+ \int_\zeta^1 \left[\frac{\cosh \omega \zeta \sinh \omega(1 - Z)}{-\omega \cosh \omega} \right] dZ$$

$$= \frac{\sinh \omega Z \sinh \omega(1 - \zeta)}{-\omega^2 \cosh \omega} \Big|_0^\zeta + \frac{\cosh \omega \zeta \cosh \omega(1 - Z)}{-\omega \cosh \omega(-\omega)} \Big|_\zeta^1 \quad (A.527)$$

$$= \frac{\sinh \omega \zeta \sinh \omega(1 - \zeta)}{-\omega^2 \cosh \omega} + \frac{\cosh \omega \zeta}{\omega^2 \cosh \omega} \quad (A.528)$$

$$- \frac{\cosh \omega \zeta \cosh \omega(1 - \zeta)}{\omega^2 \cosh \omega}$$

$$= - \frac{1}{\omega^2 \cosh \omega} \left[\sinh \omega \zeta \sinh \omega(1 - \zeta) + \cosh \omega \zeta \cosh \omega(1 - \zeta) \right]$$

$$+ \frac{\cosh \omega \zeta}{\omega^2 \cosh \omega}$$

$$(A.529)$$

$$= - \frac{1}{\omega^2 \cosh \omega} \left[\cosh(\omega \zeta + \omega(1 - \zeta)) \right] + \frac{\cosh \omega \zeta}{\omega^2 \cosh \omega} \quad (A.530)$$

So,

$$\int_0^1 g(Z, \zeta) dZ = \frac{1}{\omega^2} \left[-1 + \frac{\cosh \omega \zeta}{\cosh \omega} \right] \quad (\text{A.531})$$

Inserting this equation back into $\bar{C}_m(X, s)$ (Equation (A.525)) gives us

$$\bar{C}_m(X, s) = \frac{\bar{C}_m(X, s) \sinh \omega}{\omega \cosh \omega} - \frac{1}{\omega^2} \int_0^1 \left[-1 + \frac{\cosh \omega \zeta}{\cosh \omega} \right] F_s(X, \zeta) d\zeta \quad (\text{A.532})$$

Now we have an expression for $\bar{C}_m(X, s)$. Using this equation let's substitute it back into Equation (A.521):

$$s\bar{C}_m - F_m(X) = \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \beta [s\bar{C}_m - F_m(X)] \quad (\text{A.521})$$

Thus,

$$\begin{aligned} s\bar{C}_m - F_m(X) &= \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} \\ &\quad - \beta \left[s \left\{ \frac{\bar{C}_m \sinh \omega}{\omega \cosh \omega} - \frac{1}{\omega^2} \int_0^1 \left[-1 + \frac{\cosh \omega \zeta}{\cosh \omega} \right] F_s(X, \zeta) d\zeta \right\} - F_m(X) \right] \end{aligned} \quad (\text{A.533})$$

Rearranging this equation gives us the following

$$\begin{aligned} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - s\bar{C}_m \left(1 + \frac{\beta \sinh \omega}{\omega \cosh \omega} \right) &= -[F_m(X) + \beta F_m(X) \\ &\quad + \frac{\beta s}{\omega^2} \int_0^1 \left[-1 + \frac{\cosh \omega \zeta}{\cosh \omega} \right] F_s(X, \zeta) d\zeta] \end{aligned} \quad (\text{A.534})$$

If we define

$$\gamma = s \left(1 + \frac{\beta \sinh \omega}{\omega \cosh \omega} \right) \quad (\text{A.535})$$

and recall that $s = \omega^2$ (Equation (A.481)), then we get

$$\begin{aligned} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \gamma \bar{C}_m = & -[F_m(X) + \beta F_m(X) \\ & + \beta \int_0^1 \left[\frac{\cosh \omega \zeta}{\cosh \omega} - 1 \right] F_1(X, \zeta) d\zeta] \end{aligned} \quad (\text{A.536})$$

The right-hand side of this equation can be further simplified using the initial conditions $C_m(X, T = \hat{T}) = F_m(X)$ (Equation (A.435), $C_1(X, Z, T = \hat{T}) = F_1(X, Z)$ (Equation (A.437)), and the dimensionless expression for the volume-average immobile region solute concentration, $C_m(X, T) = v \int_0^1 Z^{v-1} C_1(X, Z, T) dZ$ where $v = 1$ (Equation (A.145)). Therefore, at time $T = \hat{T}$

$$F_m(X) = C_m(X, T = \hat{T}) = \int_0^1 C_1(X, Z, T = \hat{T}) dZ = \int_0^1 F_1(X, Z) dZ \quad (\text{A.537})$$

Putting this expression for $F_m(X)$ into the right-hand side of Equation (A.536) gives us

$$-[F_m(X) + \beta \int_0^1 F_1(X, Z) dZ + \beta \int_0^1 \left[\frac{\cosh \omega \zeta}{\cosh \omega} - 1 \right] F_1(X, \zeta) d\zeta] \quad (\text{A.538})$$

or

$$-[F_m(X) + \beta \int_0^1 F_1(X, \zeta) d\zeta + \beta \int_0^1 \left(\frac{\cosh \omega \zeta}{\cosh \omega} \right) F_1(X, \zeta) d\zeta - \beta \int_0^1 F_1(X, \zeta) d\zeta] \quad (\text{A.539})$$

Thus, Equation (A.539) becomes

$$-\left[F_m(X) + \frac{\beta}{\cosh \omega} \int_0^1 \cosh(\omega \zeta) F_i(X, \zeta) d\zeta\right] \quad (\text{A.540})$$

So, if we define

$$\bar{F}(X, s) = -\left[F_m(X) + \frac{\beta}{\cosh \omega} \int_0^1 \cosh(\omega \zeta) F_i(X, \zeta) d\zeta\right] \quad (\text{A.541})$$

then Equation (A.536) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \gamma \bar{C}_m = \bar{F}(X, s) \quad (\text{A.542})$$

Using similar techniques as in the above derivation when $\nu = 1$, we now seek the solution when $\nu = 2$.

Cylindrical Diffusion. From Equation (A.429) we have

$$\frac{\partial C_i(X, Z, T)}{\partial T} = \frac{1}{Z^{\nu-1}} \frac{\partial}{\partial Z} \left[Z^{\nu-1} \frac{\partial C_i(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (\text{A.429})$$

which is valid for all the diffusion models. As previously derived, we now take the Laplace transform of Equation (A.429) using Equation (A.437) (initial condition) and Equations (A.440) and (A.441) (boundary conditions):

$$C_i(X, Z, T = \hat{T}) = F_i(X, Z) \quad X_w < X < X_s \quad (\text{A.437})$$

$$\frac{\partial C_i(X, Z = 0, T)}{\partial Z} = 0 \quad X_w < X < X_s \quad (\text{A.440})$$

$$C_i(X, Z = 1, T) = C_m(X, T) \quad X_w < X < X_s \quad (\text{A.441})$$

So,

$$\mathcal{L}\left(\frac{\partial C_s}{\partial T}\right) = \mathcal{L}\left(\frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial C_s}{\partial Z}\right)\right) \quad (\text{A.465})$$

$$s\bar{C}_s - C_s(X, Z, T = \hat{T}) = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) \quad (\text{A.466})$$

$$s\bar{C}_s - F_s(X, Z) = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) \quad (\text{A.467})$$

thus

$$\frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) - s\bar{C}_s = -F_s(X, Z) \quad (\text{A.468})$$

with the following boundary conditions (Laplace transformed functions of Equations (A.440) and (A.441)):

$$\frac{\partial \bar{C}_s}{\partial Z}(X, Z = 0, s) = 0 \quad X_w < X < X_s \quad (\text{A.469})$$

$$\bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s) \quad X_w < X < X_s \quad (\text{A.470})$$

We seek the general solution to Equation (A.468) using the boundary conditions (A.469) and (A.470) for case of $v = 2$. That is, we seek

$$\bar{C}_s = \bar{C}_{s_c} + \bar{C}_{s_p} \quad (\text{A.471})$$

where $\bar{C}_s$ is the general solution to the differential equation, $\bar{C}_{s_c}$ is the complementary solution to the homogeneous differential equation, and $\bar{C}_{s_p}$ is the particular solution to the nonhomogeneous differential equation. For the case of $v = 2$, Equation (A.468) becomes

$$\frac{1}{Z} \frac{\partial}{\partial Z} \left(Z \frac{\partial \bar{C}_s}{\partial Z} \right) - s \bar{C}_s = -F_s(X, Z) \quad (\text{A.543})$$

Differentiating the first term of Equation (A.543) gives us

$$\frac{1}{Z} \left[Z \frac{\partial^2 \bar{C}_s}{\partial Z^2} + \frac{\partial \bar{C}_s}{\partial Z} \right] - s \bar{C}_s = -F_s(X, Z) \quad (\text{A.544})$$

or

$$\frac{\partial^2 \bar{C}_s}{\partial Z^2} + \frac{1}{Z} \frac{\partial \bar{C}_s}{\partial Z} - s \bar{C}_s = -F_s(X, Z) \quad (\text{A.545})$$

If we define

$$\hat{z} = \omega Z \quad (\text{A.546})$$

$$W(\hat{z}) = \bar{C}_s(Z) = \bar{C}_s\left(\frac{\hat{z}}{\omega}\right) \quad (\text{A.547})$$

where $\omega^2 = s$ (Equation (A.481)), then

$$\frac{\partial \bar{C}_s}{\partial Z} = \frac{\partial W}{\partial \hat{z}} \frac{d\hat{z}}{dZ} = \omega \frac{\partial W}{\partial \hat{z}} \quad (\text{A.548})$$

$$\frac{\partial^2 \bar{C}_s}{\partial Z^2} = \frac{\partial}{\partial Z} \left(\frac{\partial \bar{C}_s}{\partial Z} \right) = \frac{\partial}{\partial \hat{z}} \left(\omega \frac{\partial W}{\partial \hat{z}} \right) \frac{d\hat{z}}{dZ} = \frac{\partial}{\partial \hat{z}} \left(\omega \frac{\partial W}{\partial \hat{z}} \right) \omega = \omega^2 \frac{\partial^2 W}{\partial \hat{z}^2} \quad (\text{A.549})$$

Substituting these equations into Equation (A.545) gives us

$$\omega^2 \frac{\partial^2 W}{\partial \hat{z}^2} + \frac{\omega^2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - \omega^2 W = -F_s(X, \frac{\hat{z}}{\omega}) \equiv -\hat{F}_s(X, \hat{z}) \quad (\text{A.550})$$

Multiplying through by $1 / \omega^2$ yields

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{1}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = -\frac{\hat{F}_s(X, \hat{z})}{\omega^2} \quad (\text{A.551})$$

We now seek the complementary solution to Equation (A.551). That is,

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{1}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = 0 \quad (\text{A.552})$$

which we know to be a modified Bessel function of order zero [Abramowitz and Stegun, 1970]. Therefore, the general solution to this homogeneous differential equation is

$$W(\hat{z}) = C_1 W_1(\hat{z}) + C_2 W_2(\hat{z}) \quad (\text{A.553})$$

where $W_1(\hat{z})$ and $W_2(\hat{z})$ are of the form

$$W_1(\hat{z}) = A I_0(\hat{z}) + B K_0(\hat{z}) \quad (\text{A.554})$$

$$W_2(\hat{z}) = C I_0(\hat{z}) + D K_0(\hat{z}) \quad (\text{A.555})$$

where $C_1, C_2, A, B, C,$ and D are constants and $I_0(\hat{z})$ and $K_0(\hat{z})$ are as previously defined and are of the form

$$I_0(\hat{z}) = \sum_{k=0}^{\infty} \frac{\left(\frac{\hat{z}}{2}\right)^{2k}}{(k!)^2} \quad (\text{A.556})$$

$$K_0(\hat{z}) = -\frac{1}{2} I_0(\hat{z}) \ln \hat{z} + \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{(k!)^2} \left(1 + \frac{1}{2} + \dots + \frac{1}{k}\right) \left(\frac{\hat{z}}{2}\right)^{2k} \quad (\text{A.557})$$

To find the first solution, $W_1(\hat{z})$, we apply the zero flux boundary condition (Equation (A.469)) to $W_1(\hat{z})$ since $Z = 0$ implies $\hat{z} = 0$, thus,

$$\frac{\partial W_1(\hat{z} = 0)}{\partial \hat{z}} = 0 \quad (\text{A.558})$$

So,

$$\frac{\partial W_1}{\partial z} = 0 = A I'_0(\hat{z} = 0) + B K'_0(\hat{z} = 0) \quad (\text{A.559})$$

$$= B K'_0(\hat{z} = 0) \quad (\text{A.560})$$

since $K'_0(\hat{z} = 0)$ is not equal to zero [Abramowitz and Stegun, 1970], we take B equal to zero. Therefore,

$$W_1(\hat{z}) = A I_0(\hat{z}) \quad (\text{A.561})$$

Without loss of generality, let's take $A = 1$, so

$$W_1(\hat{z}) = I_0(\hat{z}) \quad (\text{A.562})$$

We also know the second solution, $W_2(\hat{z})$, to be of the form

$$W_2(\hat{z}) = C I_0(\hat{z}) + D K_0(\hat{z}) \quad (\text{A.563})$$

and satisfies the 'zero' boundary condition (Equation (A.470))

where $Z = 1$ implies $\hat{z} = \omega$:

$$\overline{C}_1(X, Z = 1, s) = 0 = W_2(\hat{z} = \omega) \quad (\text{A.564})$$

Thus,

$$0 = C I_0(\omega) + D K_0(\omega) \quad (\text{A.565})$$

or

$$D = - \frac{C I_0(\omega)}{K_0(\omega)} \quad (\text{A.566})$$

So,

$$W_2(\hat{z}) = C I_0(\hat{z}) - \frac{C I_0(\omega)}{K_0(\omega)} K_0(\hat{z}) \quad (\text{A.567})$$

Without loss of generality, let's take $C = K_0(\omega)$. Thus,

$$W_2(\hat{z}) = K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z}) \quad (\text{A.568})$$

Now we seek the particular solution $(\bar{C}_1)$ to the following nonhomogeneous differential equation using a Green's function:

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{1}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = -\frac{\hat{F}_1(X, \hat{z})}{\omega^2} \quad (\text{A.551})$$

First, we construct the Green's function which is of the form

$$g(\hat{z}, \zeta) = \begin{cases} \frac{W_1(\hat{z}) W_2(\zeta)}{p(\zeta) W[W_1, W_2](\zeta)} & \hat{z} < \zeta < \omega \\ \frac{W_1(\zeta) W_2(\hat{z})}{p(\zeta) W[W_1, W_2](\zeta)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.569})$$

where $W[W_1, W_2](\zeta)$ is the Wronskian of W_1 and W_2 , and $p(\zeta)$ is the coefficient of the first term in Equation (A.551). From Equation (A.551), we see that $p(\zeta) = 1$. Next we determine the Wronskian $W[W_1, W_2]$:

$$W[W_1, W_2] = \begin{vmatrix} I_0(\hat{z}) & K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z}) \\ I_0'(\hat{z}) & K_0(\omega) I_0'(\hat{z}) - I_0(\omega) K_0'(\hat{z}) \end{vmatrix} \quad (\text{A.570})$$

$$= K_0(\omega) I_0(\hat{z}) I_0'(\hat{z}) - I_0(\omega) I_0(\hat{z}) K_0'(\hat{z}) \quad (\text{A.571})$$

$$- K_0(\omega) I_0(\hat{z}) I_0'(\hat{z}) + I_0(\omega) I_0'(\hat{z}) K_0(\hat{z})$$

$$= I_0(\omega) [I_0'(\hat{z}) K_0(\hat{z}) - I_0(\hat{z}) K_0'(\hat{z})] \quad (\text{A.572})$$

$$= I_0(\omega) W[K_0(\hat{z}), I_0(\hat{z})] \quad (\text{A.573})$$

We know that $W[K_0(\hat{z}), I_0(\hat{z})] = 1/\hat{z}$ [Abramowitz and Stegun, 1970]. So,

$$W[W_1, W_2] = I_0(\omega) \frac{1}{\hat{z}} \quad (\text{A.574})$$

Therefore, the Green's function is

$$g(\hat{z}, \zeta) = \begin{cases} \frac{\zeta W_1(\hat{z}) W_2(\zeta)}{I_0(\omega)} & \hat{z} < \zeta < \omega \\ \frac{\zeta W_1(\zeta) W_2(\hat{z})}{I_0(\omega)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.575})$$

$$= \begin{cases} \frac{\zeta I_0(\hat{z}) [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} & \hat{z} < \zeta < \omega \\ \frac{\zeta I_0(\zeta) [K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})]}{I_0(\omega)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.576})$$

and

$$\bar{C}_a(\hat{z}) = - \int_0^\omega g(\hat{z}, \zeta) \left[\frac{\hat{F}_a(X, \zeta)}{\omega^2} \right] d\zeta \quad (\text{A.577})$$

So, the general solution is

$$W(\hat{z}) = \bar{C}_a(\hat{z}) = A W_1(\hat{z}) + B W_2(\hat{z}) - \int_0^\omega g(\hat{z}, \zeta) \left[\frac{\hat{F}_a(X, \zeta)}{\omega^2} \right] d\zeta \quad (\text{A.578})$$

$$\begin{aligned} &= A I_0(\hat{z}) + B [K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})] \\ &\quad - \frac{I_0(\hat{z})}{\omega^2} \int_{\hat{z}}^\omega \left[\frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} \right] \hat{F}_a(X, \zeta) d\zeta \quad (\text{A.579}) \\ &\quad - \frac{[K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})]}{\omega^2 I_0(\omega)} \int_0^{\hat{z}} \zeta I_0(\zeta) \hat{F}_a(X, \zeta) d\zeta \end{aligned}$$

To find the constants A and B we use the 'nonzero' boundary conditions (Equations (A.440) and (A.441) where $W(\hat{z}) = \bar{C}_s(Z)$). Therefore, applying the boundary condition

$$\frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 \quad (\text{A.580})$$

we get

$$\begin{aligned} \frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 = & A I'_0(0) + B [K_0(\omega) I'_0(0) - I_0(\omega) K'_0(0)] \\ & - \frac{I'_0(0)}{\omega^2 I_0(\omega)} \int_0^\omega \zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \\ & + \frac{I_0(0)}{\omega^2 I_0(\omega)} \left\{ (0) [K_0(\omega) I_0(0) - I_0(\omega) K_0(0)] \hat{F}_s(X, 0) \right\} \\ & - \frac{[K_0(\omega) I'_0(0) - I_0(\omega) K'_0(0)]}{\omega^2 I_0(\omega)} \int_0^\omega \zeta I_0(\zeta) \hat{F}_s(X, \zeta) d\zeta \\ & - \frac{[K_0(\omega) I_0(0) - I_0(\omega) K_0(0)]}{\omega^2 I_0(\omega)} [(0) I_0(0) \hat{F}_s(X, 0)] \end{aligned} \quad (\text{A.581})$$

Since $I'_0(0) = 0$ [Abramowitz and Stegun, 1970] then

$$0 = B [-I_0(\omega) K'_0(0)] \quad (\text{A.582})$$

Since $[-I_0(\omega) K'_0(0)]$ does not equal zero [Abramowitz and Stegun, 1970], we take $B = 0$. Applying the second boundary condition (Equation (A.441))

$$W(\omega) = \bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s) \quad (\text{A.583})$$

we get

$$\begin{aligned}\bar{C}_m(X, s) = & A I_0(\omega) - \frac{I_0(\omega)}{\omega^2 I_0(\omega)} \int_0^\omega \zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \\ & - \frac{[K_0(\omega) I_0(\omega) - I_0(\omega) K_0(\omega)]}{\omega^2 I_0(\omega)} \int_0^\omega \zeta I_0(\zeta) \hat{F}_s(X, \zeta) d\zeta\end{aligned}\quad (A.584)$$

Thus,

$$A = \frac{\bar{C}_m(X, s)}{I_0(\omega)} \quad (A.585)$$

So, Equation (A.578) becomes

$$W(\hat{z}) = \frac{\bar{C}_m(X, s)}{I_0(\omega)} I_0(\hat{z}) - \frac{1}{\omega^2} \int_0^\omega g(\hat{z}, \zeta) \hat{F}_s(X, \zeta) d\zeta \quad (A.586)$$

$$\begin{aligned}&= \frac{\bar{C}_m(X, s)}{I_0(\omega)} I_0(\hat{z}) \\ &- \frac{I_0(\hat{z})}{\omega^2 I_0(\omega)} \int_0^\omega \zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \quad (A.587) \\ &- \frac{[K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})]}{\omega^2 I_0(\omega)} \int_0^{\hat{z}} \zeta I_0(\zeta) \hat{F}_s(X, \zeta) d\zeta\end{aligned}$$

Recall, Equation (A.145)

$$C_{im}(X, T) = v \int_0^1 Z^{v-1} C_s(X, Z, T) dZ \quad (A.145)$$

and $W(\hat{z}) = \bar{C}_s(\hat{z} / \omega) = \bar{C}_s(Z)$ where $\hat{z} = \omega Z$. Taking the Laplace transform of Equation (145) with $v = 2$, we get

$$\bar{C}_{im}(X, s) = 2 \int_0^1 Z \bar{C}_s(X, Z, s) dZ = \frac{2}{\omega^2} \int_0^\omega Z W(\hat{z}) d\hat{z} \quad (A.588)$$

Substituting the general solution, $W(\hat{z})$ (Equation (A.586)), into this expression gives us

$$\bar{C}_m(X, s) = \frac{2\bar{C}_m(X, s)}{\omega^2 I_0(\omega)} \int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} - \frac{2}{\omega^4} \int_0^\omega \int_0^\omega \hat{z} g(\hat{z}, \zeta) \hat{F}_s(X, \zeta) d\zeta d\hat{z} \quad (\text{A.589})$$

To determine the first integral, we use the following homogeneous differential equation:

$$\hat{z}^2 \frac{d^2 I_0(\hat{z})}{d\hat{z}^2} + \hat{z} \frac{dI_0(\hat{z})}{d\hat{z}} - \hat{z}^2 I_0(\hat{z}) = 0 \quad (\text{A.590})$$

Multiplying each term by $1/\hat{z}$ produces

$$\hat{z} \frac{d^2 I_0(\hat{z})}{d\hat{z}^2} + \frac{dI_0(\hat{z})}{d\hat{z}} - \hat{z} I_0(\hat{z}) = 0 \quad (\text{A.591})$$

So,

$$\hat{z} I_0(\hat{z}) = \hat{z} \frac{d^2 I_0(\hat{z})}{d\hat{z}^2} + \frac{dI_0(\hat{z})}{d\hat{z}} \quad (\text{A.592})$$

Integrating both sides of this equation gives us

$$\int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} = \int_0^\omega \hat{z} \frac{d^2 I_0(\hat{z})}{d\hat{z}^2} d\hat{z} + \int_0^\omega \frac{dI_0(\hat{z})}{d\hat{z}} d\hat{z} \quad (\text{A.593})$$

Now, using integration by parts on the right-hand side of this equation yields

$$\int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} = \hat{z} \frac{dI_0(\hat{z})}{d\hat{z}} \Big|_0^\omega - \int_0^\omega \frac{dI_0(\hat{z})}{d\hat{z}} d\hat{z} + I_0(\hat{z}) \Big|_0^\omega \quad (\text{A.594})$$

$$\int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} = \hat{z} \frac{dI_0(\hat{z})}{d\hat{z}} \bigg|_0^\omega - I_0(\hat{z}) \bigg|_0^\omega + I_0(\hat{z}) \bigg|_0^\omega = \hat{z} \frac{dI_0(\hat{z})}{d\hat{z}} \bigg|_0^\omega \quad (\text{A.595})$$

or

$$\int_0^\omega \hat{z} I_0(\hat{z}) d\hat{z} = \hat{z} I'_0(\hat{z}) \bigg|_0^\omega = \omega I'_0(\omega) \quad (\text{A.596})$$

Thus, Equation (A.215) becomes

$$\bar{C}_m(X, s) = \frac{2\bar{C}_m(X, s)}{\omega^2 I_0(\omega)} [\omega I'_0(\omega)] - \frac{2}{\omega^4} \int_0^\omega \int_0^\omega \hat{z} g(\hat{z}, \zeta) \hat{F}_s(X, \zeta) d\zeta d\hat{z} \quad (\text{A.597})$$

$$= \frac{2\bar{C}_m(X, s) I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^4} \int_0^\omega \left(\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} \right) \hat{F}_s(X, \zeta) d\zeta \quad (\text{A.598})$$

Now we solve

$$\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} = \int_0^\zeta \hat{z} g(\hat{z}, \zeta) d\hat{z} + \int_\zeta^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} \quad (\text{A.599})$$

$$= \frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} \int_0^\zeta \hat{z} I_0(\hat{z}) d\hat{z} \quad (\text{A.600})$$

$$\begin{aligned} &+ \frac{\zeta I_0(\zeta)}{I_0(\omega)} \int_\zeta^\omega \hat{z} [K_0(\omega) I_0(\hat{z}) - I_0(\omega) K_0(\hat{z})] d\hat{z} \\ &= \frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} \int_0^\zeta \hat{z} I_0(\hat{z}) d\hat{z} \\ &+ \frac{\zeta I_0(\zeta) K_0(\omega)}{I_0(\omega)} \int_\zeta^\omega \hat{z} I_0(\hat{z}) d\hat{z} - \frac{\zeta I_0(\zeta) I_0(\omega)}{I_0(\omega)} \int_\zeta^\omega \hat{z} K_0(\hat{z}) d\hat{z} \end{aligned} \quad (\text{A.601})$$

From Equation (A.596), we know these integrals (similar derivation for $K_0(\hat{z})$). Thus, Equation (A.599) is

$$\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} = \frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} [\hat{z} I'_0(\hat{z})] \Big|_0^\zeta + \frac{\zeta I_0(\zeta) K_0(\omega)}{I_0(\omega)} [\hat{z} I'_0(\hat{z})] \Big|_\zeta^\omega \quad (\text{A.602})$$

$$- \frac{\zeta I_0(\zeta) I_0(\omega)}{I_0(\omega)} [\hat{z} K'_0(\hat{z})] \Big|_\zeta^\omega = \frac{\zeta [K_0(\omega) I_0(\zeta) - I_0(\omega) K_0(\zeta)]}{I_0(\omega)} [\zeta I'_0(\zeta)] + \frac{\zeta I_0(\zeta) K_0(\omega)}{I_0(\omega)} [\omega I'_0(\omega) - \zeta I'_0(\zeta)] \quad (\text{A.603})$$

$$- \frac{\zeta I_0(\zeta) I_0(\omega)}{I_0(\omega)} [\omega K'_0(\omega) - \zeta K'_0(\zeta)]$$

Collecting terms and simplifying,

$$\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} = -\zeta^2 I'_0(\zeta) K_0(\zeta) + \frac{\zeta \omega I_0(\zeta) K_0(\omega) I'_0(\omega)}{I_0(\omega)} - \frac{\zeta \omega I_0(\zeta) I_0(\omega) K'_0(\omega)}{I_0(\omega)} + \zeta^2 I_0(\zeta) K'_0(\zeta) \quad (\text{A.604})$$

$$= \zeta^2 [I_0(\zeta) K'_0(\zeta) - I'_0(\zeta) K_0(\zeta)] \quad (\text{A.605})$$

$$+ \frac{\zeta \omega I_0(\zeta)}{I_0(\omega)} [K_0(\omega) I'_0(\omega) - I_0(\omega) K'_0(\omega)]$$

$$= \zeta^2 (-W[K_0, I_0](\zeta)) + \frac{\zeta \omega I_0(\zeta)}{I_0(\omega)} (W[K_0, I_0](\omega)) \quad (\text{A.606})$$

$$= \zeta^2 \left(-\frac{1}{\zeta} \right) + \frac{\zeta \omega I_0(\zeta)}{I_0(\omega)} \left(\frac{1}{\omega} \right) \quad (\text{A.607})$$

So, Equation (A.599) becomes

$$\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} = \zeta \left[\frac{I_0(\zeta)}{I_0(\omega)} - 1 \right] \quad (\text{A.608})$$

Returning to Equation (A.598)

$$\bar{C}_{im}(X, s) = \frac{2\bar{C}_m(X, s)I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^4} \int_0^\omega \left(\int_0^\omega \hat{z} g(\hat{z}, \zeta) d\hat{z} \right) \hat{F}_i(X, \zeta) d\zeta \quad (\text{A.598})$$

and substituting in Equation (A.608) we get

$$\bar{C}_{im}(X, s) = \frac{2\bar{C}_m(X, s)I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^4} \int_0^\omega \left(\zeta \left[\frac{I_0(\zeta)}{I_0(\omega)} - 1 \right] \right) \hat{F}_i(X, \zeta) d\zeta \quad (\text{A.609})$$

If we let $\zeta = \omega\xi$, then when $\zeta = 0$, $\xi = 0$ and when $\zeta = \omega$, $\xi = 1$. So,

$$\bar{C}_{im}(X, s) = \frac{2\bar{C}_m(X, s)I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^4} \int_0^1 \left(\omega\xi \left[\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right] \right) F_i(X, \xi) \omega d\xi \quad (\text{A.610})$$

or

$$\bar{C}_{im}(X, s) = \frac{2\bar{C}_m(X, s)I'_0(\omega)}{\omega I_0(\omega)} - \frac{2}{\omega^2} \int_0^1 \xi \left[\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right] F_i(X, \xi) d\xi \quad (\text{A.611})$$

Using Equation (A.521)

$$s\bar{C}_m - F_m(X) = \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \beta [s\bar{C}_m - F_m(X)] \quad (\text{A.521})$$

we substitute in Equation (A.611)

$$\begin{aligned}
s\bar{C}_m - F_m(X) &= \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} + \beta F_m(X) \\
&\quad - \beta s \left\{ \frac{2\bar{C}_m}{I_0(\omega)} \frac{I'_0(\omega)}{\omega} - \frac{2}{\omega^2} \int_0^1 \xi \left[\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right] F_s(X, \xi) d\xi \right\}
\end{aligned} \tag{A.612}$$

Rearranging gives us

$$\begin{aligned}
\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - s\bar{C}_m \left[\frac{2\beta I'_0(\omega)}{\omega I_0(\omega)} + 1 \right] &= -[F_m(X) + \beta F_m(X) \\
&\quad + \frac{2\beta s}{\omega^2} \int_0^1 \xi \left(\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right) F_s(X, \xi) d\xi]
\end{aligned} \tag{A.613}$$

If we define

$$\gamma = s \left[1 + \frac{2\beta I'_0(\omega)}{\omega I_0(\omega)} \right] \tag{A.614}$$

where $I'_0(\omega) = I_1(\omega)$ [Abramowitz and Stegun, 1970] and recall that $s = \omega^2$ (Equation (A.481)), then

$$\begin{aligned}
\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \gamma \bar{C}_m &= -[F_m(X) + \beta F_m(X) \\
&\quad + 2\beta \int_0^1 \xi \left(\frac{I_0(\omega\xi)}{I_0(\omega)} - 1 \right) F_s(X, \xi) d\xi]
\end{aligned} \tag{A.615}$$

The right-hand side of this equation can be further simplified using the initial conditions $C_m(X, T = \hat{T}) = F_m(X)$ (Equation (A.435)), $C_s(X, Z, T = \hat{T}) = F_s(X, Z)$ (Equation (A.437)), and the

dimensionless expression for the volume-average immobile region solute concentration, $C_m(X, T) = v \int_0^1 Z^{v-1} C_s(X, Z, T) dZ$ where

$v = 2$ (Equation (A.145)). Therefore, at time $T = \hat{T}$

$$F_m(X) = C_m(X, T = \hat{T}) = 2 \int_0^1 Z C_s(X, Z, T = \hat{T}) dZ = 2 \int_0^1 Z F_s(X, Z) dZ \quad (A.616)$$

Putting this expression for $F_m(X)$ into the right-hand side of Equation (A.615) gives us

$$\begin{aligned} & -[F_m(X) + 2\beta \int_0^1 \xi F_s(X, \xi) d\xi + \frac{2\beta}{I_0(\omega)} \int_0^1 \xi I_0(\omega\xi) F_s(X, \xi) d\xi] \\ & -2\beta \int_0^1 \xi F_s(X, \xi) d\xi] \end{aligned} \quad (A.617)$$

So, if we define

$$\bar{F}(X, s) = -[F_m(X) + \frac{2\beta}{I_0(\omega)} \int_0^1 \xi I_0(\omega\xi) F_s(X, \xi) d\xi] \quad (A.618)$$

then Equation (A.615) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \gamma \bar{C}_m = \bar{F}(X, s) \quad (A.619)$$

Spherical Diffusion. Using the above derivation when $v = 2$, we now seek the solution when $v = 3$. From Equation (A.429) we have

$$\frac{\partial C_s(X, Z, T)}{\partial T} = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left[Z^{v-1} \frac{\partial C_s(X, Z, T)}{\partial Z} \right] \quad 0 < Z < 1 \quad (A.429)$$

which is valid for all the diffusion models. As previously derived, we now take the Laplace transform of Equation (A.429) using Equation (A.437) (initial condition) and Equations (A.440) and (A.441) (boundary conditions):

$$C_s(X, Z, T = \hat{T}) = F_s(X, Z) \quad X_w < X < X. \quad (A.437)$$

$$\frac{\partial C_s(X, Z = 0, T)}{\partial Z} = 0 \quad X_w < X < X. \quad (A.440)$$

$$C_s(X, Z = 1, T) = C_m(X, T) \quad X_w < X < X. \quad (A.441)$$

So,

$$\mathcal{L}\left(\frac{\partial C_s}{\partial T}\right) = \mathcal{L}\left(\frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial C_s}{\partial Z}\right)\right) \quad (A.465)$$

$$s\bar{C}_s - C_s(X, Z, T = \hat{T}) = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) \quad (A.466)$$

$$s\bar{C}_s - F_s(X, Z) = \frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) \quad (A.467)$$

Thus,

$$\frac{1}{Z^{v-1}} \frac{\partial}{\partial Z} \left(Z^{v-1} \frac{\partial \bar{C}_s}{\partial Z}\right) - s\bar{C}_s = -F_s(X, Z) \quad (A.468)$$

with the following boundary conditions (Laplace transformed functions of Equations (A.440) and (A.441)):

$$\frac{\partial \bar{C}_s}{\partial Z}(X, Z = 0, s) = 0 \quad X_w < X < X. \quad (A.469)$$

$$\bar{C}_s(X, Z = 1, s) = \bar{C}_m(X, s) \quad X_w < X < X. \quad (A.470)$$

We seek the general solution to Equation (A.468) using the boundary conditions (A.469) and (A.470) for case of $\nu = 3$. That is, we seek

$$\bar{C}_s = \bar{C}_{s_c} + \bar{C}_{s_p} \quad (\text{A.471})$$

where $\bar{C}_s$ is the general solution to the differential equation, $\bar{C}_{s_c}$ is the complementary solution to the homogeneous differential equation, and $\bar{C}_{s_p}$ is the particular solution to the nonhomogeneous differential equation. For the case of $\nu = 3$, Equation (A.468) becomes

$$\frac{1}{Z^2} \frac{\partial}{\partial Z} \left(Z^2 \frac{\partial \bar{C}_s}{\partial Z} \right) - s \bar{C}_s = -F_s(X, Z) \quad (\text{A.620})$$

Differentiating the first term of Equation (A.620) gives us

$$\frac{1}{Z^2} \left[Z^2 \frac{\partial^2 \bar{C}_s}{\partial Z^2} + 2Z \frac{\partial \bar{C}_s}{\partial Z} \right] - s \bar{C}_s = -F_s(X, Z) \quad (\text{A.621})$$

or

$$\frac{\partial^2 \bar{C}_s}{\partial Z^2} + \frac{2}{Z} \frac{\partial \bar{C}_s}{\partial Z} - s \bar{C}_s = -F_s(X, Z) \quad (\text{A.622})$$

Using the previously defined variables

$$\hat{z} = \omega Z \quad (\text{A.546})$$

$$W(\hat{z}) = \bar{C}_s(Z) = \bar{C}_s\left(\frac{\hat{z}}{\omega}\right) \quad (\text{A.547})$$

where $\omega^2 = s$ (Equation (A.481)), then

$$\frac{\partial \bar{C}_s}{\partial Z} = \frac{\partial W}{\partial \hat{z}} \frac{d\hat{z}}{dZ} = \omega \frac{\partial W}{\partial \hat{z}} \quad (\text{A.548})$$

$$\frac{\partial^2 \bar{C}_1}{\partial Z^2} = \frac{\partial}{\partial Z} \left(\frac{\partial \bar{C}_1}{\partial Z} \right) = \frac{\partial}{\partial \hat{z}} \left(\omega \frac{\partial W}{\partial \hat{z}} \right) \frac{d\hat{z}}{dZ} = \frac{\partial}{\partial \hat{z}} \left(\omega \frac{\partial W}{\partial \hat{z}} \right) \omega = \omega^2 \frac{\partial^2 W}{\partial \hat{z}^2} \quad (\text{A.549})$$

Substituting these equations into Equation (A.622) gives us

$$\omega^2 \frac{\partial^2 W}{\partial \hat{z}^2} + \frac{2\omega^2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - \omega^2 W = -F_1(X, \frac{\hat{z}}{\omega}) \equiv -\hat{F}_1(X, \hat{z}) \quad (\text{A.623})$$

Multiplying through by $1/\omega^2$ yields

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = -\frac{\hat{F}_1(X, \hat{z})}{\omega^2} \quad (\text{A.624})$$

We now seek the complementary solution to Equation (A.624).

That is,

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = 0 \quad (\text{A.625})$$

which we know to be a modified spherical Bessel function of order zero [Abramowitz and Stegun, 1970]. Therefore, the general solution to this homogeneous differential equation is

$$W(\hat{z}) = C_1 W_1(\hat{z}) + C_2 W_2(\hat{z}) \quad (\text{A.626})$$

where $W_1(\hat{z})$ and $W_2(\hat{z})$ are of the form

$$W_1(\hat{z}) = A i_0(\hat{z}) + B k_0(\hat{z}) \quad (\text{A.627})$$

$$W_2(\hat{z}) = C i_0(\hat{z}) + D k_0(\hat{z}) \quad (\text{A.628})$$

where $C_1, C_2, A, B, C,$ and D are constants and $i_0(\hat{z})$ and $k_0(\hat{z})$ are as previously defined and are of the form

$$i_0(\hat{z}) = \sqrt{\frac{\pi}{2}} \hat{z}^{-\frac{1}{2}} I_{\frac{1}{2}}(\hat{z}) = \frac{\sinh \hat{z}}{\hat{z}} \quad (\text{A.629})$$

$$k_0(\hat{z}) = \sqrt{\frac{\pi}{2}} \hat{z}^{-\frac{1}{2}} K_{\frac{1}{2}}(\hat{z}) = \frac{\pi e^{-\hat{z}}}{2\hat{z}} \quad (\text{A.630})$$

To find the first solution, $W_1(\hat{z})$, we apply the boundary condition (Equation (A.469)) where $\bar{C}_1(Z = 0) = W(\hat{z} = 0)$. Thus,

$$\frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 \quad (\text{A.631})$$

So,

$$\frac{\partial W}{\partial \hat{z}} = 0 = A i'_0(\hat{z} = 0) + B k'_0(\hat{z} = 0) \quad (\text{A.632})$$

since $k'_0(\hat{z} = 0)$ is undefined [Abramowitz and Stegun, 1970], we take B equal to zero. Therefore,

$$W_1(\hat{z}) = A i_0(\hat{z}) \quad (\text{A.633})$$

Without loss of generality, let's take $A = 1$, so

$$W_1(\hat{z}) = i_0(\hat{z}) \quad (\text{A.634})$$

We also know the second solution, $W_2(\hat{z})$, to be of the form

$$W_2(\hat{z}) = C i_0(\hat{z}) + D k_0(\hat{z}) \quad (\text{A.635})$$

and satisfies the 'zero' boundary condition (Equation (A.470)) where $\bar{C}_1(Z = 1) = W(\hat{z} = \omega)$:

$$\bar{C}_1(X, Z = 1, s) = 0 = W(\hat{z} = \omega) \quad (\text{A.636})$$

Thus,

$$0 = C i_0(\omega) + D k_0(\omega) \quad (\text{A.637})$$

or

$$D = -\frac{C i_0(\omega)}{k_0(\omega)} \quad (\text{A.638})$$

So,

$$W_2(\hat{z}) = C i_0(\hat{z}) - \frac{C i_0(\omega)}{k_0(\omega)} k_0(\hat{z}) \quad (\text{A.639})$$

Without loss of generality, let's take $C = k_0(\omega)$. Thus,

$$W_2(\hat{z}) = k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z}) \quad (\text{A.640})$$

Now we seek the particular solution ($\bar{C}_s$) to the following nonhomogeneous differential equation using a Green's function:

$$\frac{\partial^2 W}{\partial \hat{z}^2} + \frac{2}{\hat{z}} \frac{\partial W}{\partial \hat{z}} - W = -\frac{\hat{F}_s(X, \hat{z})}{\omega^2} \quad (\text{A.624})$$

First, we construct the Green's function which is of the form

$$g(\hat{z}, \zeta) = \begin{cases} \frac{W_1(\hat{z}) W_2(\zeta)}{p(\zeta) W[W_1, W_2](\zeta)} & \hat{z} < \zeta < \omega \\ \frac{W_1(\zeta) W_2(\hat{z})}{p(\zeta) W[W_1, W_2](\zeta)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.641})$$

where $W[W_1, W_2](\zeta)$ is the Wronskian of W_1 and W_2 , and $p(\zeta)$ is the coefficient of the first term in Equation (A.624). From Equation (A.624), we see that $p(\zeta) = 1$. Next we determine the Wronskian, $W[W_1, W_2]$:

$$W[W_1, W_2] = \begin{vmatrix} i_0(\hat{z}) & k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z}) \\ i'_0(\hat{z}) & k_0(\omega) i'_0(\hat{z}) - i_0(\omega) k'_0(\hat{z}) \end{vmatrix} \quad (\text{A.642})$$

$$= k_0(\omega) i_0(\hat{z}) i'_0(\hat{z}) - i_0(\omega) i_0(\hat{z}) k'_0(\hat{z}) \quad (\text{A.643})$$

$$- k_0(\omega) i_0(\hat{z}) i'_0(\hat{z}) + i_0(\omega) i'_0(\hat{z}) k_0(\hat{z})$$

$$= i_0(\omega) [i'_0(\hat{z}) k_0(\hat{z}) - i_0(\hat{z}) k'_0(\hat{z})] \quad (\text{A.644})$$

$$= i_0(\omega) W[k_0(\hat{z}), i_0(\hat{z})] \quad (\text{A.645})$$

We know that $W[k_0(\hat{z}), i_0(\hat{z})] = \pi / 2\hat{z}^2$ [Abramowitz and Stegun, 1970]. So,

$$W[W_1, W_2] = \frac{\pi i_0(\omega)}{2\hat{z}^2} \quad (\text{A.646})$$

Therefore, the Green's function is

$$g(\hat{z}, \zeta) = \begin{cases} \frac{2\zeta^2 W_1(\hat{z}) W_2(\zeta)}{\pi i_0(\omega)} & \hat{z} < \zeta < \omega \\ \frac{2\zeta^2 W_1(\zeta) W_2(\hat{z})}{\pi i_0(\omega)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.647})$$

$$= \begin{cases} \frac{2\zeta^2 i_0(\hat{z}) [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{\pi i_0(\omega)} & \hat{z} < \zeta < \omega \\ \frac{2\zeta^2 i_0(\zeta) [k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})]}{\pi i_0(\omega)} & 0 < \zeta < \hat{z} \end{cases} \quad (\text{A.648})$$

and

$$\bar{C}_r(\hat{z}) = - \int_0^\omega g(\hat{z}, \zeta) \left[\frac{\hat{F}_r(X, \zeta)}{\omega^2} \right] d\zeta \quad (\text{A.649})$$

So, the general solution is

$$W(\hat{z}) = \bar{C}_s(\hat{z}) = A W_1(\hat{z}) + B W_2(\hat{z}) - \int_0^\infty g(\hat{z}, \zeta) \left[\frac{\hat{F}_s(X, \zeta)}{\omega^2} \right] d\zeta \quad (A.650)$$

$$\begin{aligned} &= A i_0(\hat{z}) + B [k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})] \\ &\quad - \frac{2i_0(\hat{z})}{\pi\omega^2} \int_{\hat{z}}^\infty \left[\frac{\zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{i_0(\omega)} \right] \hat{F}_s(X, \zeta) d\zeta \quad (A.651) \\ &\quad - \frac{2[k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})]}{\pi\omega^2 i_0(\omega)} \int_0^{\hat{z}} \zeta^2 i_0(\zeta) \hat{F}_s(X, \zeta) d\zeta \end{aligned}$$

To find the constants A and B, we use the 'nonzero' boundary conditions (Equations (A.469 and (A.470) where $W(\hat{z}) = \bar{C}_s(Z)$).

Therefore, applying the boundary condition

$$\frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 \quad (A.652)$$

we get

$$\begin{aligned}
\frac{\partial W(\hat{z} = 0)}{\partial \hat{z}} = 0 = & A i'_0(0) + B [k_0(\omega) i'_0(0) - i_0(\omega) k'_0(0)] \\
& - \frac{2i'_0(0)}{\pi\omega^2 i_0(\omega)} \int_0^\infty \zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)] \hat{F}_*(X, \zeta) d\zeta \\
& + \frac{2i_0(0)}{\pi\omega^2 i_0(\omega)} \left\{ (0) [k_0(\omega) i_0(0) - i_0(\omega) k_0(0)] \hat{F}_*(X, 0) \right\} \\
& - \frac{2[k_0(\omega) i'_0(0) - i_0(\omega) k'_0(0)]}{\pi\omega^2 i_0(\omega)} \int_0^\infty \zeta^2 i_0(\zeta) \hat{F}_*(X, \zeta) d\zeta \\
& - \frac{2[k_0(\omega) i_0(0) - i_0(\omega) k_0(0)]}{\pi\omega^2 i_0(\omega)} [(0) i_0(0) \hat{F}_*(X, 0)]
\end{aligned}
\tag{A.653}$$

Since $i'_0(0) = 0$ [Abramowitz and Stegun, 1970] then

$$0 = B[-i_0(\omega) k'_0(0)] \tag{A.654}$$

Since $k'_0(0)$ is undefined [Abramowitz and Stegun, 1970], we take $B = 0$. Applying the second boundary condition (Equation (A.470))

$$W(\omega) = \bar{C}_*(X, Z = 1, s) = \bar{C}_m(X, s) \tag{A.655}$$

we get

$$\begin{aligned}\bar{C}_m(X, s) = & A i_0(\omega) - \frac{2i_0(\omega)}{\pi\omega^2 i_0(\omega)} \int_0^\omega \zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \\ & - \frac{2[k_0(\omega) i_0(\omega) - i_0(\omega) k_0(\omega)]}{\pi\omega^2 i_0(\omega)} \int_0^\omega \zeta^2 i_0(\zeta) \hat{F}_s(X, \zeta) d\zeta\end{aligned}\quad (A.656)$$

Thus,

$$A = \frac{\bar{C}_m(X, s)}{i_0(\omega)} \quad (A.657)$$

So, Equation (A.650) becomes

$$W(\hat{z}) = \frac{\bar{C}_m(X, s)}{i_0(\omega)} i_0(\hat{z}) - \frac{1}{\omega^2} \int_0^\omega g(\hat{z}, \zeta) \hat{F}_s(X, \zeta) d\zeta \quad (A.658)$$

$$\begin{aligned}&= \frac{\bar{C}_m(X, s)}{i_0(\omega)} i_0(\hat{z}) \\ &- \frac{2i_0(\hat{z})}{\pi\omega^2 i_0(\omega)} \int_0^\omega \zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)] \hat{F}_s(X, \zeta) d\zeta \\ &- \frac{2[k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})]}{\pi\omega^2 i_0(\omega)} \int_0^{\hat{z}} \zeta^2 i_0(\zeta) \hat{F}_s(X, \zeta) d\zeta\end{aligned}\quad (A.659)$$

Recall, Equation (A.145)

$$C_{im}(X, T) = \nu \int_0^1 Z^{\nu-1} C_s(X, Z, T) dZ \quad (A.145)$$

and $W(\hat{z}) = \bar{C}_s(\hat{z} / \omega) = \bar{C}_s(Z)$ where $\hat{z} = \omega Z$. Taking the Laplace transform of Equation (145) with $\nu = 3$, we get

$$\bar{C}_{im}(X, s) = 3 \int_0^1 Z^2 \bar{C}_s(X, Z, s) dZ = \frac{3}{\omega^3} \int_0^\omega \hat{z}^2 W(\hat{z}) d\hat{z} \quad (A.660)$$

Substituting the general solution, $W(\hat{z})$ (Equation (A.658)), into this expression gives us

$$\begin{aligned}\bar{C}_m(X, s) &= \frac{3\bar{C}_m(X, s)}{\omega^3 i_0(\omega)} \int_0^\infty \hat{z}^2 i_0(\hat{z}) d\hat{z} \\ &\quad - \frac{3}{\omega^5} \int_0^\infty \int_0^\infty \hat{z}^2 g(\hat{z}, \zeta) \hat{F}_1(X, \zeta) d\zeta d\hat{z}\end{aligned}\quad (A.661)$$

To determine the first integral, we use the following homogeneous differential equation:

$$\hat{z}^2 \frac{d^2 i_0(\hat{z})}{d\hat{z}^2} + 2\hat{z} \frac{di_0(\hat{z})}{d\hat{z}} - \hat{z}^2 i_0(\hat{z}) = 0 \quad (A.662)$$

So,

$$\hat{z}^2 i_0(\hat{z}) = \hat{z}^2 \frac{d^2 i_0(\hat{z})}{d\hat{z}^2} + 2\hat{z} \frac{di_0(\hat{z})}{d\hat{z}} \quad (A.663)$$

Integrating both sides of this equation gives us

$$\int_0^\infty \hat{z}^2 i_0(\hat{z}) d\hat{z} = \int_0^\infty \hat{z}^2 \frac{d^2 i_0(\hat{z})}{d\hat{z}^2} d\hat{z} + 2 \int_0^\infty \hat{z} \frac{di_0(\hat{z})}{d\hat{z}} d\hat{z} \quad (A.664)$$

Now, using integration by parts on the right-hand side of this equation yields

$$\int_0^\infty \hat{z}^2 i_0(\hat{z}) d\hat{z} = \hat{z}^2 \frac{di_0(\hat{z})}{d\hat{z}} \Big|_0^\infty - 2 \int_0^\infty \hat{z} \frac{di_0(\hat{z})}{d\hat{z}} d\hat{z} + 2 \int_0^\infty \hat{z} \frac{di_0(\hat{z})}{d\hat{z}} d\hat{z} \quad (A.665)$$

$$\int \hat{z}^2 i_0(\hat{z}) d\hat{z} = \hat{z}^2 \frac{di_0(\hat{z})}{d\hat{z}} \Big|_0^\infty \quad (A.666)$$

So,

$$\int \hat{z}^2 i_0(\hat{z}) d\hat{z} = \omega^2 i'_0(\omega) \quad (\text{A.667})$$

Thus, Equation (A.661) becomes

$$\bar{C}_m(X, s) = \frac{3\bar{C}_m(X, s)}{\omega^3 i_0(\omega)} [\omega^2 i'_0(\omega)] \quad (\text{A.668})$$

$$\begin{aligned} & - \frac{3}{\omega^5} \int_0^\infty \int_0^\infty \hat{z}^2 g(\hat{z}, \zeta) \hat{F}_s(X, \zeta) d\zeta d\hat{z} \\ & = \frac{3\bar{C}_m(X, s) i'_0(\omega)}{\omega i_0(\omega)} - \frac{3}{\omega^5} \int_0^\infty \left(\int_0^\infty \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} \right) \hat{F}_s(X, \zeta) d\zeta \end{aligned} \quad (\text{A.669})$$

Now we solve

$$\int_0^\infty \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} = \int_0^\zeta \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} + \int_\zeta^\infty \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} \quad (\text{A.670})$$

$$\begin{aligned} & = \frac{2\zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{\pi i_0(\omega)} \int_0^\zeta \hat{z}^2 i_0(\hat{z}) d\hat{z} \\ & \quad + \frac{2\zeta^2 i_0(\zeta)}{\pi i_0(\omega)} \int_\zeta^\infty \hat{z}^2 [k_0(\omega) i_0(\hat{z}) - i_0(\omega) k_0(\hat{z})] d\hat{z} \end{aligned} \quad (\text{A.671})$$

$$\begin{aligned} & = \frac{2\zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{\pi i_0(\omega)} \int_0^\zeta \hat{z}^2 i_0(\hat{z}) d\hat{z} \\ & \quad + \frac{2\zeta^2 i_0(\zeta) k_0(\omega)}{\pi i_0(\omega)} \int_\zeta^\infty \hat{z}^2 i_0(\hat{z}) d\hat{z} - \frac{2\zeta^2 i_0(\zeta) i_0(\omega)}{\pi i_0(\omega)} \int_\zeta^\infty \hat{z}^2 k_0(\hat{z}) d\hat{z} \end{aligned} \quad (\text{A.672})$$

From Equation (A.667), we know these integrals (similar derivation for $k_0(\hat{z})$). Thus, Equation (A.670) is

$$\begin{aligned}
\int_0^{\omega} z^2 g(\hat{z}, \zeta) d\hat{z} &= \frac{2\zeta^2 [k_0(\omega) i_0(\zeta) - i_0(\omega) k_0(\zeta)]}{\pi i_0(\omega)} [\zeta^2 i'_0(\zeta)] \\
&+ \frac{2\zeta^2 i_0(\zeta) k_0(\omega)}{\pi i_0(\omega)} [\omega^2 i'_0(\omega) - \zeta^2 i'_0(\zeta)] \\
&- \frac{2\zeta^2 i_0(\zeta) i_0(\omega)}{\pi i_0(\omega)} [\omega^2 k'_0(\omega) - \zeta^2 k'_0(\zeta)]
\end{aligned} \tag{A.673}$$

Collecting terms and simplifying,

$$\begin{aligned}
\int_0^{\omega} z^2 g(\hat{z}, \zeta) d\hat{z} &= \frac{2\zeta^4 i'_0(\zeta) k_0(\omega) i_0(\zeta)}{\pi i_0(\omega)} - \frac{2\zeta^4 i'_0(\zeta) k_0(\zeta) i_0(\omega)}{\pi i_0(\omega)} \\
&+ \frac{2\zeta^2 \omega^2 i_0(\zeta) i'_0(\omega) k_0(\omega)}{\pi i_0(\omega)} - \frac{2\zeta^4 i_0(\zeta) k_0(\omega) i'_0(\zeta)}{\pi i_0(\omega)} \\
&- \frac{2\omega^2 \zeta^2 i_0(\zeta) i_0(\omega) k'_0(\omega)}{\pi i_0(\omega)} + \frac{2\zeta^4 i_0(\zeta) i_0(\omega) k'_0(\zeta)}{\pi i_0(\omega)}
\end{aligned} \tag{A.674}$$

or

$$\begin{aligned}
\int_0^{\omega} z^2 g(\hat{z}, \zeta) d\hat{z} &= \frac{2\zeta^4 i_0(\omega)}{\pi i_0(\omega)} [i_0(\zeta) k'_0(\zeta) - i'_0(\zeta) k_0(\zeta)] \\
&+ \frac{2\omega^2 \zeta^2 i_0(\zeta)}{\pi i_0(\omega)} [k_0(\omega) i'_0(\omega) - i_0(\omega) k'_0(\omega)]
\end{aligned} \tag{A.675}$$

Thus,

$$\int_0^{\omega} \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} = \frac{2\zeta^4 i_0(\omega)}{\pi i_0(\omega)} (W[i_0, k_0](\zeta)) + \frac{2\omega^2 \zeta^2 i_0(\zeta)}{\pi i_0(\omega)} (W[k_0, i_0](\omega)) \quad (\text{A.676})$$

$$= \frac{2\zeta^4 i_0(\omega)}{\pi i_0(\omega)} \left(-\frac{\pi}{2\zeta^2} \right) + \frac{2\omega^2 \zeta^2 i_0(\zeta)}{\pi i_0(\omega)} \left(\frac{\pi}{2\omega^2} \right) \quad (\text{A.677})$$

So, Equation (A.670) becomes

$$\int_0^{\omega} \hat{z}^2 g(\hat{z}, \zeta) d\hat{z} = \zeta^2 \left[\frac{i_0(\zeta)}{i_0(\omega)} - 1 \right] \quad (\text{A.678})$$

Returning to Equation (A.669), with Equation (A.678) substituted in, gives us

$$\bar{C}_{im}(X, s) = \frac{3\bar{C}_m(X, s)i'_0(\omega)}{\omega i_0(\omega)} - \frac{3}{\omega^5} \int_0^{\omega} \zeta^2 \left[\frac{i_0(\zeta)}{i_0(\omega)} - 1 \right] \hat{F}_1(X, \zeta) d\zeta \quad (\text{A.679})$$

If we let $\zeta = \omega\xi$, then when $\zeta = 0$, $\xi = 0$ and when $\zeta = \omega$, $\xi = 1$. So,

$$\bar{C}_{im}(X, s) = \frac{3\bar{C}_m(X, s)i'_0(\omega)}{\omega i_0(\omega)} - \frac{3}{\omega^5} \int_0^1 \omega^2 \xi^2 \left[\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right] F_1(X, \xi) \omega d\xi \quad (\text{A.680})$$

or

$$\bar{C}_{im}(X, s) = \frac{3\bar{C}_m(X, s)i'_0(\omega)}{\omega i_0(\omega)} - \frac{3}{\omega^2} \int_0^1 \xi^2 \left[\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right] F_1(X, \xi) d\xi \quad (\text{A.681})$$

Using Equation (A.521)

$$s\bar{C}_m - F_m(X) = \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \beta[s\bar{C}_m - F_m(X)] \quad (A.521)$$

we substitute in Equation (A.681)

$$\begin{aligned} s\bar{C}_m - F_m(X) = & \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} + \beta F_m(X) \\ & - \beta s \left\{ \frac{3\bar{C}_m}{i_0(\omega)} \frac{i'_0(\omega)}{\omega} - \frac{3}{\omega^2} \int_0^1 \xi^2 \left[\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right] F_*(X, \xi) d\xi \right\} \end{aligned} \quad (A.682)$$

Rearranging gives us

$$\begin{aligned} \frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - s\bar{C}_m \left[1 + \frac{3\beta i'_0(\omega)}{\omega i_0(\omega)} \right] = & -[F_m(X) + \beta F_m(X) \\ & + \frac{3\beta s}{\omega^2} \int_0^1 \xi^2 \left(\frac{i_0(\omega\xi)}{i_0(\omega)} - 1 \right) F_*(X, \xi) d\xi] \end{aligned} \quad (A.683)$$

If we define

$$\gamma = s \left[1 + \frac{3\beta i_1(\omega)}{\omega i_0(\omega)} \right] \quad (A.684)$$

where $i'_0(\omega) = i_1(\omega)$ [Abramowitz and Stegun, 1970] and recall

that $s = \omega^2$ (Equation (A.481)), then

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m}{\partial X} - \gamma \bar{C}_m = -[F_m(X) + \beta F_{im}(X)] \quad (A.685)$$

$$+ 3\beta \int_0^1 \xi^2 \left(\frac{i_0(\omega \xi)}{i_0(\omega)} - 1 \right) F_i(X, \xi) d\xi$$

The right-hand side of this equation can be further simplified using the initial conditions $C_{im}(X, T = \hat{T}) = F_{im}(X)$ (Equation (A.435)), $C_i(X, Z, T = \hat{T}) = F_i(X, Z)$ (Equation (A.437)), and the dimensionless expression for the volume-average immobile region solute concentration, $C_{im}(X, T) = \nu \int_0^1 Z^{\nu-1} C_i(X, Z, T) dZ$ where $\nu = 3$ (Equation (A.145)). Therefore, at time $T = \hat{T}$

$$F_{im}(X) = C_{im}(X, T = \hat{T}) = 3 \int_0^1 Z^2 C_i(X, Z, T = \hat{T}) dZ = 3 \int_0^1 Z^2 F_i(X, Z) dZ \quad (A.686)$$

Putting this expression for $F_{im}(X)$ into the right-hand side of Equation (A.685) gives us

$$-[F_m(X) + 3\beta \int_0^1 \xi^2 F_i(X, \xi) d\xi + \frac{3\beta}{i_0(\omega)} \int_0^1 \xi^2 i_0(\omega \xi) F_i(X, \xi) d\xi] \quad (A.687)$$

$$-3\beta \int_0^1 \xi^2 F_i(X, \xi) d\xi]$$

So, if we define

$$\bar{F}(X, s) = -[F_m(X) + \frac{3\beta}{i_0(\omega)} \int_0^1 \xi^2 i_0(\omega \xi) F_i(X, \xi) d\xi] \quad (A.688)$$

then Equation (A.685) becomes

$$\frac{\partial^2 \bar{C}_m}{\partial X^2} + \frac{\partial \bar{C}_m}{\partial X} - X\gamma \bar{C}_m = \bar{F}(X, s) \quad (A.689)$$

Green's Function. The Laplace transform of Equation (A.428) together with the appropriate conditions for the various models resulted in a common differential equation which is of the form

$$\frac{\partial^2 \bar{C}_m(X, s)}{\partial X^2} + \frac{1}{X} \frac{\partial \bar{C}_m(X, s)}{\partial X} - \gamma \bar{C}_m(X, s) = \bar{F}(X, s) \quad (A.690)$$

where the overbar indicates the transformed function and γ and $\bar{F}(X, s)$ were developed in the previous sections.

The boundary conditions associated with this differential equation are obtained by taking the Laplace transform of Equations (A.439) and (A.449). Thus,

$$\mathcal{L}\left(\frac{\partial C_m}{\partial X}(X_w, T)\right) = 0 \quad (A.691)$$

or

$$\frac{\partial \bar{C}_m}{\partial X}(X_w, s) = 0 \quad (A.692)$$

and

$$\mathcal{L}\left(\epsilon \frac{\partial C_m}{\partial X}(X., \hat{T}) - C_m(X., \hat{T})\right) = 0 \quad (A.693)$$

or

$$\epsilon \frac{\partial \bar{C}_m}{\partial X}(X., s) - \bar{C}_m(X., s) = 0 \quad (A.694)$$

As before, we construct a Green's function by assuming that Equation (A.690) has a solution of the form

$$\bar{C}_m(X, s) = \phi(X, s) \quad (A.695)$$

such that this solution satisfies the differential equation (Equation (A.690)) and the boundary conditions (Equations (A.692) and (A.694)). Substituting Equation (A.695) into Equation (A.690) yields

$$\frac{d^2\phi(X, s)}{dX^2} + \frac{1}{X} \frac{d\phi(X, s)}{dX} - \gamma \phi(X, s) = \bar{F}(X, s) \quad (A.696)$$

In order to construct the Green's function, we first seek a simpler equation, one where the left-hand side has no constants in it. Therefore, if we define

$$y = A X \quad (A.697)$$

where A is a constant and

$$\Phi(y, s) = \phi(X, s) \quad (A.698)$$

then we can rewrite Equation (A.696) in terms of y . Thus,

$$\frac{d\phi(X, s)}{dX} = \frac{d\Phi(y, s)}{dy} \frac{dy}{dX} = A \frac{d\Phi(y, s)}{dy} \quad (A.699)$$

$$\frac{d^2\phi(X, s)}{dX^2} = \frac{d}{dy} \left(A \frac{d\Phi(y, s)}{dy} \right) \frac{dy}{dX} = A^2 \frac{d^2\Phi(y, s)}{dy^2} \quad (A.700)$$

Substituting these expression back into Equation (A.696) yields

$$A^2 \frac{d^2\Phi(y, s)}{dy^2} + \frac{1}{X} A \frac{d\Phi(y, s)}{dy} - \gamma \Phi(y, s) = \bar{F}\left(\frac{y}{A}, s\right) \quad (A.701)$$

Multiplying each term by X^2 gives us

$$X^2 A^2 \frac{d^2 \Phi(y, s)}{dy^2} + X A \frac{d\Phi(y, s)}{dy} - \gamma X^2 \Phi(y, s) = X^2 \bar{F}\left(\frac{y}{A}, s\right) \quad (\text{A.702})$$

or

$$y^2 \frac{d^2 \Phi(y, s)}{dy^2} + y \frac{d\Phi(y, s)}{dy} - \frac{\gamma}{A^2} y^2 \Phi(y, s) = \frac{y^2}{A^2} \bar{F}\left(\frac{y}{A}, s\right) \quad (\text{A.703})$$

If we choose A such that

$$\frac{\gamma}{A^2} = 1 \quad (\text{A.704})$$

or

$$A = \gamma^{\frac{1}{2}} \quad (\text{A.705})$$

then Equation (A.697) is

$$y = \gamma^{\frac{1}{2}} X \quad (\text{A.706})$$

and dividing by y^2 then Equation (A.703) becomes

$$\frac{d^2 \Phi(y, s)}{dy^2} + \frac{1}{y} \frac{d\Phi(y, s)}{dy} - \Phi(y, s) = \frac{1}{\gamma} \bar{F}\left(\frac{y}{\gamma^{1/2}}, s\right) \equiv \mathcal{F}(y, s) \quad (\text{A.707})$$

for the interval $y_w < y < y_*$.

We now look at the Laplace transformed boundary condition at the dimensionless well radius (Equation (A.692)) and convert it in terms of y_w using the above definitions. Since we defined $\bar{C}_m(X, s) = \phi(X, s)$, then

$$\frac{\partial \Phi}{\partial X}(X_w, s) = \frac{d\Phi}{dy}(y_w, s) \frac{dy}{dX} = \gamma^{\frac{1}{2}} \frac{d\Phi}{dy}(y_w, s) = 0 \quad (\text{A.708})$$

or

$$\frac{d\Phi}{dy}(y_w, s) = 0 \quad (\text{A.709})$$

where

$$y_w = \gamma^{\frac{1}{2}} X_w \quad (\text{A.710})$$

Now, we look at the boundary condition at the dimensionless radius of the contaminated zone ($X_.$) at time $\hat{T}$. Recall the boundary condition at $X_.$ (Equation (A.694)). We now rewrite this boundary condition in terms of $y_.$. Looking at the first term, we get

$$\varepsilon \frac{\partial \Phi}{\partial X}(X_., s) = \varepsilon \frac{d\Phi}{dy}(y_., s) \frac{dy}{dX} = \varepsilon \gamma^{\frac{1}{2}} \frac{d\Phi}{dy}(y_., s) \quad (\text{A.711})$$

and the second term

$$\Phi(X_., s) = \Phi\left(\frac{y_..}{\gamma^{1/2}}, s\right) = \Phi(y_., s) \quad (\text{A.712})$$

Substituting these expressions back into Equation (A.694) gives us

$$\varepsilon \gamma^{\frac{1}{2}} \frac{d\Phi}{dy}(y_., s) - \Phi(y_., s) = 0 \quad (\text{A.713})$$

where

$$y_.. = \gamma^{\frac{1}{2}} X_.. \quad (\text{A.714})$$

To derive the Green's function associated with this boundary-value problem, we first must find the general solution to the homogeneous problem. That is, we seek the complementary solution to Equation (A.707):

$$\frac{d^2\Phi(y, s)}{dy^2} + \frac{1}{y} \frac{d\Phi(y, s)}{dy} - \Phi(y, s) = 0 \quad y_w < y < y. \quad (\text{A.715})$$

which is in the form of a modified Bessel function of order zero [Abramowitz and Stegun, 1970]. The general solution to this homogeneous differential equation is of the form

$$\Phi(y, s) = C_1 \Phi_1(y, s) + C_2 \Phi_2(y, s) \quad (\text{A.716})$$

where C_1 and C_2 are constants and $\Phi_1(y, s)$ satisfies the differential equation and the boundary condition at $y = y_w$ and $\Phi_2(y, s)$ satisfies the differential equation and the boundary condition at $y = y$. Both of these solutions are of the form

$$\Phi_1(y, s) = A I_0(y) + B K_0(y) \quad (\text{A.717})$$

$$\Phi_2(y, s) = C I_0(y) + D K_0(y) \quad (\text{A.718})$$

where A, B, C , and D are constants and $I_0(y)$ and $K_0(y)$ are Bessel functions of the first kind, order zero and third kind, order zero, respectively and of the form

$$I_0(y) = \sum_{k=0}^{\infty} \frac{\left(\frac{y}{2}\right)^{2k}}{(k!)^2} \quad (\text{A.719})$$

$$K_0(y) = -\frac{1}{2} I_0(y) \ln y + \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{(k!)^2} \left(1 + \frac{1}{2} + \cdots + \frac{1}{k}\right) \left(\frac{y}{2}\right)^{2k} \quad (\text{A.720})$$

To find the first solution, $\Phi_1(y, s)$, we apply the boundary condition at the well (Equation (A.709)):

$$\frac{d\Phi_1}{dy}(y_w) = 0 = A I'_0(y_w) + B K'_0(y_w) \quad (\text{A.721})$$

Thus,

$$A = \frac{-B K'_0(y_w)}{I'_0(y_w)} \quad (\text{A.722})$$

So,

$$\Phi_1(y, s) = \frac{-B K'_0(y_w)}{I'_0(y_w)} I_0(y) + B K_0(y) \quad (\text{A.723})$$

or

$$\Phi_1(y, s) = B \left[\frac{-K'_0(y_w)}{I'_0(y_w)} I_0(y) + K_0(y) \right] \quad (\text{A.724})$$

If we choose $B = I'_0(y_w)$, without loss of generality, then Equation (A.724) becomes

$$\Phi_1(y, s) = -K'_0(y_w) I_0(y) + I'_0(y_w) K_0(y) \quad (\text{A.725})$$

To find the second solution, $\Phi_2(y, s)$, we apply the boundary condition at y . (Equation (A.713)):

$$\varepsilon \gamma^{\frac{1}{2}} \frac{d\Phi_2}{dy}(y., s) - \Phi_2(y., s) = 0 \quad (\text{A.726})$$

Thus,

$$\varepsilon \gamma^{\frac{1}{2}} [C I'_0(y.) + D K'_0(y.)] - C I_0(y.) + D K_0(y.) = 0 \quad (\text{A.727})$$

or

$$C \left[\epsilon \gamma^{\frac{1}{2}} I'_0(y.) - I_0(y.) \right] + D \left[\epsilon \gamma^{\frac{1}{2}} K'_0(y.) - K_0(y.) \right] = 0 \quad (\text{A.728})$$

Solving C in terms of D produces

$$C = \frac{-D \left[\epsilon \gamma^{\frac{1}{2}} K'_0(y.) - K_0(y.) \right]}{\left[\epsilon \gamma^{\frac{1}{2}} I'_0(y.) - I_0(y.) \right]} \quad (\text{A.729})$$

Thus,

$$\Phi_2(y, s) = \frac{-D \left[\epsilon \gamma^{\frac{1}{2}} K'_0(y.) - K_0(y.) \right]}{\left[\epsilon \gamma^{\frac{1}{2}} I'_0(y.) - I_0(y.) \right]} I_0(y) + D K_0(y) \quad (\text{A.730})$$

If we choose $D = \left[\epsilon \gamma^{\frac{1}{2}} I'_0(y.) - I_0(y.) \right]$, without loss of generality, then

$$\Phi_2(y, s) = \left[-\epsilon \gamma^{\frac{1}{2}} K'_0(y.) + K_0(y.) \right] I_0(y) + \left[\epsilon \gamma^{\frac{1}{2}} I'_0(y.) - I_0(y.) \right] K_0(y) \quad (\text{A.731})$$

We now seek the particular solution to Equation (A.707) using a Green's function which is of the form

$$g(y, \eta) = \begin{cases} \frac{\Phi_1(y) \Phi_2(\eta)}{p(\eta) W[\Phi_1, \Phi_2](\eta)} & y \leq \eta \leq y. \\ \frac{\Phi_1(\eta) \Phi_2(y)}{p(\eta) W[\Phi_1, \Phi_2](\eta)} & y_w \leq \eta \leq y \end{cases} \quad (\text{A.732})$$

where $p(\eta)$ is the coefficient of the first term in Equation (A.707), which is equal to one, and $W[\Phi_1, \Phi_2](\eta)$ is the Wronskian of Φ_1 and Φ_2 . Before we determine the Wronskian, let's define the following operators:

$$G[I_1, I_0](y_w) = \varepsilon \gamma^{\frac{1}{2}} I_1(y.) - I_0(y.) \quad (A.733)$$

where I_1 is a first kind, order one Bessel function and is equal to I'_0 [Abramowitz and Stegun, 1970] and

$$H[K_1, K_0](y_w) = \varepsilon \gamma^{\frac{1}{2}} K_1(y.) + K_0(y.) \quad (A.734)$$

where K_1 is a third kind, order one Bessel function and is equal to $-K'_0$ [Abramowitz and Stegun, 1970]. Thus,

$$\Phi_2(y, s) = H[K_1, K_0](y.) I_0(y) + G[I_1, I_0](y.) K_0(y) \quad (A.735)$$

Now we determine the Wronskian:

$$W[\Phi_1, \Phi_2](y) = \begin{vmatrix} \Phi_1 & \Phi_2 \\ \Phi_1' & \Phi_2' \end{vmatrix} \quad (\text{A.736})$$

So,

$$W[\Phi_1, \Phi_2](y) = \begin{vmatrix} -K_0'(y_w) I_0(y) + I_0'(y_w) K_0(y) & H[K_1, K_0](y) I_0(y) + G[I_1, I_0](y) K_0(y) \\ -K_0'(y_w) I_0'(y) + I_0'(y_w) K_0'(y) & H[K_1, K_0](y) I_0'(y) + G[I_1, I_0](y) K_0'(y) \end{vmatrix} \quad (\text{A.737})$$

$$\begin{aligned} &= [-K_0'(y_w) I_0(y) + I_0'(y_w) K_0(y)] [H[K_1, K_0](y) I_0'(y) + G[I_1, I_0](y) K_0'(y)] \\ &\quad - [-K_0'(y_w) I_0'(y) + I_0'(y_w) K_0'(y)] [H[K_1, K_0](y) I_0(y) + G[I_1, I_0](y) K_0(y)] \end{aligned} \quad (\text{A.738})$$

$$\begin{aligned} &= K_0'(y_w) G[I_1, I_0](y) [I_0'(y) K_0(y) - I_0(y) K_0'(y)] \\ &\quad + I_0'(y_w) H[K_1, K_0](y) [K_0(y) I_0'(y) - K_0'(y) I_0(y)] \end{aligned} \quad (\text{A.739})$$

$$= K_0'(y_w) G[I_1, I_0](y) W[K_0, I_0](y) + I_0'(y_w) H[K_1, K_0](y) W[K_0, I_0](y) \quad (\text{A.740})$$

We know that the $W[K_0, I_0](y) = 1/y$ [Abramowitz and Stegun, 1970], so

$$W[\Phi_1, \Phi_2](y) = \frac{1}{y} [K_0'(y_w) G[I_1, I_0](y) + I_0'(y_w) H[K_1, K_0](y)] \quad (\text{A.741})$$

or

$$W[\Phi_1, \Phi_2](y) = \frac{1}{y} [I_1(y_w) H[K_1, K_0](y) - K_1(y_w) G[I_1, I_0](y)] \quad (A.742)$$

where I_1 is equal to I'_0 and K_1 is equal to $-K'_0$ [Abramowitz and Stegun, 1970]. Thus, the Green's function (Equation (A.732)) is

$$g(y, \eta) = \begin{cases} \frac{\Phi_1(y) \Phi_2(\eta)}{W[\Phi_1, \Phi_2](\eta)} & y \leq \eta \leq y. \\ \frac{\Phi_1(\eta) \Phi_2(y)}{W[\Phi_1, \Phi_2](\eta)} & y_w \leq \eta \leq y \end{cases} \quad (A.743)$$

or

$$g(y, \eta) = \begin{cases} \frac{[K_1(y_w) I_0(y) + I_1(y_w) K_0(y)] [H[K_1, K_0](y) I_0(\eta) + G[I_1, I_0](y) K_0(\eta)]}{\frac{1}{\eta} [I_1(y_w) H[K_1, K_0](y) - K_1(y_w) G[I_1, I_0](y)]} \\ \frac{[K_1(y_w) I_0(\eta) + I_1(y_w) K_0(\eta)] [H[K_1, K_0](y) I_0(y) + G[I_1, I_0](y) K_0(y)]}{\frac{1}{\eta} [I_1(y_w) H[K_1, K_0](y) - K_1(y_w) G[I_1, I_0](y)]} \end{cases} \quad (A.744)$$

or

$$g(y, \eta) = \begin{cases} \frac{\eta [K_1(y_w) I_0(y) + I_1(y_w) K_0(y)] [H[K_1, K_0](y) I_0(\eta) + G[I_1, I_0](y) K_0(\eta)]}{[I_1(y_w) H[K_1, K_0](y) - K_1(y_w) G[I_1, I_0](y)]} \\ \frac{\eta [K_1(y_w) I_0(\eta) + I_1(y_w) K_0(\eta)] [H[K_1, K_0](y) I_0(y) + G[I_1, I_0](y) K_0(y)]}{[I_1(y_w) H[K_1, K_0](y) - K_1(y_w) G[I_1, I_0](y)]} \end{cases} \quad (A.745)$$

where the top expression is defined for the interval $y \leq \eta \leq y_*$ and the bottom expression is defined for the interval $y_* \leq \eta \leq y$.

The general solution to Equation (A.707) is of the form

$$\Phi(y) = \int_{y_*}^{y_*} g(y, \eta, s) \mathcal{F}(\eta, s) d\eta \quad (\text{A.746})$$

Since

$$y = \gamma^{\frac{1}{2}} X \quad (\text{A.706})$$

then

$$\eta = \gamma^{\frac{1}{2}} \xi; d\eta = \gamma^{\frac{1}{2}} d\xi \quad (\text{A.747})$$

Thus, Equation (A.746), together with the right-hand side of Equation (A.707), becomes

$$\Phi(y, s) = \int_{x_*}^{x_*} g\left(\gamma^{\frac{1}{2}} X, \gamma^{\frac{1}{2}} \xi, s\right) \mathcal{F}\left(\gamma^{\frac{1}{2}} \xi, s\right) \gamma^{\frac{1}{2}} d\xi \quad (\text{A.748})$$

$$= \int_{x_*}^{x_*} g\left(\gamma^{\frac{1}{2}} X, \gamma^{\frac{1}{2}} \xi, s\right) \gamma^{-1} \bar{F}(\xi, s) \gamma^{\frac{1}{2}} d\xi \quad (\text{A.749})$$

$$= \int_{x_*}^{x_*} g\left(\gamma^{\frac{1}{2}} X, \gamma^{\frac{1}{2}} \xi, s\right) \gamma^{-\frac{1}{2}} \bar{F}(\xi, s) d\xi \quad (\text{A.750})$$

Since $\bar{C}_m(X, s) = \phi(X, s)$ (Equation (A.695)), and $\Phi(y, s) = \phi(X, s)$ (Equation (A.698)) then

$$\bar{C}_m(X, s) = \int_{x_*}^{x_*} g\left(\gamma^{\frac{1}{2}} X, \gamma^{\frac{1}{2}} \xi, s\right) \gamma^{-\frac{1}{2}} \bar{F}(\xi, s) d\xi \quad (\text{A.751})$$

If we define

$$b(X, \xi, s) = g\left(\gamma^{\frac{1}{2}} X, \gamma^{\frac{1}{2}} \xi, s\right) \quad (\text{A.752})$$

then

$$\bar{C}_m(X, s) = \int_{x_*}^{x_*} b(X, \xi, s) \gamma^{-\frac{1}{2}} \bar{F}(\xi, s) d\xi \quad (\text{A.753})$$

Substituting in the constructed Green's function (Equation (A.745)) using Equations (A.706) and (A.747) gives us

$$\bar{C}_m(X, s) =$$

$$\int_{x_*}^x \gamma^{\frac{1}{2}} \xi \frac{\left[K_1(y_*) I_0(\gamma^{\frac{1}{2}} \xi) + I_1(y_*) K_0(\gamma^{\frac{1}{2}} \xi) \right] \left[H[K_1, K_0](y_*) I_0(\gamma^{\frac{1}{2}} X) + G[I_1, I_0](y_*) K_0(\gamma^{\frac{1}{2}} X) \right]}{I_1(y_*) H[K_1, K_0](y_*) - K_1(y_*) G[I_1, I_0](y_*)} \gamma^{-\frac{1}{2}} \bar{F}(\xi, s) d\xi$$

+

$$\int_x^{x_*} \gamma^{\frac{1}{2}} \xi \frac{\left[K_1(y_*) I_0(\gamma^{\frac{1}{2}} X) + I_1(y_*) K_0(\gamma^{\frac{1}{2}} X) \right] \left[H[K_1, K_0](y_*) I_0(\gamma^{\frac{1}{2}} \xi) + G[I_1, I_0](y_*) K_0(\gamma^{\frac{1}{2}} \xi) \right]}{I_1(y_*) H[K_1, K_0](y_*) - K_1(y_*) G[I_1, I_0](y_*)} \gamma^{-\frac{1}{2}} \bar{F}(\xi, s) d\xi$$

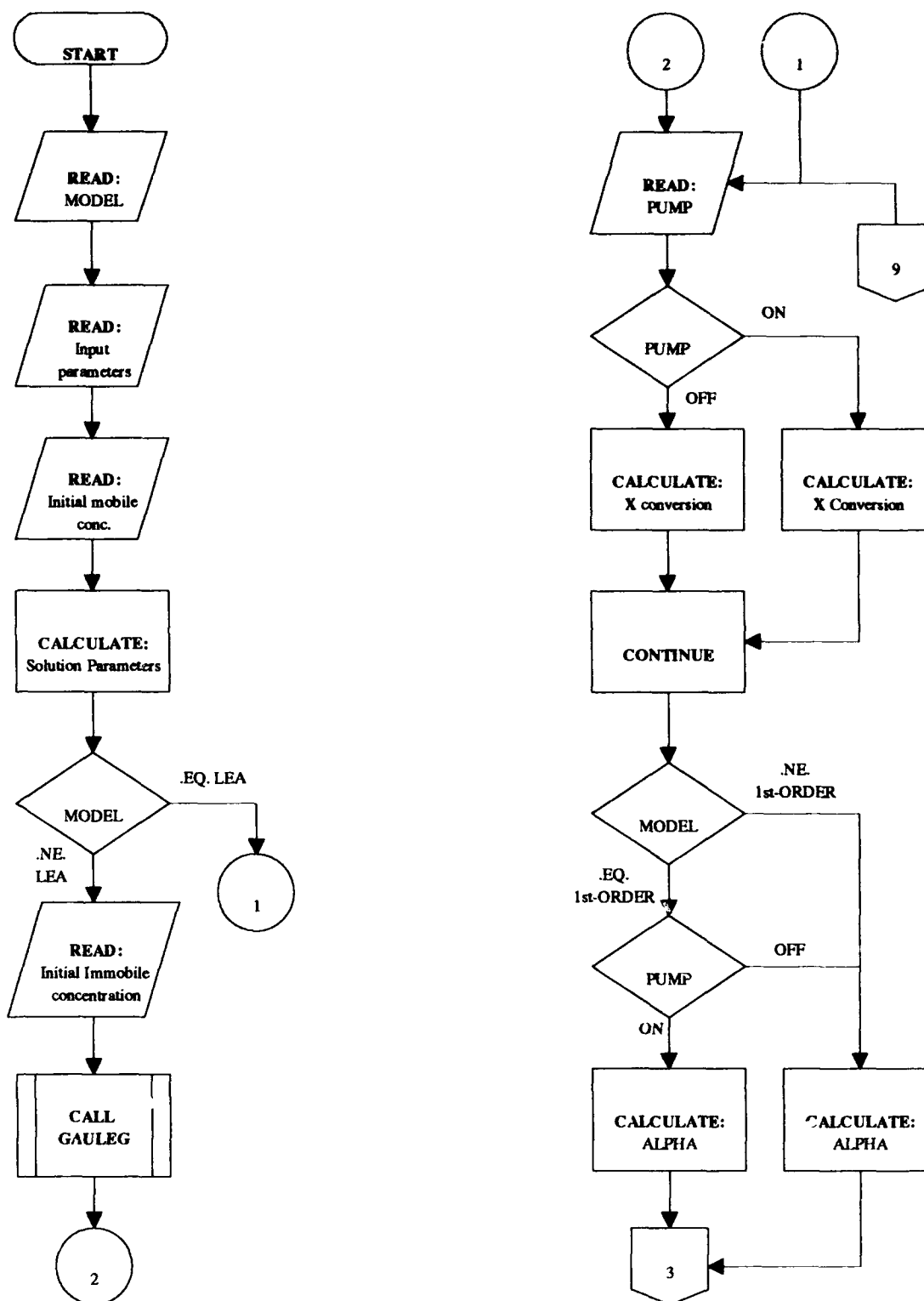
(A.754)

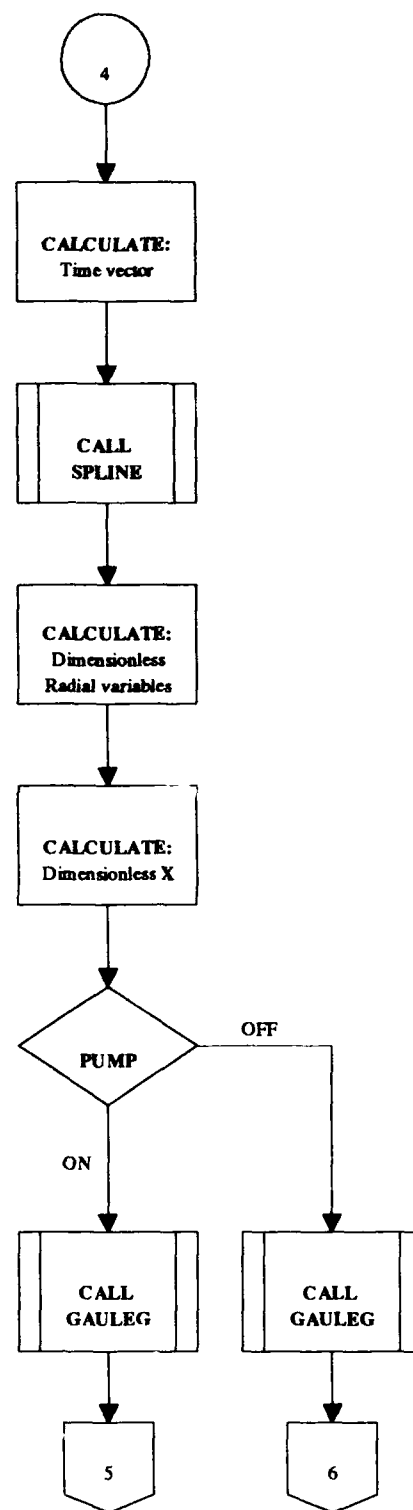
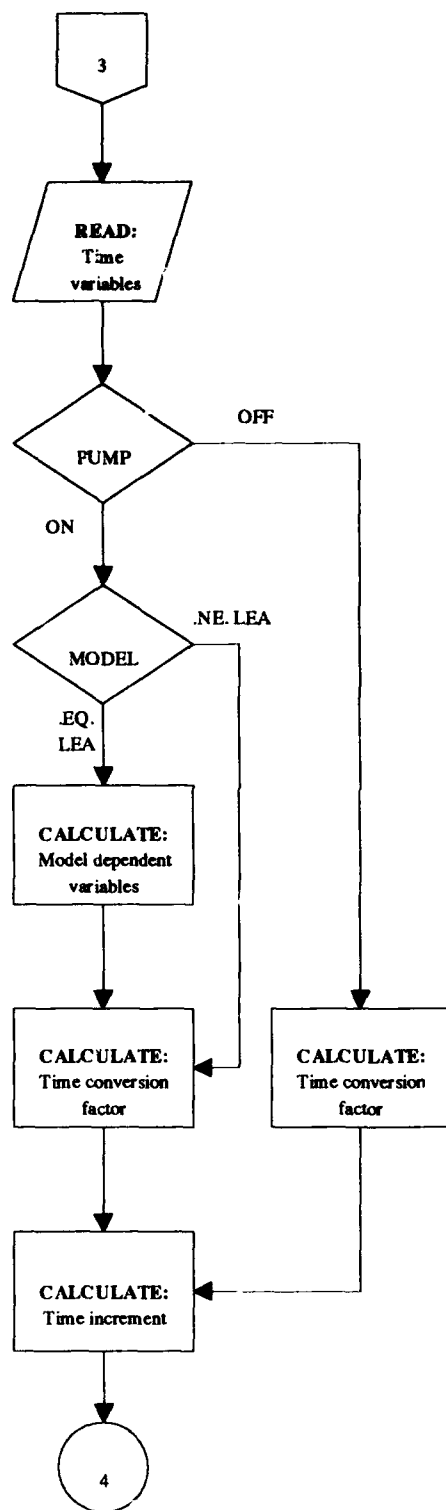
Simplifying yields

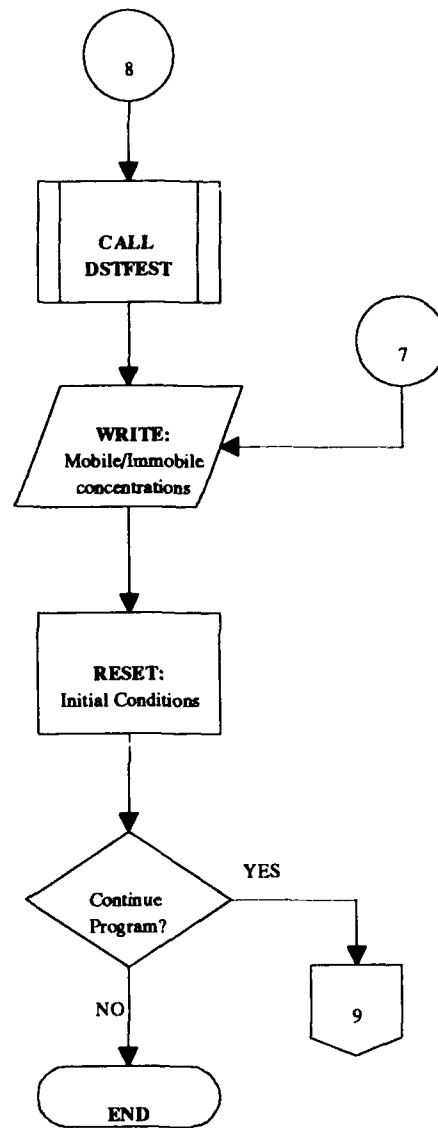
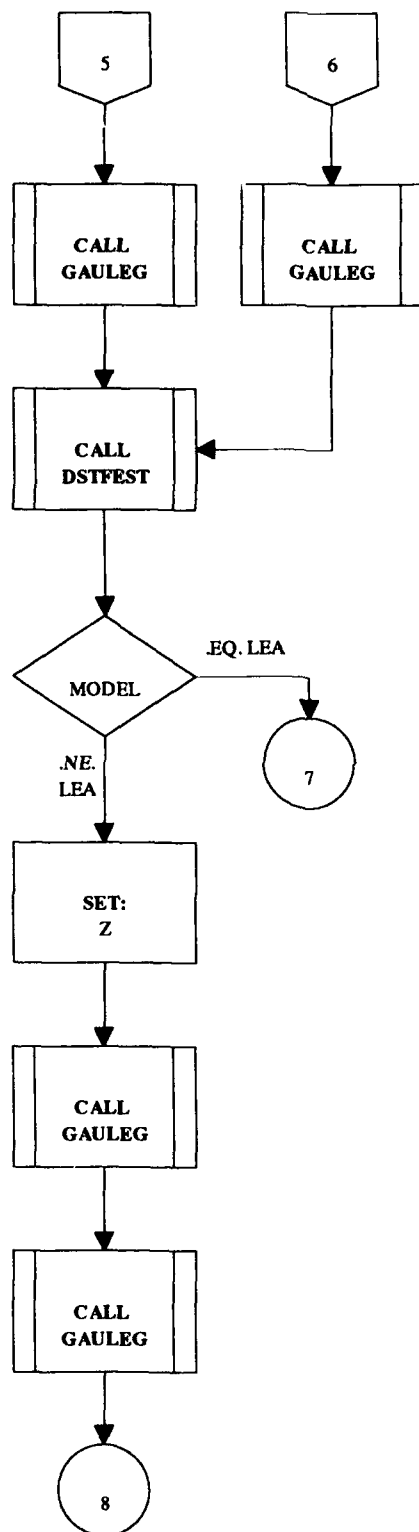
$$\begin{aligned} \bar{C}_m(X, s) = & \left\{ \frac{1}{I_1(y_w)H[K_1, K_0](y.) - K_1(y_w)G[I_1, I_0](y.)} \right\} \cdot \\ & \left\{ \left[H[K_1, K_0](y.)I_0(\gamma^{\frac{1}{2}}X) + G[I_1, I_0](y.)K_0(\gamma^{\frac{1}{2}}X) \right] K_1(y_w) \int_{x_w}^x \xi I_0(\gamma^{\frac{1}{2}}\xi) \bar{F}(\xi, s) d\xi \right. \\ & + \left[H[K_1, K_0](y.)I_0(\gamma^{\frac{1}{2}}X) + G[I_1, I_0](y.)K_0(\gamma^{\frac{1}{2}}X) \right] I_1(y_w) \int_{x_w}^x \xi K_0(\gamma^{\frac{1}{2}}\xi) \bar{F}(\xi, s) d\xi \\ & + \left[K_1(y_w)I_0(\gamma^{\frac{1}{2}}X) + I_1(y_w)K_0(\gamma^{\frac{1}{2}}X) \right] H[K_1, K_0](y.) \int_x^{x_w} \xi I_0(\gamma^{\frac{1}{2}}\xi) \bar{F}(\xi, s) d\xi \\ & \left. + \left[K_1(y_w)I_0(\gamma^{\frac{1}{2}}X) + I_1(y_w)K_0(\gamma^{\frac{1}{2}}X) \right] G[I_1, I_0](y.) \int_x^{x_w} \xi K_0(\gamma^{\frac{1}{2}}\xi) \bar{F}(\xi, s) d\xi \right\} \end{aligned}$$

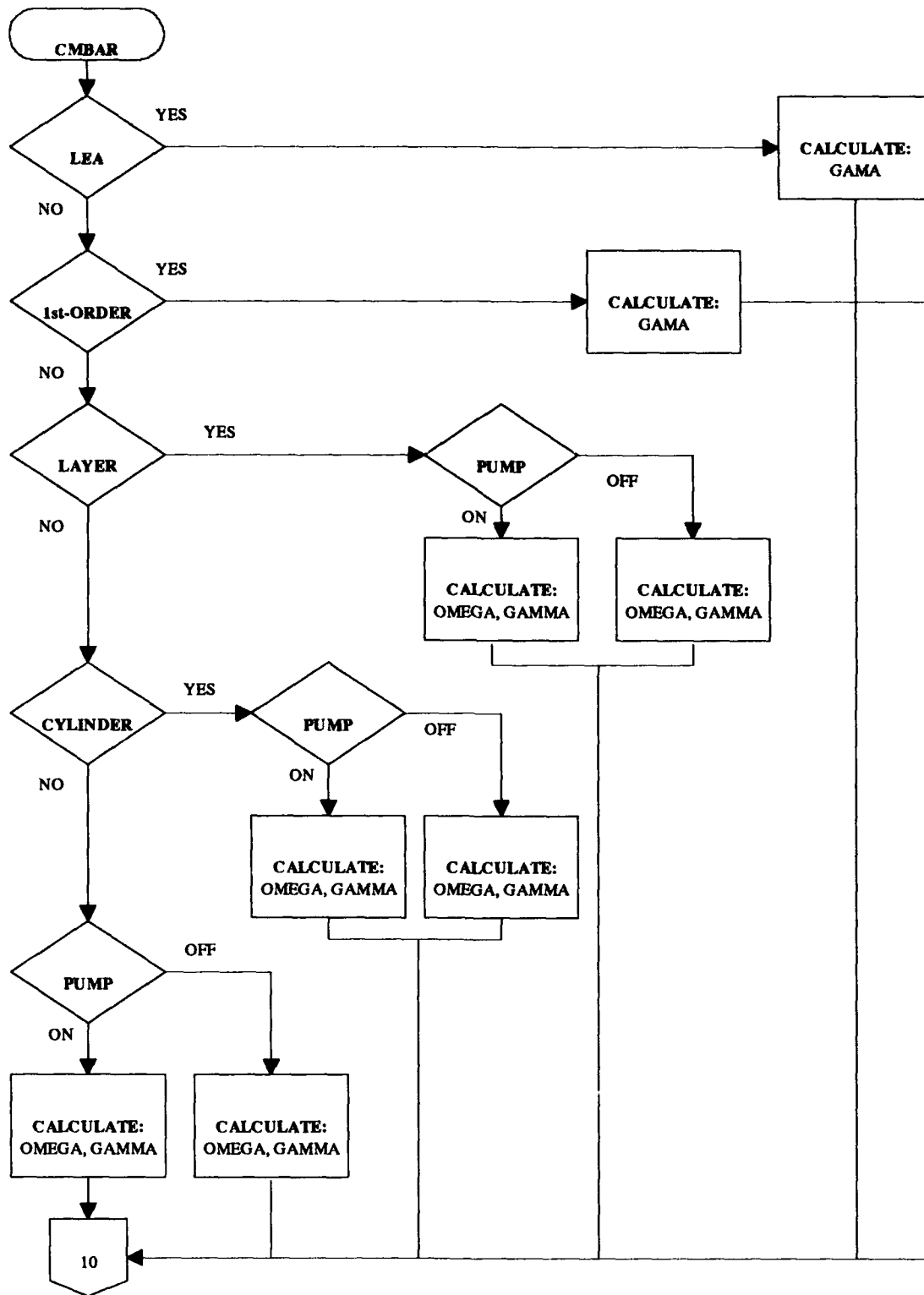
(A.755)

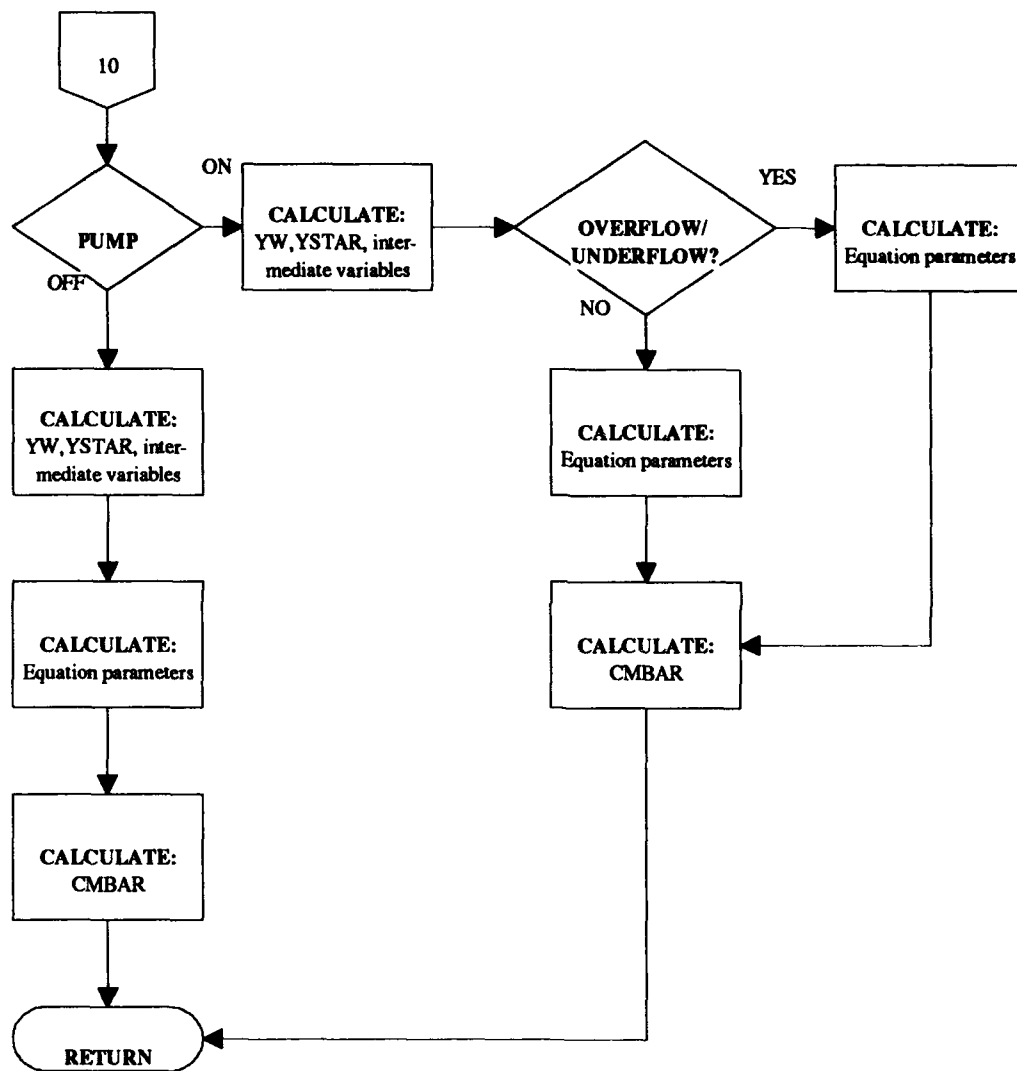
Appendix B: Flowchart

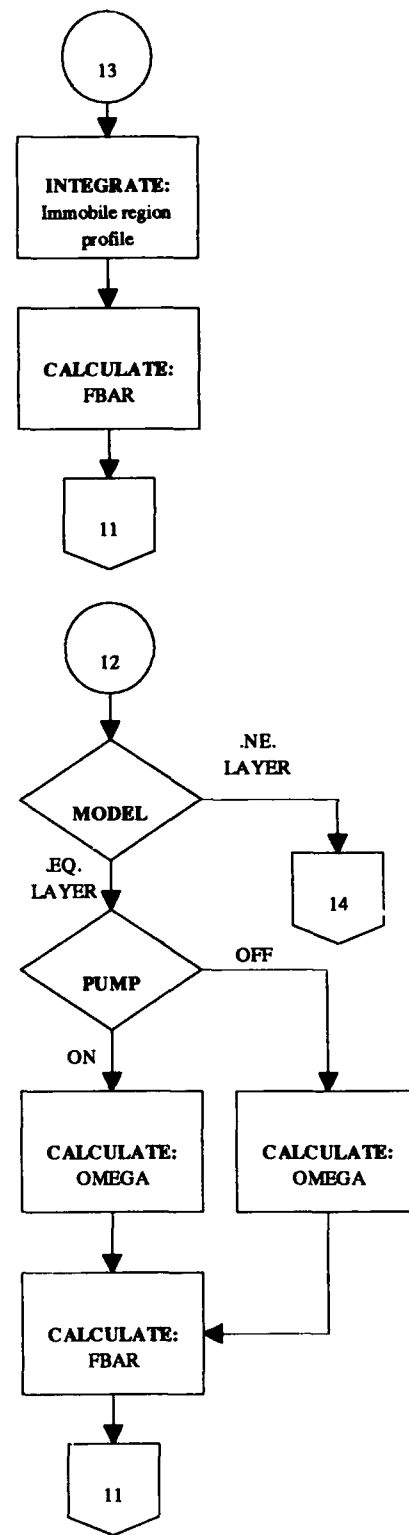
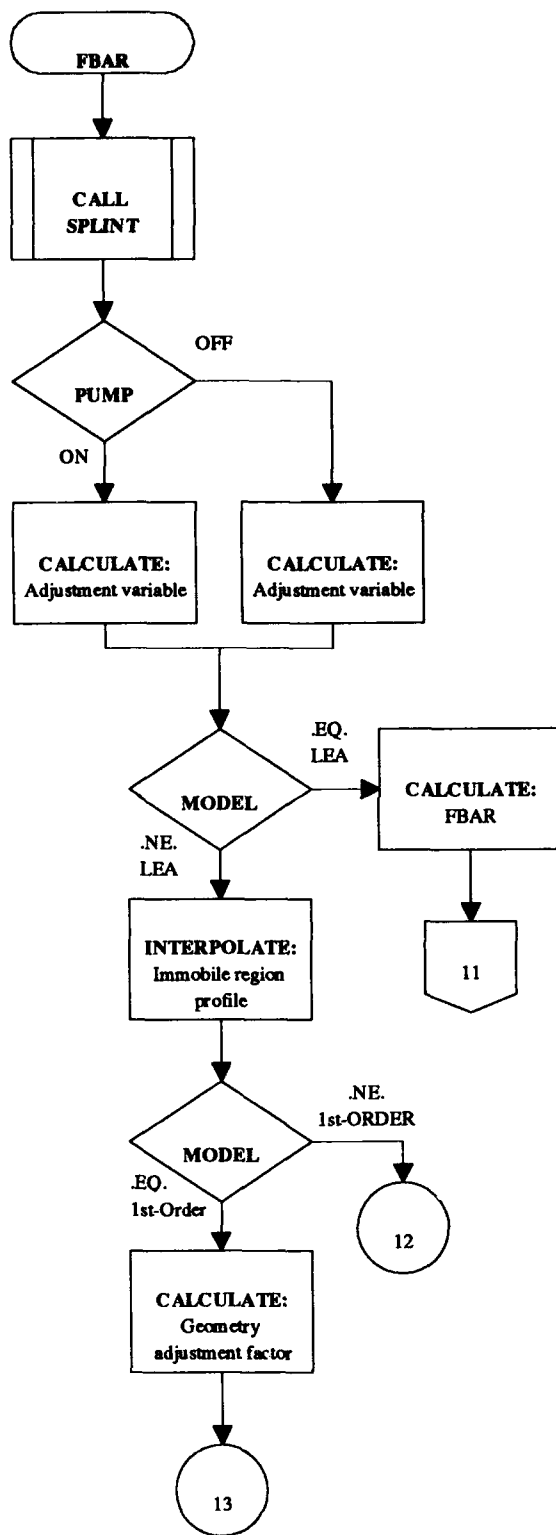


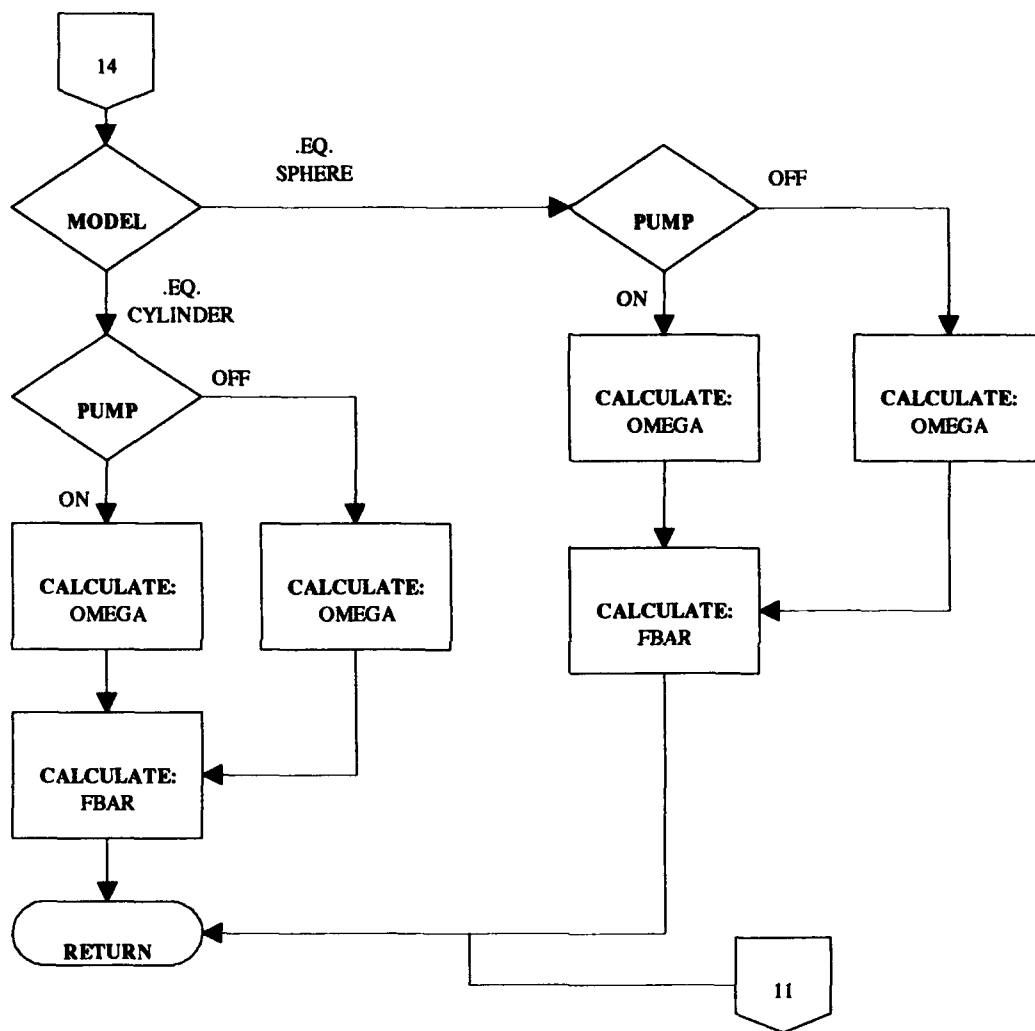


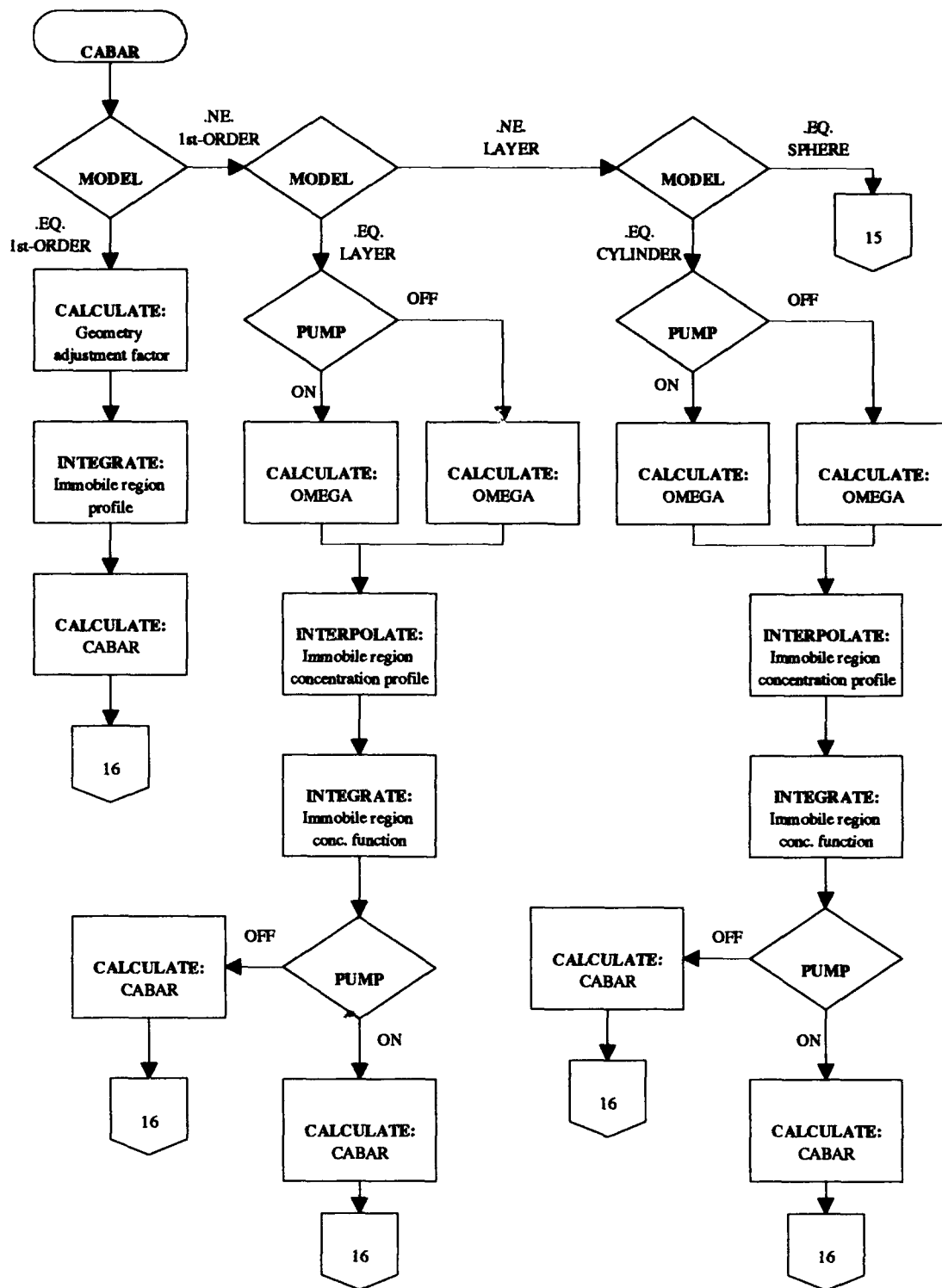


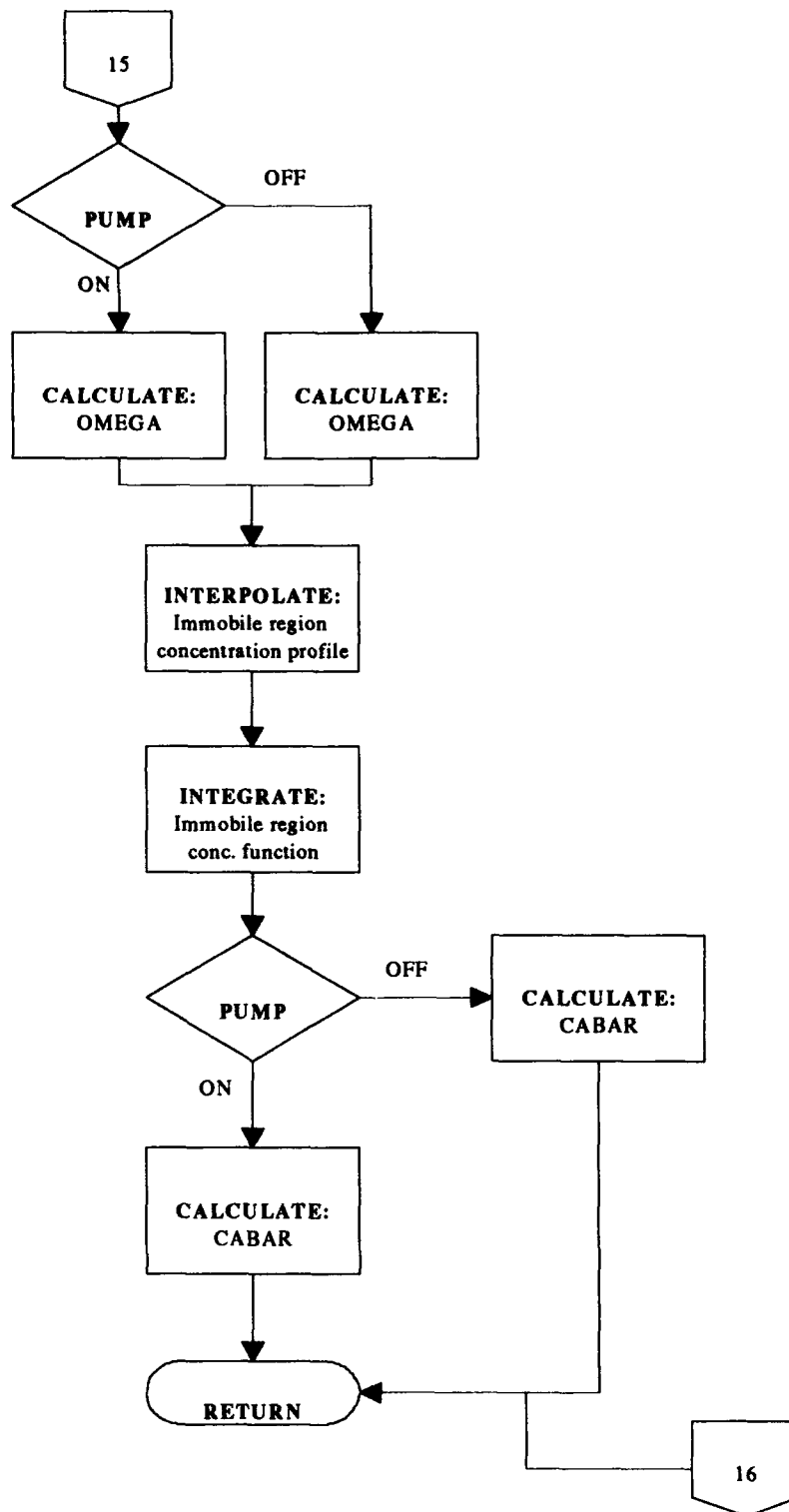












Appendix C: Source Code

C Program Pulsepmp.FOR
C
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C
C Source Code created Sep 93
C
C Title: Analytical Modeling of Aquifer Decontamination By
C Pulsed Pumping When Contaminant Transport Is Affected
C By Rate-Limited Sorption/Desorption
C
C This code calculates the solute concentration out from an
C extraction well located at the center of a circular
C contaminated plume to some radius r^* . The code uses the
C equations governing the transport of an organic contaminant
C during aquifer remediation by pulsed pumping. Contaminant
C transport is assumed to be affected by advection, dispersion,
C and sorption/desorption. Sorption is modeled assuming
C equilibrium or rate-limited, with the rate-limitation
C described by either a first-order equation, or by Fickian
C diffusion of contaminant through layered, cylindrical, or
C spherical immobile water regions. The code is designed to
C use an arbitrary initial distribution of contaminant in both
C the mobile and immobile regions.
C
C The purpose of the code is to numerically invert the
C analytically derived Laplace domain solute concentrations
C solutions to obtain the concentration versus time and radial
C distance profiles (breakthrough curves). The code uses the
C Stehfest algorithm as the Laplace inversion routine, the
C International Mathematical and Statistical Library (IMSL),
C SFUN Library, to evaluate the Bessel functions associated
C with the solutions, and numerous subroutines and external
C functions from Press and others. Changes to the code will
C require compiling and linking with the IMSLIB.LIB.
C
C References:
C
C Carlson, David, Mark E. Oxley, and Mark N. Goltz. "A Green's
C Function Solution to Aquifer Decontamination by Pulsed
C Pumping with Arbitrary Radial Initial Conditions," (in
C preparation). School of Engineering, Air Force
C Institute of Technology (AETU), Wright-Patterson AFB,
C OH, 1993.
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C Goltz, Mark N. and Mark E. Oxley. "Analytical Modeling of
C Aquifer Decontamination by Pumping When Transport is
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C Affected by Rate-Limited Sorption," Water Resources
 C Research, 27 (4): 547-556 (April 1991).
 C
 C International Mathematical and Statistical Library,
 C International Mathematical and Statistical Library
 C User's Manual Version 2.1. Houston, TX: January 1989.
 C
 C Press, William H., Saul A. Teukolsky, William T.
 C Vetterling, and Brian P. Flannery. Numerical
 C Recipes in FORTRAN. Cambridge, MA: Cambridge
 C University Press, 1992.
 C
 C Stehfest, Harold. "Numerical Inversion of Laplace
 C Transforms," Communications of the ACM, 13 (1): 47-49
 C (January 1970).
 C
 C *****
 C The following are the input parameters located in the file
 C "INPUT.DAT". They are defined in the order in which they are
 C read in.
 C
 C
 C QW Pumping rate [L^3/T]
 C
 C B Aquifer thickness [L]
 C
 C AL Longitudinal dispersivity [L]
 C
 C THETA Total porosity
 C
 C RHO Soil bulk density [M/L^3]
 C
 C KD Sorption distribution coefficient [L^3/M]
 C
 C PHI Ratio of mobile to total water
 C
 C EF Fraction of sorption sites in contact with mobile
 C water
 C
 C ALFA First-order rate constant [$1/T$]
 C
 C DE Fickian diffusion coefficient in the immobile
 C region [L^2/T]
 C
 C A Half-width of immobile layer or radius of immobile
 C spherical/cylindrical zones [L]
 C
 C DO Mobile region molecular diffusion coefficient
 C [L^2/T]
 C
 C CP Proportionality constant used in deriving the
 C coefficient of leakage of the solute from the
 C contaminated zone to the outer boundary (EPS)

C

C XF1 The radial distance from the well out to the edge
C of the contaminated zone [L]
C

C F1 Initial concentration in the mobile region at a
C given XF1 location. Entered in as a dimensionless
C value
C

C Q Temporary variable used to set the number of
C points along the radial axis (RPOINT)
C

C ACA The number of points in the immobile region along
C the a-axis. Entered in as a dimensionless value
C

C CA Initial concentration in the immobile region of a
C certain geometry at a given ACA location. Entered
C in as a dimensionless value
C

C The following are key program variables or calculated
C parameters:
C

C N An even integer that affects the accuracy of the
C Laplace inversion routine
C

C TSTEP Number of time intervals within the pump on/off
C condition
C

C TFIN Length of time pump is on or off in a given cycle
C

C PUMP Flag used to determine if the user wants to model
C the pump on or off
C

C ALPHA This parameter takes on different meanings
C depending on whether the pump is on or off and
C whether a diffusion or first-order assumption is
C modeled. If the pump is on and a diffusion
C assumption is modeled, then ALPHA is the
C dimensionless immobile region solute diffusion
C coefficient. If the pump is off then this value
C is not used. If a first-order assumption is
C modeled, then ALPHA is the dimensionless first-
C order rate constant for when the pump is on and
C off. However, the magnitude of this parameter
C differs for the two conditions.
C

C BETA Solute capacity ratio of immobile to mobile
C regions
C

C X Dimensionless radial distance
C

C XW Dimensionless well radius
C

C	XSTAR	Dimensionless radius of initially contaminated
C		zone
C	CONCM	The dimensionless mobile region solute
C		concentration as a function of radial distance and
C		time
C		
C	CONCIM	The dimensionless immobile region solute
C		concentration as a function of radial distance
C		from the well, location along the a-axis in the
C		immobile region, and time
C		
C	CIM	The dimensionless immobile region solute
C		concentration as function of radial distance from
C		the well and time. This is for the first-order
C		rate model and uses the diffusion models geometry
C		as a comparison for the immobile region
C		concentration
C		
C	T	Dimensionless time
C		
C	APOINT	The number of points along the immobile region
C		axis
C		
C	RPOINT	The number of points along the radial axis
C		
C	RETARD	Retardation factor when the LEA model is assumed
C		
C	RM	Mobile region retardation factor
C		
C	RIM	Immobile region retardation factor
C		
C	THETAM	Mobile region water content
C		
C	THETAIM	Immobile region water content
C		
C	TCNV	Conversion factor used to convert dimensionable
C		time to dimensionless time. This value takes on
C		different magnitudes for the pump on and off
C		
C	XCONV	Conversion factor used to convert dimensionable
C		distance to dimensionless distance. This value
C		takes on different magnitudes for the pump on and
C		off
C		
C	EPS	Coefficient of leakage, epsilon, of the solute
C		from the contaminated zone to the outer boundary.
C		Used when the pump is off
C		
C	S	Laplace transform variable
C		
C	*****	
C		

```

REAL*8 ALPHA,PI,DE,BETA,X,XW,XSTAR,XLOW,XHI,WLOW,WHI,ACA,
&Y2,Z,ZHI,ZLOW,WZHI,WZLOW,AL,XF1,F1,Y2X,AXROOT,AWAIT,
&CONCM,CONCIM,T,YP1,YTEMP,KD,CA,YPN,ALIM,BLIM,TMP4,TMP5,
&TMP6,TMP7,TMP8,TMP9,TMP10,F1F,CAF,DO,
&CP,XCONV,EPS,TMP11

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C

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DIMENSION XLOW(100),XHI(100),WLOW(100),WHI(100),ACA(10),
&Y2(10),ZHI(10),ZLOW(10),WZHI(10),WZLOW(10),XF1(10),
&F1(10),Y2X(10),T(10),AXROOT(10),AWAIT(10),CONCM(10),
&CONCIM(10,10),YTEMP(10),CA(10,10),TMP4(10),TMP5(10),
&TMP6(10),TMP7(10),TMP8(10),TMP9(10),TMP10(10),F1F(10),
&CAF(10,10),TMP11(8)

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C

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REAL*8 CMBAR,CABAR
EXTERNAL CMBAR,CABAR

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C

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CHARACTER*21 MODEL

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C

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INTEGER CHOICE,TEN,APOINT,IX,RPOINT,TSTEP,N,GEOM,PULSE,
&PUMP,TWEN

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C

```

COMMON /ALL/ CHOICE,ALPHA,PUMP
COMMON /MCMCA/ TEN,PI
COMMON /MCMF/ BETA
COMMON /MCAF/ APOINT,ACA,CA,GEOM,AWAIT,AXROOT
COMMON /MCM/ X,XW,XSTAR,XLOW,XHI,WLOW,WHI,TMP11,EPS,TWEN
COMMON /MCA/ Z,ZHI,ZLOW,WZHI,WZLOW,IX,TMP4,TMP5,TMP6,Y2
COMMON /MF/ AL,RPOINT,XF1,F1,Y2X,TMP7,TMP8,TMP9,TMP10,
&XCONV

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C

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OPEN(7,FILE='INPUT.DAT',STATUS='OLD')
OPEN(8,FILE='REPORT.DAT',STATUS='UNKNOWN')
OPEN(9,FILE='F1.DAT',STATUS='OLD')
OPEN(10,FILE='CA.DAT',STATUS='OLD')
OPEN(11,FILE='OUT.DAT',STATUS='UNKNOWN')
PRINT*,' Select model number for simulation:'
PRINT*,'      1 = LEA'
PRINT*,'      2 = FIRST-ORDER RATE'
PRINT*,'      3 = LAYERED DIFFUSION'
PRINT*,'      4 = CYLINDRICAL DIFFUSION'
PRINT*,'      5 = SPHERICAL DIFFUSION'
READ*,CHOICE
GEOM=0
IF(CHOICE.EQ.1)MODEL='LEA'
  IF(CHOICE.EQ.2)THEN
    MODEL='FIRST-ORDER RATE'
    PRINT*,' Which diffusion model do you wish to compare
& to the First-Order model?'
    PRINT*,' 1 = LAYERED DIFFUSION'
    PRINT*,' 2 = CYLINDRICAL DIFFUSION'
    PRINT*,' 3 = SPHERICAL DIFFUSION'
    READ*,GEOM
  ENDIF

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      IF(CHOICE.EQ.3)MODEL='LAYERED DIFFUSION'
      IF(CHOICE.EQ.4)MODEL='CYLINDRICAL DIFFUSION'
      IF(CHOICE.EQ.5)MODEL='SPHERICAL DIFFUSION'
C
C Set precision, 'N', for Stehfest subroutine and precision
C 'TEN' and 'TWEN' for GAULEG computations. Note that 'TWEN'
C is used for Gauss-Quadrature integration for pump off and
C 'TEN' is used likewise for pump on conditions. 'TWEN' is
C larger due to ill-behaved modified Bessel functions in the
C pump off solution. Set the values for the first derivatives
C 'YPl' and 'YPN' for the Spline fit, time offset, and PI.
C
      PRINT*,'Enter Stehfest precision'
      READ*,N
      PRINT*,'Enter integration precision (100 max)'
      READ*,TWEN
      TEN=10
      YP1=0.D0
      YPN=1.D30
      TOFFSET=0.
      PI=4.*DATAN(1.0D0)
C
C Read in input data
C
      READ(7,*)QW,B,Al,
      READ(7,*)THETA,RHO,KD
      READ(7,*)PHI
      READ(7,*)EF
C
C Read in First-Order rate constant
C
      READ(7,*) ALFA
C
C Read in values for Fickian diffusion coefficient in the
C immobile region (DE), half-width of immobile layer or radius
C of immobile cylindrical and spherical geometries (A), mobile
C region diffusion coefficient (DO), and proportionality
C constant (CP) for EPS
C
      READ(7,*)DE,A,DO,CP
C
C Read in the mobile region concentrations at a given radial
C location
C
      DO 6 I1=1,10
          READ(9,*,END=11) XF1(I1), F1(I1)
          RPOINT=I1
      6  CONTINUE
      11 CONTINUE
C
C Set up headings
C
      IF(MODEL.EQ.'LEA')THEN

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        WRITE(6,20)
        WRITE(8,20)
C
20      FORMAT(25X,'EQUILIBRIUM SORPTION/DESORPTION')
C
      ELSE IF(MODEL.EQ.'FIRST-ORDER RATE') THEN
        WRITE(6,30)
        WRITE(8,30)
C
30      FORMAT(13X,'SORPTION/DESORPTION CONTROLLED BY FIRST-
& ORDER RATE PROCESS')
      IF(GEOM.EQ.1) THEN
        WRITE(6,31)
        WRITE(8,31)
31      FORMAT(13X,'IMMOBILE REGION COMPARED WITH LAYERED
& DIFFUSION')
      ELSE IF(GEOM.EQ.2) THEN
        WRITE(6,32)
        WRITE(8,32)
32      FORMAT(13X,'IMMOBILE REGION COMPARED WITH CYLINDRICAL
& DIFFUSION')
      ELSE
        WRITE(6,33)
        WRITE(8,33)
33      FORMAT(13X,'IMMOBILE REGION COMPARED WITH SPHERICAL
& DIFFUSION')
      ENDIF
C
      ELSE IF(MODEL.EQ.'LAYERED DIFFUSION') THEN
        WRITE(6,40)
        WRITE(8,40)
C
40      FORMAT(13X,'SORPTION/DESORPTION CONTROLLED BY DIFFUSION
& WITHIN LAYERS')
C
      ELSE IF(MODEL.EQ.'CYLINDRICAL DIFFUSION') THEN
        WRITE(6,50)
        WRITE(8,50)
C
50      FORMAT(13X,'SORPTION/DESORPTION CONTROLLED BY DIFFUSION
& WITHIN CYLINDERS')
C
      ELSE
        WRITE(6,60)
        WRITE(8,60)
C
60      FORMAT(13X,'SORPTION/DESORPTION CONTROLLED BY DIFFUSION
& WITHIN SPHERES')
      ENDIF
C
C Print out the input parameters and set up the retardation
C factor (RETARD) for the LEA model when the pump is on
C

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WRITE(6,70)QW,B,AL
WRITE(8,70)QW,B,AL
70  FORMAT(' QW=',F15.4,4X,'B=',F17.2,3X,' AL=',F15.4)
C
WRITE(6,80)THETA,RHO,KD
WRITE(8,80)THETA,RHO,KD
80  FORMAT(' THETA=',F12.4,3X,' RHO=',F16.3,2X,' KD=',F13.2)
C
RETARD=1.+RHO*KD/THETA
WRITE(6,100)RETARD,PHI,EF
WRITE(8,100)RETARD,PHI,EF
100  FORMAT(' R=',F15.4,4X,'PHI=',F17.4,2X,'EF=',F14.3)
C
C Set up the First-Order Rate and Diffusion models and print
C out the input parameters associated with the pump on and pump
C off
C
C If we assume only a fraction, PHI, of the total aquifer
C porosity, THETA, is mobile, then THETAM = PHI * THETA
C
C If we assume only a fraction of sorption sites are in contact
C with mobile water, EF, then RM = 1 + RHO*EF*KD/THETAM and
C RIM = 1 + RHO*(1-EF)*KD/THETAIM
C
WRITE(6,160)DE,A,DO,CP,ALFA,N
WRITE(8,160)DE,A,DO,CP,ALFA,N
160  FORMAT(5H DE=E15.5,4X,2HA = F19.4,2.,3HDO=E14.5,/,
&4H CP=F15.4,4X,5HALFA=,4X,E12.5,2X,2HN=,13X,I2)
C
C Set up mobile and immobile porosities and retardation factors
C
THETAM=PHI*THETA
THETAIM=THETA-THETAM
RM=1.+RHO*EF*KD/THETAM
RIM=1.+RHO*(1.-EF)*KD/THETAIM
BETA=THETAIM*RIM/(THETAM*RM)
C
C Set up the dimensionless immobile region solute diffusion
C coefficient when the pump is on. This parameter is used
C whenever the diffusion models are activated (pump on) and is
C not a used parameter when the pump is off
C
ALPHA=(DE*AL*AL*2.*PI*B*THETAM*RM)/(A*A*QW*RIM)
C
C Set up the coefficient of leakage of the solute from the
C contaminated zone to the outer boundary. This parameter is
C used when the pump is off
C
EPS=DO/CP/A*DSQRT(DE*RM/DO/RIM)
C
C Print out the calculated variables
C

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        WRITE(6,180)RM,RIM,BETA,ALPHA,EPS,TWEN
        WRITE(8,180)RM,RIM,BETA,ALPHA,EPS,TWEN
180  FORMAT(' RM=',F15.5,4X,' RIM=',F17.5,2X,
        &' BETA=',F12.5,2X,/,,' ALPHA=',E12.5,4X,' EPS= ',E17.5,
        &2X,5HTWEN=9X,I3,/)

C
C  Read in the initial concentration in the immobile region at a
C  given location along the a-axis. This value is read in as a
C  dimensionless value. Restriction: For every radial point
C  from the well each location must have the same number of
C  immobile region points, (i.e., number of a-points along the
C  z-axis is constant).
C
        IF(MODEL.NE.'LEA') THEN
            Q=0.0
            DO 21 I2=1,RPOINT
                DO 16 I3=1,10
                    READ(10,*,END=25)Q,ACA(I3),CA(I2,I3)
                    IF (ABS(Q-XF1(I2)).GE.(.0001)) THEN
                        BACKSPACE(10)
                        GOTO 21
                    ENDIF
                    APOINT=I3
16          CONTINUE
21          CONTINUE
25          REWIND(10)

C
C  Call GAULEG subroutine (Gauss-Legendre) to find the
C  orthogonal roots (abscissas) and weights of the immobile
C  region for Gauss Quadrature integration. This is required to
C  find FBAR.
C
        ALIM=0.D0
        BLIM=1.D0
        CALL GAULEG(ALIM,BLIM,AXROOT,AWAIT,APOINT)
        ENDIF

C
C  Ask the user what they want to model: Pump On or Pump Off
C
5      PRINT*,'Do you want the pump on or off? (1=on : 0=off)'
        READ*,PUMP

C
C  Setup conversion factors used to convert dimensionable
C  distance (radial) to dimensionless distance for the pump on
C  and pump off
C
        IF(PUMP.EQ.1) THEN
            XCONV=1./AL
            WRITE(6,10)
            WRITE(8,10)
10          FORMAT(/,15X,'BREAKTHROUGH CONCENTRATIONS WHEN THE PUMP
        & IS ON',/)
        ELSE

```



```

        XCONV=DSQRT(DE*RM/DO/RIM)/A
        WRITE(6,15)
        WRITE(8,15)
15      FORMAT(/,15X,'BREAKTHROUGH CONCENTRATIONS WHEN THE PUMP
        & IS OFF',/)
        ENDIF
C
C Set up ALPHA for the First-Order Model (pump on/pump off)
C
        IF(CHOICE.EQ.2) THEN
            IF(PUMP.EQ.1) THEN
                ALPHA=(ALFA*2.*PI*B*AL*AL)/(BETA*QW)
            ELSE
                ALPHA=ALFA*A*A/THETAIM/DE
            ENDIF
        ENDIF
C
C Set up the time interval and convert to a dimensionless
C value. Time takes on different values when the pump is on
C and off
C
        PRINT*,' Enter time increment & number of time intervals
        &(10 max) '
        PRINT*,' (Tf,# time steps) '
        READ*,TFIN,TSTEP
C
C For the LEA model (pump on) time is dependent upon RETARD and
C THETA
C
        IF(PUMP.EQ.1) THEN
            IF(CHOICE.EQ.1) THEN
                RM=RETARD
                THETAM=THETA
            ENDIF
            TCONV=QW/(2.*PI*B*THETAM*AL*AL*RM)
        ELSE
            TCONV=DE/RIM/A/A
        ENDIF
        DELTT=(TFIN)/REAL(TSTEP)
        DO 200 JJ=1,TSTEP
            T(JJ)=(JJ)*DELTT*TCONV
            WRITE(8,195)T(JJ)
195      FORMAT(1X,'DIMENSIONLESS TIME = ',F11.5)
200    CONTINUE
C
C Call SPLINE subroutine to cubic spline fit the mobile
C concentration profile
C
        CALL SPLINE(XF1,F1,RPOINT,YP1,YPN,Y2X)
C
C Find dimensionless boundary values on the radial axis:
C XW and XSTAR. These values differ for the pump on and pump
C off

```

```

C
      XSTAR=XF1(RPOINT)*XCONV
      XW=XF1(1)*XCONV
C
C   Enter the main calculation loop
C
      DO 1000 IX=1,RPOINT
C
C   Convert dimensionable r to dimensionless X
C
      X=XF1(IX)*XCONV
      WRITE(6,349)XF1(IX),F1(IX)
349      FORMAT(/,19(' ',27H Calculating at (R,F1) ...
      & F5.2,1XF9.6,1X,18(' '))
C
C   Call GAULEG subroutine (Gauss-Legendre) to find the
C   orthogonal roots (abscissas) and weights over the two
C   intervals: XW - X and X - XSTAR in the mobile region for
C   Gauss-Quadrature integration.
C
      IF(PUMP.EQ.1) THEN
        CALL GAULEG(XW,X,XLOW,WLOW,TEN)
        CALL GAULEG(X,XSTAR,XHI,WHI,TEN)
      ELSE
        CALL GAULEG(XW,X,XLOW,WLOW,TWEN)
        CALL GAULEG(X,XSTAR,XHI,WHI,TWEN)
      ENDIF
C
C   Call DSTFEST subroutine (Stehfest) to invert the
C   dimensionless Laplace transformed mobile region solute
C   concentration (CMBAR). DSTFEST returns with the
C   dimensionless mobile region solute concentration (CONCM)
C
      CALL DSTFEST(CMBAR,N,T,CONCM,TSTEP)
C
      DO 482 N3=1,TSTEP
        WRITE(6,583)T(N3)/TCONV,CONCM(N3)
583      FORMAT(7H Time =2X,F10.5,3X,7HCONCM =,2X,E12.5)
482      CONTINUE
C
C   Setup parameters for calculating and inverting the
C   dimensionless Laplace transformed concentration at points
C   within the immobile region (CABAR). Call GAULEG subroutine
C   (Gauss-Legendre) to find the orthogonal roots (abscissas) and
C   weights in this region for Gauss-Quadrature integration.
C
      IF(MODEL.NE.'LEA') THEN
        DO 225 I7=1,APOINT
          Z=ACA(I7)
          CALL GAULEG(ALIM,Z,ZLOW,WZLOW,TEN)
          CALL GAULEG(Z,BLIM,ZHI,WZHI,TEN)
C

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```

C Print out the immobile concentration at a given radial
C location and location within the immobile region
C
      WRITE(6,749)XF1(IX),Z,CA(IX,I7)
749      FORMAT(29H Calculating at (R,Z,CA) ...
      &      2X,F5.2,2X,F4.2,2X,F9.6)
C
C Call DSTFEST subroutine (Stehfest) to invert the
C dimensionless Laplace transformed concentration at points
C within the immobile region (CABAR). DSTFEST returns with the
C dimensionless concentration at points with the immobile
C region (YTEMP)
C
      CALL DSTFEST(CABAR,N,T,YTEMP,TSTEP)
      CAF(IX,I7)=YTEMP(TSTEP)
      DO 215 K6=1,TSTEP
        WRITE(6,748)T(K6)/TCONV,YTEMP(K6)
748        FORMAT(7H Time =2X,F10.5,2X,9HCONCIM = E12.5)
        CONCIM(I7,K6)=YTEMP(K6)
215      CONTINUE
225      CONTINUE
      M16=APOINT
      ELSE
        M16=1
      ENDIF
C
C Convert dimensionless time to real time and print out
C results: distance or radius from the well, real time, and
C concentration at the fixed distance for both the mobile and
C immobile regions
C
      WRITE(8,501)
501      FORMAT(/,4X,3HXF1,10X,4HTIME,10X,5HCONCM,10X,3HACA,9X,
      &      6HCONCIM/)
      DO 500 K8=1,TSTEP
        DO 510 K9=1,M16
          WRITE(8,520)XF1(IX),((T(K8)/TCONV)+TOFFSET),
          &      CONCM(K8),ACA(K9),CONCIM(K9,K8)
520          FORMAT(5(E11.5,3X))
510          CONTINUE
500          CONTINUE
          F1F(IX)=CONCM(TSTEP)
1000 CONTINUE
C
C Reset mobile and immobile region initial conditions
C
      DO 700 ICX=1,RPOINT
        F1(ICX)=F1F(ICX)
        IF(F1(ICX).LT.0.)F1(ICX)=0.
        WRITE(6,730)XF1(ICX),F1(ICX)
        WRITE(8,730)XF1(ICX),F1(ICX)
730      FORMAT(/,5H R = F5.2,3X,16HInitial CONCM = F12.6,/)
        DO 710 ICZ=1,APOINT

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      CA(ICX,ICZ)=CAF(ICX,ICZ)
      IF(CA(ICX,ICZ).LT.0.)CA(ICX,ICZ)=0.
      WRITE(6,740)ACA(ICZ),CA(ICX,ICZ)
      WRITE(8,740)ACA(ICZ),CA(ICX,ICZ)
740    FORMAT(5H Z = F5.3,3X,17H Initial CONCIM = F11.6)
710    CONTINUE
700    CONTINUE
      TOFFSET=TFIN+TOFFSET
C
C   Ask the user if he/she wants to continue running the
C   simulation
C
      PRINT*,' Do you wish to continue the program? (1=y | 0=n) '
      READ*,PULSE
      IF(PULSE.EQ.1)GOTO 5
C
C   Close all files that were previously opened
C
      CLOSE(7)
      CLOSE(8)
      CLOSE(9)
      CLOSE(10)
      CLOSE(11)
      END
C
C*****
C
      DOUBLE PRECISION FUNCTION CMBAR(S)
C
C   This is an external function used to set up the parameters
C   and calculate the variables associated with the
C   dimensionless Laplace transformed mobile region solute
C   concentration (CMBAR). CMBAR is defined by Equation 3.66 or
C   A.394 for the pump on and 3.105 or A.755 for the pump off
C
      REAL*8 S,ALPHA,PI,BETA,X,XW,XSTAR,XLOW,XHI,WLOW,WHI,GAMA,
&OMEGA,XCONST,DENOM,CONST1,CONST2,CONST3,CONST4,CONST5,
&CONST6,CONST7,CONST8,YW,YSTAR,CEYEO,CEYE1,EYE1,EYEO,EPS,
&Y1,Y2,Y3,Y4,Y5,Y6,Y7,Y8,HK,GI,YTMP,DA,DB,GA,GB,HA,HB,
&DENOM1,DENOM2,YD1,YD2
C
      REAL*8 FBAR,DBSI1E,DBSI0E,CMINT1,CMINT2,CMINT3,CMINT4,
&DTANH,DBSK0E,DBSK1E,DAIE,DBIE,DAIDE,DBIDE
      EXTERNAL FBAR,DBSI1E,DBSI0E,CMINT1,CMINT2,CMINT3,CMINT4,
&DTANH,DBSK0E,DBSK1E,DAIE,DBIE,DAIDE,DBIDE
C
      INTEGER CHOICE,TEN,PUMP,TWEN
C
      DIMENSION XLOW(100),XHI(100),WLOW(100),WHI(100),YTMP(8)
C
      COMMON /ALL/ CHOICE,ALPHA,PUMP
      COMMON /MCMCA/TEN,PI

```

```

COMMON /MCMF/ BETA
COMMON /MCM/ X,XW,XSTAR,XLOW,XHI,WLOW,WHI,YTMP,EPS,TWEN
C
C LEA model (pump on/pump off)
C
  IF(CHOICE.EQ.1) THEN
    GAMA=S
C
C First-order model (pump on/pump off)
C
  ELSE IF(CHOICE.EQ.2) THEN
    GAMA=S*(1.+(BETA*ALPHA/(S+ALPHA)))
C
C Layered diffusion model
C
  ELSE IF(CHOICE.EQ.3) THEN
    IF(PUMP.EQ.1) THEN
      OMEGA=DSQRT(S/ALPHA)
    ELSE
      OMEGA=DSQRT(S)
    ENDIF
    GAMA=S*(1.+(BETA*DTANH(OMEGA)/OMEGA))
C
C Cylindrical model
C
  ELSE IF(CHOICE.EQ.4) THEN
    IF(PUMP.EQ.1) THEN
      OMEGA=DSQRT(S/ALPHA)
    ELSE
      OMEGA=DSQRT(S)
    ENDIF
C
C Set up the Bessel functions I1 and I0. These are IMSL calls
C
    CEYE1=DBSI1E(OMEGA)/(DEXP(-ABS(OMEGA)))
    CEYEO=DBSI0E(OMEGA)/(DEXP(-ABS(OMEGA)))
    GAMA=S*(1.+2.*BETA*CEYE1/(OMEGA*CEYEO))
C
C Spherical model
C
  ELSE
    IF(PUMP.EQ.1) THEN
      OMEGA=DSQRT(S/ALPHA)
    ELSE
      OMEGA=DSQRT(S)
    ENDIF
C
C Set up the Bessel functions i1 and i0.
C
    EYE1=(OMEGA*DCOSH(OMEGA)-DSINH(OMEGA))/OMEGA**2.
    EYEO=DSINH(OMEGA)/OMEGA
    GAMA=S*(1.+3.*BETA*EYE1/(OMEGA*EYEO))
  ENDIF

```

```

C
C Set up the CMBAR equations and constants for the pump on
C
C This X is the the dimensionless radial distance that was
C defined in the main program and is equal to  $X = XF1 * XCONV$ 
C
C Set up the constants associated with Equations 3.66 and A.394
C (pump on). These constants call IMSL external functions to
C solve the Airy (DAIE) and Bairy (DBIE) functions and their
C derivatives, DAIDE (Airy), DBIDE (Bairy). Additionally, due
C to the exponential scaling associated with IMSL routines and
C probles with overflow errors, we establish intermediate
C constants Y1,2,3,4,5,6,7,8 that scale back the Airy and Bairy
C functions and check for overflow and underflow
C
      IF (PUMP.EQ.1) THEN
        YW=(XW+1./(4.*GAMA))*GAMA**(1./3.)
        YSTAR=(XSTAR+1./(4.*GAMA))*GAMA**(1./3.)
        XCONST=(X+1./(4.*GAMA))*GAMA**(1./3.)
        DA=DAIE(XCONST)
        DB=DBIE(XCONST)
        GA=-.5*DAIE(YW)+GAMA**(1./3.)*DAIDE(YW)
        GB=-.5*DBIE(YW)+GAMA**(1./3.)*DBIDE(YW)
        HA=.5*DAIE(YSTAR)+GAMA**(1./3.)*DAIDE(YSTAR)
        HB=.5*DBIE(YSTAR)+GAMA**(1./3.)*DBIDE(YSTAR)
        DENOM1=GB*HB
        DENOM2=GB*HA
        YD1=-2./3.*(YW**1.5)+2./3.*(YSTAR**1.5)
        YD2=2./3.*(YW**1.5)-2./3.*(YSTAR**1.5)
C
C Check for under/overflow. If there is no under/overflow
C potential then we use the equations as derived, if there is a
C potential under/overflow error then we modify the equations
C
      IF (YDW.LT.(-700).OR.(YD2+DLOG(ABS(DENOM2))).LT.(-700))
& THEN
        CONST1=PI*GB*DA/GA
        CONST2=-PI*GB*HA*DB/GA/HB
        CONST3=PI*HA*DB/HB
        CONST4=-PI*DA
        CONST5=PI*GB*DA/GA
        CONST6=-PI*DB
        CONST7=PI*HA*DB/HB
        CONST8=-PI*GB*HA*DA/GA/HB
        Y1=-.5*X+4./3.*(YW**1.5)-2./3.*(XCONST**1.5)
        Y2=-.5*X+4./3.*(YW**1.5)-4./3.*(YSTAR**1.5)+2./3.*
& (XCONST**1.5)
        Y3=-.5*X-4./3.*(YSTAR**1.5)+2./3.*(XCONST**1.5)
        Y4=-.5*X-2./3.*(XCONST**1.5)
        Y5=-.5*X+4./3.*(YW**1.5)-2./3.*(XCONST**1.5)
        Y6=-.5*X+2./3.*(XCONST**1.5)
        Y7=-.5*X-4./3.*(YSTAR**1.5)+2./3.*(XCONST**1.5)

```

```

      Y8=-.5*X+4./3.*(YW**1.5)-4./3.*(YSTAR**1.5)-2./3.*
&      (XCONST**1.5)
C
      ELSE
C
      DENOM=DENOM1*DEXP*YD1)-DENOM2*DEXP (YD2)
      CONST1=PI*GB*HB*DA/DENOM
      Y1=-.5*X+2./3*(YW**1.5)+2./3.*(YSTAR**1.5)-2./3.*
&      (XCONST**1.5)
      CONST2=-PI*GB*HA*DB/DENOM
      Y2=-.5*X+2./3*(YW**1.5)-2./3.*(YSTAR**1.5)+2./3.*
&      (XCONST**1.5)
      CONST3=PI*GA*HA*DB/DENOM
      Y3=-.5*X-2./3*(YW**1.5)-2./3.*(YSTAR**1.5)+2./3.*
&      (XCONST**1.5)
      CONST4=-PI*GA*HB*DA/DENOM
      Y4=-.5*X-2./3*(YW**1.5)+2./3.*(YSTAR**1.5)-2./3.*
&      (XCONST**1.5)
      CONST5=PI*GB*HB*DA/DENOM
      Y5=-.5*X+2./3*(YW**1.5)+2./3.*(YSTAR**1.5)-2./3.*
&      (XCONST**1.5)
      CONST6=-PI*GA*HB*DB/DENOM
      Y6=-.5*X-2./3*(YW**1.5)+2./3.*(YSTAR**1.5)+2./3.*
&      (XCONST**1.5)
      CONST7=PI*GA*HA*DB/DENOM
      Y7=-.5*X-2./3*(YW**1.5)-2./3.*(YSTAR**1.5)+2./3.*
&      (XCONST**1.5)
      CONST8=-PI*GB*HA*DA/DENOM
      Y8=-.5*X+2./3*(YW**1.5)-2./3.*(YSTAR**1.5)-2./3.*
&      (XCONST**1.5)
      ENDIF
C
C Set up the integrals in Equations 3.66 and A.394 by calling
C the external functions CMINT1 and CMINT2. The XLOW and XHI
C arguments passed correspond to the orthogonal roots
C (abscissas) that were calculated by the GAULEG subroutine
C (Gauss-Legendre) in the main program over the two intervals:
C XW - X and X -XSTAR, and s comes from the DSTFEST subroutine
C Note: The number of integrals set up do not correspond to the
C actual number of integrals shown in Equations 3.66/A.394
C due to scaling requirements and overflow/underflow checks
C
      DO 98 I15=1,8
      YTMP(I15)=0.
98      CONTINUE
      DO 100 I20=1,TEN
      YTMP(1)=CMINT1(CONST1,Y1,GAMA,XLOW(I20),S)*WLOW(I20)
&      +YTMP(1)
      YTMP(2)=CMINT1(CONST2,Y2,GAMA,XLOW(I20),S)*WLOW(I20)
&      +YTMP(2)
      YTMP(3)=CMINT2(CONST3,Y3,GAMA,XLOW(I20),S)*WLOW(I20)
&      +YTMP(3)
      YTMP(4)=CMINT2(CONST4,Y4,GAMA,XLOW(I20),S)*WLOW(I20)

```

```

&      +YTMP (4)
      YTMP (5)=CMINT1 (CONST5,Y5,GAMA,XHI (I20),S) *WHI (I20)
&      +YTMP (5)
      YTMP (6)=CMINT1 (CONST6,Y6,GAMA,XHI (I20),S) *WHI (I20)
&      +YTMP (6)
      YTMP (7)=CMINT2 (CONST7,Y7,GAMA,XHI (I20),S) *WHI (I20)
&      +YTMP (7)
      YTMP (8)=CMINT2 (CONST8,Y8,GAMA,XHI (I20),S) *WHI (I20)
&      +YTMP (8)
100    CONTINUE
C
C Solve for CMBAR (Equations 3.66/A.394) by perform the
C numerical integrations by summing CMBAR and YTMP using the
C WLOW and WHI weights that were calculated by the GAULEG
C subroutine (Gauss-Legendre) in the main program over the two
C intervals: XW - X and X -XSTAR
C
      CMBAR=0.
      DO 102 I24=1,8
        CMBAR=CMBAR+YTMP (I24)
102    CONTINUE

C
      ELSE
C
C Set up the constants associated with Equations 3.105 and
C A.755 (pump off). These constants call IMSL routines K1
C (DBSK1E), K0 (DBSK0E), I1 (DBSI1E), and I0 (DBSI0E).
C Additionally, due to the exponential scaling associated with
C IMSL routines and troubles with overflow errors, we establish
C intermediate constants Y1,2,3,4,5,6,7,8 that scale back the
C Bessel functions and check for overflow and underflow
C
      YW=DSQRT (GAMA) *XW
      YSTAR=DSQRT (GAMA) *XSTAR
      HK=EPS*DSQRT (GAMA) *DBSK1E (YSTAR)+DBSK0E (YSTAR)
      GI=EPS*DSQRT (GAMA) *DBSI1E (YSTAR)-DBSI0E (YSTAR)
      CONST1=-HK*DBSI0E (DSQRT (GAMA) *X) /GI
      Y1=DSQRT (GAMA) * (X-2.*XSTAR)
      CONST2=-DBSK0E (DSQRT (GAMA) *X)
      Y2=DSQRT (GAMA) * (-X)
      CONST3=-HK*DBSI0E (DSQRT (GAMA) *X) *DBSI1E (YW) /GI/
&      DBSK1E (YW)
      Y3=DSQRT (GAMA) * (X+2.*XW-2.*XSTAR)
      CONST4=-DBSK0E (DSQRT (GAMA) *X) *DBSI1E (YW) /DBSK1E (YW)
      Y4=DSQRT (GAMA) * (2.*XW-X)
      CONST5=-DBSI0E (DSQRT (GAMA) *X) *hK/GI
      Y5=DSQRT (GAMA) * (X-2.*XSTAR)
      CONST6=-DBSI1E (YW) *DBSK0E (DSQRT (GAMA) *X) *HK/DBSK1E (YW) /
&      GI
      Y6=DSQRT (GAMA) * (2.*XW-2.*XSTAR-X)
      CONST7=-DBSI0E (DSQRT (GAMA) *X)
      Y7=DSQRT (GAMA) *X

```



```

CONST8=-DBSI1E(YW)*DBSK0E(DSQRT(GAMA)*X)/DBSK1E(YW)
Y8=DSQRT(GAMA)*(2.*XW-X)
C
C Set up the integrals in Equations 3.105 and A.755 by calling
C the external functions CMINT3 and CMINT4. The XLOW and XHI
C arguments passed correspond to the orthogonal roots
C (abscissas) that were calculated by the GAULEG subroutine
C (Gauss-Legendre) in the main program over the two intervals:
C XW - X and X -XSTAR, and s comes from the DSTFEST subroutine
C Note: The number of integrals set up do not correspond to the
C actual number of integrals shown in Equations 3.105/A.755 due
C to scaling requirements and overflow/underflow checks
C
      DO 198 I25=1,8
        YTMP(I25)=0.
198      CONTINUE
      DO 200 I30=1,TWEN
        YTMP(1)=CMINT3(CONST1,Y1,GAMA,XLOW(I30),S)*WLOW(I30)
        & +YTMP(1)
        YTMP(2)=CMINT3(CONST2,Y2,GAMA,XLOW(I30),S)*WLOW(I30)
        & +YTMP(2)
        YTMP(3)=CMINT4(CONST3,Y3,GAMA,XLOW(I30),S)*WLOW(I30)
        & +YTMP(3)
        YTMP(4)=CMINT4(CONST4,Y4,GAMA,XLOW(I30),S)*WLOW(I30)
        & +YTMP(4)
        YTMP(5)=CMINT3(CONST5,Y5,GAMA,XHI(I30),S)*WLOW(I30)
        & +YTMP(5)
        YTMP(6)=CMINT3(CONST6,Y6,GAMA,XHI(I30),S)*WLOW(I30)
        & +YTMP(6)
        YTMP(7)=CMINT4(CONST7,Y7,GAMA,XHI(I30),S)*WLOW(I30)
        & +YTMP(7)
        YTMP(8)=CMINT4(CONST8,Y8,GAMA,XHI(I30),S)*WLOW(I30)
        & +YTMP(8)
200      CONTINUE
C
C Solve for CMBAR (Equations 3.105/A.755) by perform the
C numerical integrations by summing CMBAR and YTMP using the
C WLOW and WHI weights that were calculated by the GAULEG
C subroutine (Gauss-Legendre) in the main program over the two
C intervals: XW - X and X -XSTAR
C
      CMBAR=0.
      DO 202 I35=1,8
        CMBAR=CMBAR+YTMP(I35)
202      CONTINUE
C
      ENDIF
      RETURN
      END
C
C*****
C

```

C These functions (CMINT1/CMINT2) set up the integrands in the
 C integrals of CMBAR for when the pump is on (Equations (3.66)
 C and A.394). These functions call on the external function
 C FBAR and the AIRY subroutine

C

```
DOUBLE PRECISION FUNCTION CMINT1(CONST,Y,GAMA,XARG,S)
REAL*8 CONST,Y,GAMA,XARG,S,ARG,DAIE,FBAR,Z
EXTERNAL DAIE,FBAR
ARG=(XARG+1./(4.*GAMA))*GAMA**(1./3.)
CMINT1=CONST*DAIE(ARG)*FBAR(XARG,S)*GAMA**(-1./3.)
```

C

C Because we are numerically unable to scale back the the
 C Airy/Bairy functions at the evaluated arguments, we perform a
 C check of the exponential power and determine if this value is
 C too small for computer computation

C

```
Z=Y-2./3.*(ARG**1.5)+.5*XARG
A=Z+DLOG(ABS(CMINT1))
IF(Z.GT.-700..AND.A.GT.-700)THEN
  CMINT1=CMINT1*DEXP(Z)
ELSE
  CMINT1=0.
ENDIF
RETURN
END
```

C

```
DOUBLE PRECISION FUNCTION CMINT2(CONST,Y,GAMA,XARG,S)
REAL*8 CONST,Y,GAMA,XARG,S,ARG,DBIE,FBAR,Z
EXTERNAL DBIE,FBAR
ARG=(XARG+1./(4.*GAMA))*GAMA**(1./3.)
CMINT2=CONST*DBIE(ARG)*FBAR(XARG,S)*GAMA**(-1./3.)
Z=Y+2./3.*(ARG**1.5)+.5*XARG
A=Z+DLOG(ABS(CMINT2))
IF(Z.GT.-700..AND.A.GT.-700)THEN
  CMINT2=CMINT2*DEXP(Z)
ELSE
  CMINT2=0.
ENDIF
RETURN
END
```

C

C These functions (CMINT3/CMINT4) set up the integrands in the
 C integrals of CMBAR for when the pump is off (Equations
 C (3.105) and A.755). These functions call the external
 C function FBAR, and the IMSL routines

C

```
REAL*8 FUNCTION CMINT3(CONST,Y,GAMA,XARG,S)
REAL*8 CONST,Y,GAMA,XARG,S,ARG,DBSI0E,FBAR,Z
EXTERNAL DBSI0E,FBAR
ARG=CONST*XARG*DBSI0E(DSQRT(GAMA)*XARG)*FBAR(XARG,S)
```

C

C Because we are numerically unable to scale back the the
 C Bessel functions at the evaluated arguments, we perform a

```

C  check of the exponential power and determine if this value is
C  too small for computer computation
C
      Z=Y+DSQRT(GAMA)*XARG
      A=Z+DLOG(ABS(ARG))
      IF(Z.GT.-700..AND.A.GT.-700.) THEN
        CMINT3=ARG*DEXP(Z)
      ELSE
        CMINT3=0.
      ENDIF
      RETURN
      END

C
      REAL*8 FUNCTION CMINT4(CONST,Y,GAMA,XARG,S)
      REAL*8 CONST,Y,GAMA,XARG,S,ARG,DBSK0E,FBAR,Z
      EXTERNAL DBSK0E,FBAR
      ARG=CONST*XARG*DBSK0E(DSQRT(GAMA)*XARG)*FBAR(XARG,S)
      Z=Y-DSQRT(GAMA)*XARG
      A=Z+DLOG(ABS(ARG))
      IF(Z.GT.-700..AND.A.GT.-700.) THEN
        CMINT4=ARG*DEXP(Z)
      ELSE
        CMINT4=0.
      ENDIF
      RETURN
      END

C
C*****
C
      DOUBLE PRECISION FUNCTION FBAR(XARG,S)
C
C  This is an external function used to set up the parameters
C  and calculate the variables associated with FBAR.  FBAR is
C  defined in the case of the pump on by Equations 3.37/A.62
C  (LEA), 3.39/A.81 (First-order), 3.41/A.166 (Layered),
C  3.43/A.244 (Cylindrical), 3.45/A.315 (Spherical) and in the
C  case of the pump off by Equations 3.78/A.455 (LEA),
C  3.80/A.463 (First-order), 3.82/A.541 (Layered), 3.84/A.618
C  (Cylindrical), and 3.86/A.688 (Spherical). Notice that FBAR
C  in both cases only differ by the dimensionless variable XARG
C  or the radial distance X
C
      REAL*8 XARG,S,ALPHA,BETA,AL,XF1,F1,Y2X,AXROOT,AWAIT,OMEGA,
      &INTGRL,YTEMP,XTEMP,YF1,YF1,YPN,YARG,Y2TEMP,Y3TEMP,
      &Y4TEMP,ACA,CA,ACIM,XCONV
C
      REAL*8 LAYER,CYLNDR,SPHERE,DBSI0E
      EXTERNAL LAYER,CYLNDR,SPHERE,DBSI0E
C
      INTEGER CHOICE,APOINT,RPOINT,GEOM,PUMP
C
      DIMENSION XF1(10),F1(10),Y2X(10),AXRCOT(10),AWAIT(10),

```

```

      &YTEMP(10),Y2TEMP(10),Y3TEMP(10),Y4TEMP(10),CA(10,10),
      &ACA(10)
C
      COMMON /ALL/ CHOICE,ALPHA,PUMP
      COMMON /MCMF/ BETA
      COMMON /MCAF/ APOINT,ACA,CA,GEOM,AWAIT,AXROOT
      COMMON /MF/ AL,RPOINT,XF1,F1,Y2X,YTEMP,Y2TEMP,Y3TEMP,
      &Y4TEMP,XCONV
C
C XARG corresponds to the XLOW and XHI arguments passed
C from the CMBAR function through the CMINT functions and are
C the orthogonal roots (abscissas) that were calculated by the
C GAULEG subroutine (Gauss-Legendre) in the main program over
C the intervals: XW - X and X -XSTAR. In order to find the
C concentrations associated with these locations we call on the
C SPLINT subroutine to find these values. Since XARG is a
C dimensionless variable and input parameters are in the
C dimensioned domain, we first convert it back before
C interpolating
C
      XTEMP=XARG/XCONV
      CALL SPLINT(XF1,F1,Y2X,RPOINT,XTEMP,YF1)
C
C The variable STAGNT is used so that a common FBAR can be used
C for when the pump is on and off
C
      IF(PUMP.EQ.1)THEN
        STAGNT=1.
      ELSE
        STAGNT=XARG
      ENDIF
C
C LEA model
C
      IF(CHOICE.EQ.1)THEN
C
C Calculate FBAR
C
        FBAR=-XARG/STAGNT*YF1
C
      ELSE
C
C First-order model and diffusion models.
C
C Since GAULEG (Gaussian Quadrature) determines the location of
C the abscissas at nonequally spaced intervals or at intervals
C that do not correspond to the input immobile locations, we
C call on the SPLINE subroutine to give us the second
C derivative of the function at the input values. SPLINE uses
C the first derivative information at the boundaries (YP1/YPN),
C the radial locations (input), and the immobile concentrations
C (input). In turn, SPLINT uses the second derivative
C information from SPLINE and returns a cubic fit immobile

```

```

C region concentration (y-values) associated with the GAULEG
C locations
C
      YP1=0.
      YPN=1.D30
      DO 20 I1=1,APOINT
        DO 10 I2=1,RPOINT
          YTEMP(I2)=CA(I2,I1)
10      CONTINUE
        CALL SPLINE(XF1,YTEMP,RPOINT,YP1,YPN,Y2TEMP)
        CALL SPLINT(XF1,YTEMP,Y2TEMP,RPOINT,XTEMP,YARG)
        Y3TEMP(I1)=YARG
20      CONTINUE
C
C Find y-values at AXROOT perpendicular to radial arm at XARG
C (see above discussion)
C
      CALL SPLINE(ACA,Y3TEMP,APOINT,YP1,YPN,Y2TEMP)
      DO 30 I3=1,APOINT
C
C Set up the first-order comparison (integral) for the immobile
C region. Recall, we are comparing the immobile region with
C the diffusion models (Equations 3.19/A.145)
C
      CALL SPLINT(ACA,Y3TEMP,Y2TEMP,APOINT,AXROOT(I3),
&      Y4TEMP(I3))
      IF(GEOM.EQ.2)Y4TEMP(I3)=2.D0*AXROOT(I3)*Y4TEMP(I3)
      IF(GEOM.EQ.3)Y4TEMP(I3)=3.D0*(AXROOT(I3)**2.)
&      *Y4TEMP(I3)
30      CONTINUE
      IF(CHOICE.EQ.2)THEN
C
C Perform the numerical integration by calling the AREA
C subroutine
C
      CALL AREA(Y4TEMP,AWAIT,APOINT,ACIM)
C
C Calculate FBAR
C
      FBAR=-XARG/STAGNT*(YF1+(BETA*ALPHA*ACIM)/(S+ALPHA))
C
C Layered model
C
      ELSE IF(CHOICE.EQ.3)THEN
        IF(PUMP.EQ.1)THEN
          OMEGA=DSQRT(S/ALPHA)
        ELSE
          OMEGA=DSQRT(S)
        ENDIF
        DO 100 I7=1,APOINT
C
C Call the LAYER function to set up the integrand in the
C integral within FBAR

```

```

C
      YTEMP(I7)=LAYER(OMEGA,AXROOT(I7),Y4TEMP(I7))
100    CONTINUE
C
C   Perform the numerical integration by calling the AREA
C   subroutine
C
      CALL AREA(YTEMP,AWAIT,APOINT,INTGRL)
C
C   Calculate FBAR
C
      FBAR=-XARG/STAGNT*(YF1+BETA/DCOSH(OMEGA)*INTGRL)
C
C   Cylindrical model
C
      ELSE IF(CHOICE.EQ.4) THEN
        IF(PUMP.EQ.1) THEN
          OMEGA=DSQRT(S/ALPHA)
        ELSE
          OMEGA=DSQRT(S)
        ENDIF
        DO 200 I8=1,APOINT
C
C   Call the CYLNDR function to set up the integrand in the
C   integral within FBAR
C
          YTEMP(I8)=CYLNDR(OMEGA,AXROOT(I8),Y4TEMP(I8))
200    CONTINUE
C
C   Perform the numerical integration by calling the AREA
C   subroutine
C
      CALL AREA(YTEMP,AWAIT,APOINT,INTGRL)
C
C   Calculate FBAR
C
      FBAR=-XARG/STAGNT*(YF1+2.*BETA/(DBSIOE(OMEGA)/(DEXP
&      (-ABS(OMEGA)))))*INTGRL)
C
C   Spherical model
C
      ELSE
        IF(PUMP.EQ.1) THEN
          OMEGA=DSQRT(S/ALPHA)
        ELSE
          OMEGA=DSQRT(S)
        ENDIF
        DO 300 I9=1,APOINT
C
C   Call the SPHERE function to set up the integrand in the
C   integral within FBAR
C

```

```

      YTEMP(I9)=SPHERE(OMEGA,AXROOT(I9),Y4TEMP(I9))
300      CONTINUE
C
C Perform the numerical integration by calling the AREA
C subroutine
C
      CALL AREA(YTEMP,AWAIT,APOINT,INTGRL)
C
C Calculate FBAR
C
      FBAR=-XARG/STAGNT*(YF1+3.*BETA/(DSINH(OMEGA)/OMEGA)
&      *INTGRL)
C
      ENDIF
      ENDIF
      RETURN
      END
C
C*****
C
C These external functions set up the integrands within FBAR
C for the layered, cylindrical, and spherical diffusion models
C (pump on/pump off)
C
      DOUBLE PRECISION FUNCTION LAYER(OMEGA,Z,R)
      REAL*8 OMEGA,Z,R
      LAYER=DCOSH(OMEGA*Z)*R
      RETURN
      END
C
      DOUBLE PRECISION FUNCTION CYLNDR(OMEGA,Z,R)
      REAL*8 OMEGA,Z,R,DBSIOE
      CYLNDR=Z*(DBSIOE(OMEGA*Z)/(DEXP(-ABS(Z*OMEGA))))*R
      RETURN
      END
C
      DOUBLE PRECISION FUNCTION SPHERE(OMEGA,Z,R)
      REAL*8 OMEGA,Z,R
      SPHERE=Z**2.+(DSINH(OMEGA*Z))/(OMEGA*Z)*R
      RETURN
      END
C
C*****
C
      DOUBLE PRECISION FUNCTION CABAR(S)
C
C This is an external function used to set up the
C parameters and calculate the variables associated with CABAR
C for the diffusion models. CABAR is defined in the case of
C the pump on by Equations A.138 (Layered), A.213
C (Cylindrical), A.286 (Spherical) and in the case of the pump
C off by Equations A.516 (Layered), A.587 (Cylindrical), and
C A.659 (Spherical). Notice that CABAR in both cases only

```

```

C differ by the dimensionless immobile region region solute
C diffusion coefficient (ALPHA). Also note that CABAR for
C cylinders and spheres uses limits in terms of 'Z' rather than
C  $\hat{z}$ . This is so we can evaluate R between 0 and 1
C
      REAL*8 S, ALPHA, PI, CA, ACA, Y2, Z, ZHI, ZLOW, WZHI, WZLOW, IOW,
      &AWAIT, CIM, IOZHAT, KOW, KOZHAT, NTGRL1, NTGRL2, YTEMP, Y2TEMP,
      &Y3TEMP, OMEGA, YP1, YPN, AXROOT
C
      REAL*8 CMBAR, CAINT1, CAINT2, CAINT3, CAINT4, CAINT5, CAINT6,
      &DBSI0E, DBSK0E
      EXTERNAL CMBAR, CAINT1, CAINT2, CAINT3, CAINT4, CAINT5, CAINT6,
      &DBSI0E, DBSK0E
C
      INTEGER CHOICE, TEN, APOINT, IX, GEOM, PUMP
C
      DIMENSION CA(10,10), ACA(10), Y2(10), ZHI(10), ZLOW(10),
      &AWAIT(10), WZHI(10), WZLOW(10), YTEMP(10), Y2TEMP(10),
      &Y3TEMP(10), AXROOT(10)
C
      COMMON /ALL/ CHOICE, ALPHA, PUMP
      COMMON /MCMCA/ TEN, PI
      COMMON /MCAF/ APOINT, ACA, CA, GEOM, AWAIT, AXROOT
      COMMON /MCA/ Z, ZHI, ZLOW, WZHI, WZLOW, IX, YTEMP, Y2TEMP,
      &Y3TEMP, Y2
C
      YP1=0.D0
      YPN=1.D0
C
C Set up the first-order immobile region comparison with the
C diffusion models (Equations 3.19/A.145)
C
      DO 100 J1=1, APOINT
        YTEMP(J1)=CA(IX, J1)
        IF (GEOM.EQ.2) YTEMP(J1)=2.D0*AXROOT(J1)*YTEMP(J1)
        IF (GEOM.EQ.3) YTEMP(J1)=3.D0*(AXROOT(J1)**2.)*YTEMP(J1)
100 CONTINUE
C
      IF (CHOICE.EQ.2) THEN
C
C Perform the numerical integration by calling the AREA
C subroutine
C
        CALL AREA(YTEMP, AWAIT, APOINT, CIM)
C
C Solve for CABAR
C
        CABAR=(CIM+ALPHA*CMBAR(S))/(S+ALPHA)
C
      ENDIF
C
C Set up the diffusion models. Note: these models use SPLINE
C and SPLINT to interpolate R at the appropriate GAULEG points

```



```

C
C Layered model
C
      IF (CHOICE.EQ.3) THEN
        IF (PUMP.EQ.1) THEN
          OMEGA=DSQRT(S/ALPHA)
        ELSE
          OMEGA=DSQRT(S)
        ENDIF
        CALL SPLINE(ACA,YTEMP,APOINT,YP1,YPN,Y2)
        DO 200 J2=1,TEN
          CALL SPLINT(ACA,YTEMP,Y2,APOINT,ZHI(J2),Y2TEMP(J2))
          Y2TEMP(J2)=CAINT1(ZHI(J2),Y2TEMP(J2),OMEGA)
          CALL SPLINT(ACA,YTEMP,Y2,APOINT,ZLOW(J2),Y3TEMP(J2))
          Y3TEMP(J2)=CAINT2(ZLOW(J2),Y3TEMP(J2),OMEGA)
200      CONTINUE
C
C Perform the numerical integration by calling the AREA
C subroutine
C
      CALL AREA(Y2TEMP,WZHI,TEN,NTGRL1)
      CALL AREA(Y3TEMP,WZLOW,TEN,NTGRL2)
C
C Solve for CABAR pump on/pump off
C
      IF (PUMP.EQ.1) THEN
        CABAR=CMBAR(S)/DCOSH(OMEGA)*DCOSH(OMEGA*Z)
&      +DCOSH(OMEGA*Z)/OMEGA*ALPHA*DCOSH(OMEGA)*NTGRL1
&      +DSINH(OMEGA*(1-Z))/(OMEGA*ALPHA*DCOSH(OMEGA))*NTGRL2
      ELSE
        CABAR=CMBAR(S)/DCOSH(OMEGA)*DCOSH(OMEGA*Z)+
&      DCOSH(OMEGA*Z)/(OMEGA*DCOSH(OMEGA))*NTGRL1+
&      DSINH(OMEGA*(1-Z))/(OMEGA*DCOSH(OMEGA))*NTGRL2
      ENDIF
C
C Cylindrical model
C
      ELSE IF (CHOICE.EQ.4) THEN
        IF (PUMP.EQ.1) THEN
          OMEGA=DSQRT(S/ALPHA)
        ELSE
          OMEGA=DSQRT(S)
        ENDIF
        CALL SPLINE(ACA,YTEMP,APOINT,YP1,YPN,Y2)
        DO 300 J4=1,TEN
          CALL SPLINT(ACA,YTEMP,Y2,APOINT,ZHI(J4),Y2TEMP(J4))
          Y2TEMP(J4)=CAINT3(ZHI(J4),Y2TEMP(J4),OMEGA)
          CALL SPLINT(ACA,YTEMP,Y2,APOINT,ZLOW(J4),Y3TEMP(J4))
          Y3TEMP(J4)=CAINT4(ZLOW(J4),Y3TEMP(J4),OMEGA)
300      CONTINUE
C
C Perform the numerical integration by calling the AREA
C subroutine

```

```

C
      CALL AREA(Y2TEMP,WZHI,TEN,NTGRL1)
      CALL AREA(Y3TEMP,WZLOW,TEN,NTGRL2)
C
C Set up the Bessel functions I0 and K0
C
      I0W=DBSIOE(OMEGA)*DEXP(ABS(OMEGA))
      I0ZHAT=DBSIOE(OMEGA*Z)*DEXP(ABS(OMEGA*Z))
      K0W=DBSK0E(OMEGA)*DEXP(-OMEGA)
      K0ZHAT=DBSK0E(OMEGA*Z)*DEXP(-OMEGA*Z)
C
C Solve for CABAR (pump on/pump off)
C
      IF(PUMP.EQ.1) THEN
        CABAR=CMBAR(S)/I0W*I0ZHAT-I0ZHAT/((OMEGA**2.)
&      *ALPHA*I0W)*NTGRL1-(K0W*I0ZHAT-I0W*K0ZHAT)/
&      ((OMEGA**2.)*ALPHA*I0W)*NTGRL2
      ELSE
        CABAR=CMBAR(S)/I0W*I0ZHAT-I0ZHAT/((OMEGA**2.)*I0W)
&      *NTGRL1-(K0W*I0ZHAT-I0W*K0ZHAT)/((OMEGA**2.)*I0W)
&      *NTGRL2
      ENDIF
C
C Spherical model
C
      ELSE IF(CHOICE.EQ.5) THEN
        CALL SPLINE(ACA,YTEMP,APOINT,YP1,YPN,Y2)
        IF(PUMP.EQ.1) THEN
          OMEGA=DSQRT(S/ALPHA)
        ELSE
          OMEGA=DSQRT(S)
        ENDIF
        DO 400 J6=1,TEN
          CALL SPLINT(ACA,YTEMP,Y2,APOINT,ZHI(J6),Y2TEMP(J6))
          Y2TEMP(J6)=CAINT5(ZHI(J6),Y2TEMP(J6),OMEGA)
          CALL SPLINT(ACA,YTEMP,Y2,APOINT,ZLOW(J6),Y3TEMP(J6))
          Y3TEMP(J6)=CAINT6(ZLOW(J6),Y3TEMP(J6),OMEGA)
400      CONTINUE
C
C Perform the numerical integration by calling the AREA
C subroutine
C
      CALL AREA(Y2TEMP,WZHI,TEN,NTGRL1)
      CALL AREA(Y3TEMP,WZLOW,TEN,NTGRL2)
C
C Set up the Bessel functions i0 and k0
C
      I0W=DSINH(OMEGA)/OMEGA
      I0ZHAT=DSINH(OMEGA*Z)/(OMEGA*Z)
      K0W=PI*DEXP(-OMEGA)/2.D0/OMEGA
      K0ZHAT=PI*DEXP(-OMEGA*Z)/2.D0/OMEGA/Z
C
C Solve for CABAR (pump on/pump off)

```

```

C
      IF (PUMP.EQ.1) THEN
        CABAR=CMBAR(S)/IOW*I0ZHAT-2.D0*I0ZHAT/(PI*(OMEGA**2.)*
&      ALPHA*IOW)*NTGRL1-2.D0*(KOW*I0ZHAT-IOW*K0ZHAT)/
&      (PI*(OMEGA**2.)*ALPHA*IOW)*NTGRL2
      ELSE
        CABAR=CMBAR(S)/IOW*I0ZHAT-2.D0*I0ZHAT/(PI*(OMEGA**2.)*
&      IOW)*NTGRL1-2.D0*(KOW*I0ZHAT-IOW*K0ZHAT)/(PI*
&      (OMEGA**2.)*IOW)*NTGRL2
      ENDIF
    ENDIF
  RETURN
END

C
C*****
C
C These external functions set up the integrands within CABAR
C for the layered, cylindrical, and spherical diffusion models
C (pump on/pump off)
C
      DOUBLE PRECISION FUNCTION CAIN1(Z,R,OMEGA)
      REAL*8 OMEGA,Z,R
      CAIN1=DSINH( (OMEGA) * (1-Z) ) *R
      RETURN
      END

C
      DOUBLE PRECISION FUNCTION CAIN2(Z,R,OMEGA)
      REAL*8 OMEGA,Z,R
      CAIN2=DCOSH(OMEGA*Z) *R
      RETURN
      END

C
      DOUBLE PRECISION FUNCTION CAIN3(Z,R,OMEGA)
      REAL*8 OMEGA,Z,R,DBSK0E,DBSI0E
      EXTERNAL DBSK0E,DBSI0E
      CAIN3=(DBSK0E(OMEGA)*DBSI0E(Z*OMEGA)*DEXP(OMEGA*(Z-1.))
&-DBSI0E(OMEGA)*DBSK0E(Z*OMEGA))*DEXP
&(OMEGA*(1.-Z))*R*Z*OMEGA**2.
      RETURN
      END

C
      DOUBLE PRECISION FUNCTION CAIN4(Z,R,OMEGA)
      REAL*8 Z,R,DBSI0E,OMEGA
      EXTERNAL DBSI0E
      CAIN4=Z*OMEGA*DBSI0E(Z*OMEGA)*DEXP(ABS(Z*OMEGA))*R*OMEGA
      RETURN
      END

C
      DOUBLE PRECISION FUNCTION CAIN5(Z,R,OMEGA)
      REAL*8 OMEGA,Z,R,PI
      PI=4.*DATAN(1.D0)
      CAIN5=PI*(DEXP(-OMEGA)/(2.*OMEGA)*DSINH(Z*OMEGA)/
&(Z*OMEGA)-DSINH(OMEGA)/OMEGA*DEXP(-Z*OMEGA)/

```

```

&(2.*Z*OMEGA))*R*Z*Z*OMEGA**3.
RETURN
END

C
DOUBLE PRECISION FUNCTION CAINT6(Z,R,OMEGA)
REAL*8 Z,R,OMEGA
CAINT6=DSINH(Z*OMEGA)/(Z*OMEGA)*R*Z*Z*OMEGA**3.
RETURN
END

C
C*****
C
C SPLINE subroutine
C
C SPLINE (X,Y,N,YP1,YPN,Y2)
C
C Purpose - To get an interpolation formula that is smooth in
C           the first derivative, and continuous in the second
C           derivative, both within an interval and at its
C           boundaries
C
C Usage - CALL SPLINE
C
C Reference - Press, William H., Saul A. Teukolsky, William T.
C            Vetterling, and Brian P. Flannery. Numerical
C            Recipes in FORTRAN. Cambridge, MA: Cambridge
C            University Press, 1992.
C
C Arguments - Given arrays X(1:N) and Y(1:N) containing a
C            tabulated function, with  $X_1 < X_2 < X_3 < \dots < X_N$ ,
C            and given values YP1 and YPN for the first
C            derivative of the interpolating function at
C            points 1 and N, respectively, this routine
C            returns an array Y2(1:N) of length N which
C            contains the second derivatives of the
C            interpolated function at the tabulated
C            points  $X_{sub\ i}$ . If YP1 and/or YPN are equal to
C            1.E30 or larger, the routine is signaled to set
C            the corresponding boundary condition for a
C            natural spline, with zero second derivative on
C            that boundary. Parameter NMAX is the largest
C            anticipated value of N.
C
C
SUBROUTINE SPLINE(X,Y,N,YP1,YPN,Y2)
INTEGER N,NMAX
REAL*8 YP1,YPN,X(N),Y(N),Y2(N)
PARAMETER (NMAX=500)
INTEGER I,K
REAL*8 P,QN,SIG,UN,U(NMAX)
IF(YP1.GT.0.99E30) THEN
    Y2(1)=0.
    U(1)=0.
ELSE

```

```

      Y2(1)=-0.5
      U(1)=(3./(X(2)-X(1)))*(Y(2)-Y(1))/(X(2)-X(1))-Y(1)
    ENDIF
    DO 1550, I=2,N-1
      SIG=(X(I)-X(I-1))/(X(I+1)-X(I-1))
      P=SIG*Y2(I-1)+2.
      Y2(I)=(SIG-1.)/P
      U(I)=(6.*(Y(I+1)-Y(I))/(X(I+1)-X(I))-(Y(I)-
& Y(I-1))/(X(I)-X(I-1)))/(X(I+1)-X(I-1))-SIG*U(I-1))/P
1550 CONTINUE
      IF(YPN.GT.0.99E30)THEN
        QN=0.
        UN=0.
      ELSE
        QN=0.5
        UN=(3./(X(N)-X(N-1)))*(YPN-(Y(N)-Y(N-1))/(X(N)-X(N-1)))
      ENDIF
      Y2(N)=(UN-QN*U(N-1))/(QN*Y2(N-1)+1.)
      DO 1510 K=N-1,1,-1
        Y2(K)=Y2(K)*Y2(K+1)+U(K)
1510 CONTINUE
      RETURN
    END

C
C*****
C
C  SPLINT subroutine
C
C  SPLINT (XA,YA,Y2A,N,X,Y)
C
C  Purpose - To obtain values of the interpolated function for
C            any value of X (for "SPLINE interpolation")
C
C  Usage - CALL SPLINT
C
C  Reference - Press, William H., Saul A. Teukolsky, William T.
C            Vetterling, and Brian P. Flannery. Numerical
C            Recipes in FORTRAN. Cambridge, MA: Cambridge
C            University Press, 1992.
C
C  Arguments - Given the arrays XA(1:n) and YA(1:N) of length
C            N, which tabulate a function (with XA's in
C            order), and given the array Y2A(1:N), which is
C            the output from SPLINE, and given a value X,
C            this routine returns a cubic-spline interpolated
C            value Y.
C
C
      SUBROUTINE SPLINT(XA,YA,Y2A,N,X,Y)
      INTEGER N,K,KHI,KLO
      REAL*8 X,Y,XA(N),Y2A(N),YA(N),A,B,H
      KLO=1
      KHI=N
1520 IF (KHI-KLO.GT.1) THEN

```

```

      K=(KHI+KLO)/2
      IF(XA(K).GT.X)THEN
        KHI=K
      ELSE
        KLO=K
      ENDIF
      GOTO 1520
    ENDIF
    H=XA(KHI)-XA(KLO)
    IF(H.EQ.0.)PAUSE ' BAD XA INPUT IN SPLINT'
    A=(XA(KHI)-X)/H
    B=(X-XA(KLO))/H
    Y=A*YA(KLO)+B*YA(KHI)+((A**3-A)*Y2A(KLO)+(B**3-
&B)*Y2A(KHI))* (H**2)/6.
    RETURN
  END

```

```

C
C*****

```

```

C
C GAULEG subroutine
C
C GAULEG (X1,X2,X,W,N)
C
C Purpose - To achieve integration formulas of higher order by
C           providing the freedom to choose the weighting
C           coefficients and the location of the abscissas at
C           which the function is to be evaluated
C
C Usage - CALL GAULEG
C
C Reference - Press, William H., Saul A. Teukolsky, William T.
C            Vetterling, and Brian P. Flannery. Numerical
C            Recipes in FORTRAN. Cambridge, MA: Cambridge
C            University Press, 1992.
C
C Arguments - Given the lower and upper limits of integration
C            'X1' and 'X2,' and given the number of points
C            'N,' this routine returns arrays X(1:N) and
C            W(1:N) of length N, containing the abscissas and
C            weights of the Gauss-Legendre N-point Quadrature
C            formula.
C

```

```

SUBROUTINE GAULEG(X1,X2,X,W,N)
  INTEGER N
  REAL*8 X1,X2,X(N),W(N)
  DOUBLE PRECISION EPS
  PARAMETER (EPS=3.D-14)
  INTEGER I,J,M
  DOUBLE PRECISION P1,P2,P3,PP,XL,XM,Z,Z1,PIE
  M=(N+1)/2
  XM=0.5D0*(X2+X1)
  XL=0.5D0*(X2-X1)
  PIE=4.D0*DATAN(1.D0)

```

```

DO 1600 I=1,M
  Z=COS(PIE*(I-.25D0)/(N+0.5D0))
1601 CONTINUE
  P1=1.D0
  P2=0.D0
  DO 1610, J=1,N
    P3=P2
    P2=P1
    P1=((2.D0*J-1.D0)*Z*P2-(J-1.D0)*P3)/J
1610 CONTINUE
  PP=N*(Z*P1-P2)/(Z*Z-1.D0)
  Z1=Z
  Z=Z1-P1/PP
  IF(ABS(Z-Z1).GT.EPS) GOTO 1601
  X(I)=XM-XL*Z
  X(N+1-I)=XM+XL*Z
  W(I)=2.D0*XL/((1.D0-Z*Z)*PP*PP)
  W(N+1-I)=W(I)
1600 CONTINUE
  RETURN
  END

C
C*****
C
  SUBROUTINE AREA(Y,W,N,SUM)
C
C  This is a user defined subroutine used to numerically
C  calculates the integral of a function, using values Y(i), of
C  length N, at the roots of the Legendre polynomial. The
C  weight functions, W(i), are calculated from subroutine
C  GAULEG. Function values, Y(i), come from subroutine SPLINT.
C
  INTEGER I,N
  REAL*8 Y(N),W(N),SUM
  SUM=0.D0
  DO 1700 I=1,N
    SUM=SUM+Y(I)*W(I)
1700 CONTINUE
  RETURN
  END

C
C*****
C
C  Stehfest subroutine
C
C  DSTFEST (F,N,T,FA,ICOUNT)
C
C  Purpose - Inverse Laplace transform of a user supplied double
C            precision function
C
C  Usage - CALL DSTFEST (F,N,T,FA,ICOUNT)
C

```

C Reference - Stehfest, H., Numerical inversion of Laplace
C transforms, Communications of the ACM, 13(1),
C 47-49, 1970.
C
C Arguments F - A user supplied double precision function,
C F(S), specifying the Laplace transform whose
C inverse is to be calculated (INPUT). The
C calling sequence of this function must be of the
C form F(S) where s is a double precision
C variable. F should be type EXTERNAL in the main
C program.
C
C N - An even number which affects the precision of
C the calculation (INPUT). For double precision,
C N=18 has been shown to provide maximum accuracy
C (Stehfest, 1970).
C
C T - A vector of length ICOUNT containing the
C points at which the inverse Laplace transform is
C to be calculated (INPUT).
C
C FA - Output vector of length ICOUNT. FA(I)
C contains the value of the inverse Laplace
C transform of the user supplied function at T(I).
C
C ICOUNT - The number of points at which the
C inverse Laplace transform is to be calculated
C INPUT).
C

```

SUBROUTINE DSTFEST (F,N,T,FA,ICOUNT)
IMPLICIT REAL*8 (A-H,O-Z)
INTEGER SN,N
DIMENSION G(20), H(10), V(20), T(ICOUNT), FA(ICOUNT)
M=0
DO 999 J=1,ICOUNT
  IF (M.EQ.N) GOTO 10
  G(0)=1.0
  NH=N/2
  DO 20 I=1,N
    G(I)=G(I-1)*I
20  CONTINUE
  H(1)=2./G(NH-1)
  DO 30 I=2,NH
    H(I)=I**NH*G(2*I)/(G(NH-I)*G(I)*G(I-1))
30  CONTINUE
  SN=(-1)**(NH+1)
  DO 40 I=1,N
    V(I)=0.
    KM=INT((I+1)/2)
    IF (I.LT.NH) GOTO 140
    DO 41 K=KM,NH
      V(I)=V(I)+H(K)/(G(I-K)*G(2*K-I))
41  CONTINUE

```



```

        GOTO 45
140      DO 42 K=KM, I
          V(I)=V(I)+H(K)/(G(I-K)*G(2*K-I))
42      CONTINUE
45      V(I)=SN*V(I)
          SN=-SN
40      CONTINUE
          M=N
10      FA(J)=0.
          A=DLOG(2.D0)/T(J)
          DO 50 I=1, N
            FA(J)=FA(J)+V(I)*F(I*A)
50      CONTINUE
999    FA(J)=A*FA(J)
        RETURN
        END
C
C*****

```

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Vita

Capt Thomas A. Adams was born in Uniontown, Pennsylvania on 6 November 1961. He graduated from Cleveland State University with a Bachelor of Mechanical Engineering degree in March 1984. Shortly afterwards, he entered the Air Force through Officers Training School and was commissioned on 26 April 1985. After completing six months of Communications Officer School at Keesler AFB, Mississippi, he was assigned to the 1931 Communications Wing at Elmendorf AFB, Alaska. Serving as a program manager for long-range high frequency (HF) radio systems, Capt Adams implemented and tested an adaptive troposcatter voice/data HF network that significantly improved the reliability of HF communications throughout the theater. Working as the local area network (LAN) program manager for the Alaskan Command and Control Systems Military Automated Network (ACCSMAN), Capt Adams helped implement a state-of-the-art, secure, high-speed fiber optic network. In August 1989, he was reassigned to the 97 Civil Engineering Squadron, Eaker AFB, Arkansas. While working as the base mechanical engineer, Capt Adams obtained his Professional Engineering license. Afterwards, he was appointed to serve as Chief, Construction Management, and then as Chief, Engineering Branch before being reassigned to the Air Force Institute of Technology.

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