Asymptotic Methods Applied to the Geoenvironmental Problems of Ground Subsidence and Soil Vapor Extraction

by

Chiu-On Ng

M.Phil., University of Hong Kong, Hong Kong, 1990
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ABSTRACT

Part I
Finite-Strain Ground Subsidence Theory

In Chapter 1, we develop a finite-strain theory for the joint effects of water pumping and surface loads on ground subsidence in a soil system consisting of a hard aquifer sandwiched by two soft and semipervious layers. Pumping is highly localized and is represented by a single well. On the uncovered part of the ground surface, the pore pressure is assumed to be maintained at a constant value. Beneath a building foundation two types of boundary conditions are considered: one for a monolithic large foundation and one for numerous small and unconnected foundations. The total area covered by the building foundation is assumed to be large in horizontal dimensions compared with the soil thickness. In terms of the small permeability ratio, a perturbation analysis is performed to yield the leading order asymptotic equations. Numerical results are obtained for circular foundations. Space and time variations of the ground settlement is examined for unsealed or sealed foundations. It is found that a rigid and well-sealed foundation can settle much faster than its surrounding soil. With pumping the contact stress between the soil and the rigid foundation will be redistributed with time, resulting in increased stress near the outer edge of the foundation and diminished stress at the center. The physical mechanism is explained by examining the pore pressure and void ratio directly beneath the foundation.

Part II
Transport Theories for Soil Vapor Extraction in Aggregated Soils

In the second part of the thesis, a theoretical study on soil vapor extraction in a vadose zone composed of aggregated soils is presented. In Chapter 2, the macroscale transport equations are derived systematically using the multiple-scale method of homogenization, based on the assumptions that (i) the soil matrix is composed of nearly periodic array of spherical aggregates; within an aggregates water is immobile because of capillary forces; (ii) the aggregates are much smaller than the macroscale;
and (iii) diffusion in the aggregates is much weaker than that in the pore air. Local equilibrium is confirmed as a limiting case of the theory when the aggregate diffusion time is much shorter than the global advection time. In Chapter 3, we first compare the theoretical predictions with some published experiments. On further applying the model to simulate some field-scale soil venting under radial flows, we discuss the effects of the soil, chemical and flow parameters on the performance of soil vapor extraction. In Chapter 4, we develop a vapor transport theory for a layered vadose zone where a thin and semipervious lens is sandwiched by highly porous sand layers. An asymptotic analysis is carried out for an axi-symmetric geometry, yielding quasi-one-dimensional governing equations for individual layers. At the leading order the flow and chemical transport are horizontal in the coarse layers but vertical in the semipervious lens. In Chapter 5, the aggregate diffusion model is extended for the multicomponent vapor transport in the presence of free and trapped phases of residual NAPL. The trapped NAPL is distributed inside aggregates, while the free NAPL is directly in contact with mobile air. While the free NAPL can readily be in equilibrium with macropore vapor, the mass transfer from aggregates is rate-limited by aqueous diffusion. With this model we can solve for the component concentrations and the NAPL saturations, macroscopically and microscopically. The distinctive features of multicomponent transport are confirmed with experimental data, and studied in detail by numerical simulations of a field-scale venting problem.

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List of Symbols

Chapter 1

\( a_v \) \quad \text{coefficient of soil compressibility}
\( b_i \) \quad \text{instantaneous thickness of soil layer } i
\( B_i \) \quad \text{initial thickness of soil layer } i
\( C_c \) \quad \text{virgin compression index}
\( C_s \) \quad \text{swelling and recompression index}
\( D_i \) \quad \text{constrained modulus of soil in layer } i
\( e_i \) \quad \text{void ratio in soil layer } i
\( \mathbf{e}_r, \mathbf{e}_z \) \quad \text{unit vectors along the radial and vertical directions}
\( g \) \quad \text{acceleration due to gravity}
\( J \) \quad \text{Jacobian determinant}
\( K_i \) \quad \text{hydraulic conductivity of soil layer } i
\( n_i \) \quad \text{porosity of soil in layer } i
\( \mathbf{n} \) \quad \text{unit normal vector}
\( p \) \quad \text{pore water pressure}
\( Q \) \quad \text{pumping rate}
\( r, R \) \quad \text{Eulerian and Lagrangian radial coordinate}
\( r_w \) \quad \text{radius of pumping well}
\( s_i \) \quad \text{drawdown in soil layer } i
\( s^* \) \quad \text{transformed drawdown defined in (1.103)}
\( S_i \) \quad \text{storage coefficient of layer } i
$t$  
  time

$t_c$  
  threshold time of foundation losing full bearing support

$u$  
  radial component of solid velocity

$v_s$  
  solid velocity vector

$v_w$  
  pore water velocity vector

$w$  
  vertical component of solid velocity

$W$  
  building weight

$Y$  
  transformed radial coordinate defined in (1.104)

$z, Z$  
  Eulerian and Lagrangian vertical coordinate

$\beta$  
  parameter defined in (1.102)

$\Gamma_i$  
  soil layer interface $i$ (see Figure 1-1)

$\delta$  
  small perturbation parameter defined in (1.28)

$\delta_{ij}$  
  Kronecker delta

$\kappa$  
  parameter defined in (1.102)

$\rho_s$  
  soil grain density

$\rho_w$  
  water density

$\sigma_{ij}$  
  effective stress tensor

$\tau_{ij}$  
  total stress tensor

$\cdot^\prime$  
  initial state

$\cdot^\prime$  
  deviation from initial state

$\cdot$  
  physical scale

$\cdot^{\prime\prime}$  
  normalized quantity

$\cdot^{(m)}$  
  the $m$th perturbation expansion of a quantity

**Chapters 2 and 3**

$a$  
  radius of a spherical aggregate

$C_a$  
  aggregate concentration (total mass per aggregate volume)

$C_g$  
  vapor concentration in macropores

$C_{g0}$  
  characteristic vapor concentration
\( C_g \)  
Laplace transform of \( C_g \)

\( C_j^\alpha \)  
concentration of component \( \alpha \) in phase \( j \)

\( C_s \)  
mass of chemical sorbed per mass of soil

\( C_w \)  
aqueous concentration in an aggregate

\( D_e \)  
sorption-retarded effective diffusivity in an aggregate defined in (2.54)

\( D_g \)  
molecular diffusivity in pure air

\( (D_g^*)_{il} \)  
effective diffusivity in pore air

\( D_w \)  
diffusivity in aggregate solution

\( f_{om} \)  
mass fraction of organic matter in soil

\( F = 0 \)  
mathematical description of \( \Gamma_{ga} \)

\( H \)  
Henry's law constant

\( I_{ga} \)  
total flux from an aggregate into macropore

\( I_j^\alpha_{ji} \)  
rate of mass transfer of component \( \alpha \) from phase \( i \) to phase \( j \)

per bulk volume

\( \bar{J}_j^\alpha \)  
dispersive flux of component \( \alpha \) in phase \( j \)

\( k \)  
soil permeability divided by air dynamic viscosity

\( K_d \)  
solid-water sorption partition coefficient

\( K_{ij} \)  
permeability tensor

\( K_{om} \)  
organic matter-water partition coefficient

\( l \)  
microscopic length scale

\( L \)  
macroscopic length scale

\( M \)  
molecular weight

\( n_i \)  
unit vector to \( \Gamma_{ga} \) directing into aggregate

\( N \)  
number of terms computed in an infinite series

\( N_l \)  
cell function governed by (2.67)–(2.68)

\( p \)  
absolute air pressure

\( p' \)  
pressure deviation = \( p_a - p \)

\( p_0 \)  
pressure in the suction well

\( p_a \)  
atmospheric pressure

\( \hat{p}_a \)  
dimensionless well pressure parameter defined by (3.21)
$Pe$ microscale Péclet number $= U_g l / D_g$

$\overline{Pe}$ macroscale Péclet number $= U_g L / D_g^*$

$r$ microscale radial distance from the center of aggregate (Chapter 2), or macroscale radial distance from the center of contaminated site (Chapter 3)

$r_0$ radius of suction well

$R$ retardation factor $= 1 + \xi$

$Re$ microscale Reynolds number $= U_g l / \nu$

$R_g$ universal gas constant

$s$ independent variable in Laplace transformed space

$S_j$ saturation of phase $j$

$t$ time

$t_p$ duration of pulse input of chemical vapor into a column

$T$ time scale (Chapter 2), or the time before pumping starts (Chapter 3)

$T_a$ time scale for diffusion in an aggregate

$T_t$ transient flow time scale

$u_i$ air velocity components in macropores

$U_g$ air velocity scale

$x_i$ microscale coordinates

$X_i$ macroscale coordinates

$z$ coordinate along a column

$\alpha_N$ dimensionless parameter defined in (3.32)

$\alpha'_N$ dimensionless parameter defined in (3.37)

$\delta_{ij}$ Kronecker delta

$\epsilon$ small perturbation parameter $= l / L$

$\Gamma_{ga}$ interface between macropore and aggregate

$\theta$ total porosity

$\theta_a$ volume fraction of aggregates in soil

$\theta_g$ macroporosity

$\Theta$ absolute temperature
\( \lambda_n \)  parameter defined in (2.81)
\( \mu \)  air dynamic viscosity
\( \nu \)  air kinematic viscosity
\( \xi \)  dimensionless parameter defined in (2.89)
\( \rho \)  air density
\( \rho_b \)  bulk soil density
\( \rho_s \)  solid density of soil grain
\( \sigma \)  dimensionless parameter defined in (2.90)
\( \phi \)  microporosity
\( \Omega \)  a unit cell
\( \Omega_a \)  aggregate domain in \( \Omega \)
\( \Omega_g \)  macropore domain in \( \Omega \)
\( (\cdot) \)  a normalized quantity
\( \langle \cdot \rangle_a \)  bulk average of a quantity in aggregate, defined in (2.18)
\( \langle \cdot \rangle_g \)  bulk average of a quantity in macropore, defined in (2.18)
\( \langle \cdot \rangle \)  average over an aggregate
\( \langle \cdot \rangle^{(m)} \)  the \( m \)th perturbation expansion of a quantity

**Chapter 4**

\( a \)  radius of a spherical aggregate
\( A \)  vapor-aggregate exchange term defined in (4.73)
\( C_g \)  vapor concentration in pore air
\( C_{g0} \)  vapor concentration in the source
\( C_w \)  aqueous concentration in an aggregate
\( d \)  thickness of a layer
\( D \)  effective diffusivity in pore air
\( D_e \)  sorption-retarded effective diffusivity in an aggregate defined in (4.7)
\( D_w \)  aqueous diffusivity in an aggregate
\( F_1, F_2 \)  functions for lower and upper boundaries of the lens
\( H \)  Henry's law constant
\( k \)  air conductivity divided by air specific weight
\( K_d \)  sorption partition coefficient
\( M \)  molecular weight of air mixture
\( p \)  absolute air pressure
\( p' \)  pressure deviation defined by (4.39)
\( p_0 \)  pressure in the suction well
\( P_a \)  atmospheric pressure
\( \dot{P}_a \)  dimensionless well pressure parameter defined by (4.37)
\( Pe \)  Péclet number defined in (4.30)
\((r, z)\)  cylindrical coordinates
\( r_0 \)  radius of the contamination source and the suction well
\( r_b \)  maximum radius of the lens
\( R_g \)  universal gas constant
\( t \)  time variable
\( T \)  time of contamination before pumping
\((u, w)\)  radial and vertical components of air specific discharge
\( \beta_f \)  retardation factor in the lens
\( \delta \)  perturbation parameter defined by (4.20)
\( \delta_D \)  ratio of effective diffusivities in pore air defined by (4.25)
\( \delta_k \)  ratio of air conductivities defined by (4.23)
\( \Gamma_1, \Gamma_2 \)  lower and upper boundaries of the lens
\( \lambda_n \)  parameter defined by (4.6)
\( \Omega \)  layer domain
\( \phi \)  microporosity of aggregate
\( \rho \)  air density
\( \rho_s \)  aggregate solid density
\( \sigma \)  dimensionless parameter defined by (4.75)
\( \theta_a \)  volume fraction of aggregate
\( \theta_g \)  air-filled porosity
\( \Theta \) absolute air temperature

\( \xi \) dimensionless parameter defined by (4.74)

\( \langle \cdot \rangle \) depth-averaged quantity

\( \tilde{\cdot} \) physical scale

\( \tilde{\cdot} \) normalized quantity

\( \langle \cdot \rangle_{i=1,2,3} \) a quantity for the respective coarse layer

\( \langle \cdot \rangle_c \) a quantity for all coarse layers

\( \langle \cdot \rangle_f \) a quantity for the lens

Chapter 5

\( a \) radius of an aggregate

\( C_{ai} \) aggregate concentration of component

\( C_{gi} \) concentration of component \( i \) in trapped air

\( C_{oi} \) concentration of component \( i \) in trapped NAPL

\( C_{wi} \) concentration of component \( i \) in immobile water

\( C'_{gi} \) concentration of component \( i \) in free air

\( C'_{oi} \) concentration of component \( i \) in free NAPL

\( C'_{ti} \) total bulk concentration of component \( i \)

\( C^{sat}_{gi} \) saturation vapor concentration of component \( i \)

\( C^{sat}_{wi} \) saturation aqueous concentration of component \( i \)

\( D_{gi} \) diffusivity of component \( i \) in interaggregate air

\( D^o_{g} \) diffusivity of component \( i \) in pure air

\( D^{*}_{wi} \) diffusivity of component \( i \) in immobile water

\( f_{om} \) mass fraction of organic matter in soil

\( H_i \) Henry's law constant of component \( i \)

\( k \) soil permeability divided by air dynamic viscosity

\( K_{di} \) sorption partition coefficient of component \( i \)

\( K_{omi} \) organic matter-water partition coefficient of component \( i \)
$L'$ macroscopic length scale

$M_i$ molecular weight of component $i$

$N$ number of components in NAPL

$p'$ soil air pressure

$p'_w$ pressure in the pumping well

$P_a$ atmospheric pressure

$P_i^*$ vapor pressure of pure component $i$

$Pe_i$ Péclet number defined in (5.38)

$r$ microscale radial distance from the center of an aggregate

$r'$ macroscale radial distance from the center of spill site

$r'_e$ position of the far evaporation front

$r'_o$ radius of spill site

$r'_w$ radius of screen of pumping well

$R$ universal gas constant

$S_g$ saturation of trapped air in aggregate

$S_o$ saturation of trapped NAPL in aggregate

$S_{o0}$ initial saturation of trapped NAPL in aggregate

$S_w$ saturation of immobile water in aggregate

$S'_o$ saturation of free NAPL in interaggregate space

$S'_{o0}$ initial saturation of free NAPL in interaggregate space

$t$ time

$T$ time before pumping starts

$\bar{u}$ air seepage velocity

$U'$ air seepage velocity scale

$x'$ macroscale coordinates

$y$ transformed radial coordinate defined in (I.1)

$z'$ distance from the bottom of column

$\alpha_i$ dimensionless parameter defined in (5.13)

$\alpha'_i$ dimensionless parameter defined in (5.27)

$\beta_i$ dimensionless parameter defined in (5.14)
\( \gamma_i \)  activity coefficient of component \( i \) in NAPL
\( \theta \)  total porosity
\( \theta_a \)  volume fraction of aggregates in soil
\( \theta_g \)  macroporosity
\( \Theta \)  absolute temperature
\( \Theta_{bi} \)  absolute boiling temperature of component \( i \)
\( \lambda_{ni} \)  parameter defined in (5.20)
\( \xi_i \)  dimensionless parameter defined in (5.39)
\( \rho_{oi} \)  liquid density of component \( i \)
\( \rho_s \)  solid density of soil grain
\( \sigma_i \)  dimensionless parameter defined in (5.44)
\( \phi \)  microporosity
\( \chi_i \)  mole fraction of component \( i \) in trapped NAPL
\( \chi_{i0} \)  initial mole fraction of component \( i \) in trapped and free NAPL
\( \chi_i' \)  mole fraction of component \( i \) in free NAPL
\( \psi \)  transformed aqueous concentration defined in (I.4)
\( \Omega \)  a microscopic unit cell inside an aggregate
\( \Omega_g \)  trapped air in aggregate
\( \Omega_o \)  trapped NAPL in aggregate
\( \Omega_s \)  solid phase in aggregate
\( \Omega_w \)  immobile water in aggregate
\( \Omega' \)  a unit cell containing an aggregate
\( \Omega'_a \)  an aggregate
\( \Omega'_g \)  free air in interaggregate space
\( \Omega'_o \)  free NAPL in interaggregate space
\( \hat{\cdot} \)  normalized quantities defined according to (5.33)
\( \langle \cdot \rangle \)  average over an aggregate
Part I

Finite-Strain Ground Subsidence Theory
Chapter 1

Ground Subsidence of Finite Amplitude Due to Pumping and Surface Loading

1.1 Introduction

Pintung is a county on the western coast of Taiwan. In the past three decades, local economy has been boosted by artificial breeding of giant shrimps for export; the population has also tripled. Fresh water consumption by the inhabitants, the aquaculture and other industries has been mainly supplied by pumping from underground. In an area of 40 km$^2$ where the soil stratum consists of alternating sand and clay layers, over three thousand wells are now known to exist. Thirty years of unregulated pumping have resulted in severe subsidence with a maximum settlement of 2.30 m. A particularly striking and common phenomenon is the faster settlement of buildings relative to the surrounding ground surface. The street floors of many buildings including the local high school have become cellars. New buildings are now constructed on raised foundations such that the street floors are a few meters above the street, in order to anticipate later settlement. While remedies by stricter control of the groundwater usage, and by seeking alternate water resources, are being introduced, the intriguing
phenomenon of enhanced subsidence of the ground surface under buildings has so far not been explained scientifically (Survey of land subsidence in the County of Pintung including Districts of Linbian, Jiatung and Fonliao, Internal Report by the Seventh Engineering Division, Taiwan Provincial Bureau of Water Conservancy, 1986).

Another prominent example of place suffering from ground subsidence is Mexico City which has settled as much as 9 m over the past century as a result of groundwater extraction for domestic and industrial consumptions (e.g., Zeevaert, 1957; Figueroa-Vega, 1984; Poland, 1984). Mexico City is underlain by sediments of volcanic origin deposited during late Pleistocene. Typically, the subsoil consists of two highly compressible silty clay formations of 35 m and 10 m thickness sandwiching a 5 m thick sandy bed. The clays are composed of 80% montmorillonite and 15% kaolinite and have a maximum void ratio 15 and water content as high as 650%. The soils are known to be normally consolidated or slightly overconsolidated. The total rate of groundwater extraction was estimated in early 1970's to be in the order of 12 m$^3$/s and is expected to be much higher nowadays. Operating wells are as deep as 500 m. However, by comparison of casing protrusion and ground settlement, Figueroa-Vega (1984) concluded that about 75–80% of the total subsidence is due to compaction of the clayey strata in the top 50 m. In Mexico City buildings not taller than 5 stories are usually founded on shallow foundations resting on the fill while many of the high-rise buildings are supported by point-bearing piles driven down to the hard sandy stratum at 35 m below ground (Zeevaert, 1957; Marsal, 1957). Ground subsidence therefore poses a great threat to the building safety and must be thoroughly analyzed in the design process.

There are now many comprehensive reports and practical analyses of ground subsidence (Poland and Davis, 1969; Bolt et al., 1977). Mathematical theories, dating back to the seminal work of Hantush and Jacob (1954, 1955a,b) have also been reviewed by many (e.g., Helm, 1982, 1984; Fallou et al., 1992; Lee et al., 1992). Most theories are, however, for small settlement due to pumping alone and are based on the linearized poroelasticity theory of Biot (e.g., Gambolati, 1973; Lewis and Schrefler, 1978; Bear and Corapcio, 1981; Helm, 1987). Only a few authors have taken
into account the effect of finite soil strain (Helm, 1976; Rivera et al., 1991; Fallou et al., 1992; Lee et al., 1992). Apparently there are not any published theories on the combined effects of surface loads and pumping. For finite strains the soil constitutive behavior is necessarily nonlinear, hence the combined effects cannot be obtained by superimposing the two treated separately. A new theory is therefore needed.

The theoretical approach of this study is an extension of Fallou et al. (1992) and Lee et al. (1992) who considered the subsidence due to a single well pumping water from an aquifer in a three-layer soil. The permeability in the semipervious layer is assumed to be much smaller than that in the aquifers, as is often the case in nature. Extensive use of perturbation analysis and the Lagrangian coordinates is a main feature of this approach. By the former, the heuristic quasi-three-dimensional approximation of Hantush and Jacob (1955a,b) that the flow is nearly vertical in the semipervious layer and nearly horizontal in the aquifer, is rendered more systematic. The Lagrangian coordinates which are first used for strictly one-dimensional consolidation in a single layer by Gibson et al. (1967) and Philip (1968), are shown to be particularly powerful for describing the present quasi-three-dimensional problem involving finite deformation and several layers. Physically, Fallou et al. (1992) and Lee et al. (1992) have confirmed the importance of gravity in a soil deformation of finite amplitude. The assumption of constant total stress in time, commonly invoked to simplify Biot's theory, is no longer valid when the consolidating layer is soft and thick.

In the present work we shall consider a soil stratum with three horizontal layers: a confined artesian aquifer sandwiched by two semipervious layers. We assume that all layers are fully saturated, and that the pore pressure at the ground surface remains constant. The last condition implies that any evaporation or drawdown from the ground surface is replenished by recharge from rainfall or regional irrigation. These assumptions are approximately consistent with the observations in Mexico City. During decades of extensive pumping, the water table in the central part of Mexico City has remained at a steady depth of 1–2 m below the ground surface (Zeevaert, 1983). Probable causes of the steadiness in the water table have been attributed to regional
recharge, drainage from an old buried canal and rupture of the existing sewage system (Zeevaert, 1983).

Although the theoretical arguments here resemble those in Lee et al. (1992), the basic governing equations, the essential steps of order estimates and the Lagrangian coordinates are first explained for the sake of clarity. The perturbation analysis of Lee et al. will be modified to derive the leading order asymptotic equations. The initial-boundary-value problem is then solved by an implicit, alternating-direction scheme of finite differences. Numerical results are presented and discussed and their physical meanings revealed for various cases of pumping and surface loading.

1.2 Conservation Laws

As shown in Figure 1-1, the soil stratum consists of two layers of semipervious formation sandwiching an aquifer from which groundwater is pumped directly. Pumping is concentrated in a small region near the origin, and can be due to a cluster of wells, but for simplicity they are symbolically represented by a single well screened over the full depth of the aquifer. The lower confining layer rests on rigid impermeable rock. To study the physical essence without excessive computation, axial symmetry about the well is assumed. An \((r, z)\) coordinate system is defined in Figure 1-1. The surface loading exists only in a concentric circle or annulus centered at the well. Before pumping starts and surface loading is applied, the soil is in static equilibrium; therefore the pore pressure \(\bar{p}\) is hydrostatic, i.e.,

\[
\frac{d\bar{p}}{dz} = -\rho_w g
\]  \hspace{1cm} (1.1)

where \(\rho_w\) is the density of water and \(g\) is the gravitational acceleration. The overhead bar is used to distinguish a quantity of the initial state. The transient change in pore pressure is defined as the drawdown \(s\):

\[
s(r, z, t) = (p(r, z, t) - \bar{p}(z))/\rho_w g.
\]  \hspace{1cm} (1.2)

35
Figure 1-1: Definition sketch of an aquitard-aquifer-aquitard system with a water pumping well and concentric surface loading.

Clearly \( s(r, z, 0) = 0 \) everywhere.

Mass conservation of the water phase requires that

\[
\frac{\partial n \rho_w}{\partial t} + \nabla \cdot (n \rho_w v_w) = 0
\]  \hspace{1cm} (1.3)

for the pore water, where \( n \) denotes the porosity and \( v_w \) the pore water velocity. Mass conservation of the solid matrix requires that

\[
\frac{\partial (1 - n) \rho_s}{\partial t} + \nabla \cdot [(1 - n) \rho_s v_s] = 0,
\]  \hspace{1cm} (1.4)

where \( v_s = u e_r + w e_z \) is the solid velocity and \( \rho_s \) is the soil grain density. The fluid
momentum balance is given by the law of Darcy,

\[ n(v_w - v_s) = -K \nabla s \]  \hspace{1cm} (1.5)

where \( K \) is the hydraulic conductivity. In the present study, isotropy within a layer is assumed, and \( \rho_w \) and \( \rho_s \) are taken to be constant. The preceding three laws can be combined to give the storage equation

\[ \nabla \cdot (K \nabla s) = \nabla \cdot v_s. \]  \hspace{1cm} (1.6)

Note that the right-hand side of (1.6) is the rate of volumetric strain of the soil matrix.

We now turn to the momentum balance of the soil matrix. Adopting the convention of positive tension, we define, after Terzaghi, the effective stress \( \sigma_{ij} \) in the soil matrix by

\[ \sigma_{ij} = \tau_{ij} + p \delta_{ij} \]  \hspace{1cm} (1.7)

where \( \tau_{ij} \) is the total stress and \( \delta_{ij} \) is the Kronecker delta. Neglecting inertia, the solid phase is in quasi-static equilibrium so that

\[ \nabla \cdot \sigma_{ij} = \rho_w g \nabla s + (1 - n)(\rho_s - \rho_w) g e_z. \]  \hspace{1cm} (1.8)

Since the initial drawdown is identically zero, the initial geostatic stress must satisfy

\[ \frac{\partial \sigma_{zz}}{\partial z} = (1 - \bar{n})(\rho_s - \rho_w) g. \]  \hspace{1cm} (1.9)

Further distinguishing deviations from the initial state by a prime, we express a physical quantity as the sum of the initial value and the transient perturbations,

\[ n = \bar{n} + n'; \quad p = \bar{p} + p'; \quad \sigma_{ij} = \bar{\sigma}_{ij} + \sigma'_{ij}; \]
\[ K = \bar{K} + K'; \quad v_s = v'_s; \quad b = \bar{b} + b'; \]  \hspace{1cm} (1.10)
\[ s = s' = \bar{s} + s' = p' / \rho_w g. \]

where \( B \) is the initial thickness of a layer. The above primed quantities are defined
in Eulerian coordinates as functions of \((r, z, t)\). As will be seen in (1.21) and (1.49), the Lagrangian relation between \(s'\) and \(p'\) has a form different from the last of (1.10). Note that the perturbations from the initial state need not be infinitesimal. In terms of the perturbations, (1.8) reads:

\[
\nabla \cdot \sigma'_{ij} = \rho_w g \nabla s' - n'(\rho_s - \rho_w)g e_z.
\]

(1.11)

Thus the change in the effective stress is the combined effect of the changes in the pore pressure and in the porosity. In many existing works on soil consolidation (see, e.g., Verruijt, 1969), it is customary to ignore the vertical variation in the total stress, which amounts to neglecting the effect of the change in porosity, or equivalently, the body force. While this assumption can lead to mathematical simplification by decoupling the drawdown from the soil deformation, its physical fallacies have been pointed out before by Gibson et al. (1967) and discussed by Fallou et al. (1992) and Lee et al. (1992).

In most of the existing theories, only infinitesimal soil deformation is considered and the linear Hooke’s law between stress and strain is assumed. However for finite strains, a more realistic stress-strain relationship is needed. It will be shown after an asymptotic analysis in §1.6.3 that the stress-strain relationship is needed only in one-dimensional form, which is also the only form well established by experiments.

1.3 Boundary and Initial Conditions

1.3.1 Radial Boundary Conditions

We assume that groundwater is pumped at the given rate of \(Q(t)\) from the well

\[
\int_{b_1}^{b_1+b_2} 2\pi r_w K \frac{\partial s'}{\partial r} dz = Q(t), \quad r = r_w, \quad b_1 < z < b_1 + b_2
\]

(1.12)

where \(r_w\) is the outer well radius and \(b_1(r, t)\) and \(b_2(r, t)\) are the instantaneous thicknesses of the lower confining layer and the aquifer respectively.
Far from the well, \( r \to \infty \), all the perturbation (primed) quantities must diminish to zero.

### 1.3.2 Interface Boundary Conditions

Along the fixed and impermeable bottom supporting the solid stratum \( \Gamma_0 : z = 0 \), the solid remains stationary,

\[ u' = w' = 0 \]  \hspace{1cm} (1.13)

where \( u', w' \) are the radial and vertical components of the solid velocity \( v'_s \) respectively, and there is no fluid flux,

\[ \frac{\partial s'}{\partial z} = 0. \]  \hspace{1cm} (1.14)

Along the moving interfaces between the confining layers and the aquifer defined by \( \Gamma_1 : z = b_1(r, t) \) and \( \Gamma_2 : z = b_1(r, t) + b_2(r, t) \), we require the continuity of solid phase velocity

\[ [v'_s]_- = [v'_s]_+, \]  \hspace{1cm} (1.15)

fluid flux relative to the solid phase

\[ [K \nabla s' \cdot n]_- = [K \nabla s' \cdot n]_+, \]  \hspace{1cm} (1.16)

effective stress in the soil

\[ [\sigma'_{ij} \cdot n]_- = [\sigma'_{ij} \cdot n]_+, \]  \hspace{1cm} (1.17)

and drawdown

\[ [s']_- = [s']_+. \]  \hspace{1cm} (1.18)

The subscripts \(-\) and \(+\) denote the quantities approaching the interface from below and above respectively and \( n \) is the unit normal vector.
1.3.3 Ground Surface Conditions

On the ground surface, \( \Gamma_3 : z = b_1(r, t) + b_2(r, t) + b_3(r, t) \) a building foundation rests on a circle centered at the well, \( \Gamma_3^I : r_w \leq r \leq r_o \). The rest of the ground surface is uncovered by surface load. Several types of boundary conditions for the covered part of the surface will be considered.

Uncovered Area

In the uncovered area, denoted by \( \Gamma_3^{U} \), the ground surface is stress-free,

\[
\tau_{z_j} n_j = 0 \quad \text{on} \quad \Gamma_3^{U}.
\]  \hspace{1cm} (1.19)

We also assume that water can freely be discharged or recharged across this unloaded surface such that the pore pressure remains constant, i.e.,

\[
p(r, Z_3 + z', t) = \bar{p}(Z_3)
\]  \hspace{1cm} (1.20)

where \( Z_3 \) and \( z' \) are the initial height and the vertical displacement of the ground surface respectively. From (1.2) we obtain the change in drawdown on the ground surface

\[
s'(r, Z_3 + z', t) = (p(r, Z_3 + z', t) - \bar{p}(Z_3 + z'))/\rho wg
\]

\[
= (p(r, Z_3 + z', t) - \bar{p}(Z_3) + \rho wg z')/\rho wg
\]

\[
= z'
\]  \hspace{1cm} (1.21)

on account of (1.1), and (1.20).

Covered Area

Let the total surface load be \( W \). The area covered by surface load is denoted by \( \Gamma_3^{L} \). Two cases will be distinguished:
Case i. The foundation is a rigid monolithic slab which seals the supporting ground surface perfectly. Therefore the normal water flux is zero

\[ \nabla s' \cdot \mathbf{n} = 0 \quad \text{on} \quad \Gamma_3^L. \quad (1.22) \]

The ground settlement must equal the rigid displacement of the foundation. For a foundation which is rigid in both radial and azimuthal directions, the displacement is vertical and uniform. The unknown displacement is determined by requiring that the integration of the total vertical stress over the foundation must balance the building weight \( W \):

\[ \int_{r_w}^{r_o} 2\pi r r_z' n_j dr = -W \quad \text{on} \quad \Gamma_3^L. \quad (1.23) \]

Case ii. The foundation is a collection of small and unconnected footings. The vertical contact stress is the total load divided by the covered area

\[ \tau_{zj}' n_j = \frac{-W}{\pi (r_o^2 - r_w^2)} \quad (1.24) \]

and invariant with time. Two sub-cases are considered.

(a) The loaded ground surface is perfectly sealed by the foundation so that condition (1.22) applies.

(b) The loaded surface is unsealed to allow free water passage. Thus (1.21) applies.

We remark that in reality, the area may in fact be covered by a few large blocks of buildings, which altogether will give the ground surface some extent of rigidity and sealing. Therefore one may view that the above ground surface conditions, encompassing perfect rigidity/softness and sealing/drainage, represent extreme cases.

Finally, all perturbation quantities are zero at the initial instant.
1.4 Scale Estimates and Normalization

As in Fallou et al. (1992) and Lee et al. (1992), we begin by an estimate of scales for the various quantities. Let us distinguish all scales by a hat. Where necessary, a subscript 1, 2 or 3 will be used to distinguish a scale for the bottom semipervious layer, the middle aquifer or the upper semipervious layer respectively. The arguments leading to these estimates are outlined as follows.

1.4.1 Drawdown and Discharge

By continuity of pressure across the interfaces, the drawdowns in the three layers must all have the same scale. This common scale can be related to the well discharge by (1.12):

\[ \hat{s} = O \left( \frac{\hat{Q}}{2\pi \hat{b}\hat{K}_2} \right) \]  

(1.25)

where \( \hat{b} \) is the common thickness scale for all three layers. In order that the drawdown be comparable to the layer thickness, \( \hat{s} = \hat{b} \) it is necessary that

\[ \hat{Q} = 2\pi \hat{b}^2 \hat{K}_2. \]  

(1.26)

As a numerical illustration, to cause a drawdown of \( \hat{s} = 5 \) m in a semipervious layer with \( \hat{b} = 20 \) m, and \( \hat{K}_2 = 5 \times 10^{-5} \) m/s, the pumping rate must be roughly \( \hat{Q} = 0.03 \) m\(^3\)/s = 2,700 m\(^3\) per day.

1.4.2 Radial Length Scale

By assuming that the well discharge is comparably contributed by radial flow in the aquifer and the vertical flows from the semipervious layers, we can deduce the order relation between \( \hat{b} \) and the horizontal length scale \( \hat{r} \),

\[ \frac{\hat{b}}{\hat{r}} = \left( \frac{\hat{K}_i}{\hat{K}_2} \right)^{1/2} \quad i = 1, 3. \]  

(1.27)
The scale \( \hat{r} \) is known as the *radius of influence*. The hydraulic conductivity of a typical aquifer is of the order \( 10^{-4} - 10^{-6} \) m/s, while that of a semipervious layer is of the order \( 10^{-8} - 10^{-12} \) m/s. Thus the ratio \( \hat{K}_i/\hat{K}_2 \) \((i = 1, 3)\) varies over a wide range of small values \( 10^{-2} - 10^{-8} \), and the ratio of length scales \( \hat{b}/\hat{r} \) varies between \( 10^{-1} - 10^{-4} \). The large contrast in the permeabilities therefore implies shallowness.

As in Fallou *et al.* and Lee *et al.*, the small parameter

\[
\delta = \frac{\hat{K}_i}{\hat{K}_2} = O(\hat{b}/\hat{r})^2 \quad i = 1, 3
\]

(1.28)

will be used in the subsequent asymptotic analyses to gauge all small quantities.

### 1.4.3 Solid Velocity

For the sake of scale estimate only, the linear law of Hooke may be used in the solid momentum equation (1.8). It follows by using (1.27) that in each layer

\[
\frac{\hat{u}}{\hat{w}} = O\left(\frac{\hat{b}}{\hat{r}}\right) = \delta^{\frac{1}{2}},
\]

(1.29)

i.e., the solid matrix deforms faster in the vertical direction. From the storage equation (1.6), we may relate the scale of the vertical solid velocity to that of the hydraulic conductivity for the two semipervious layers

\[
\hat{w}_i = O(\hat{K}_i) \quad i = 1, 3.
\]

(1.30)

Note that isotropy of \( K \) within a layer has been assumed. By continuity, the scales of vertical solid velocity in all layers are the same. However due to the larger stiffness, the rate of vertical strain in the aquifer which is proportional to the differential vertical velocity must be much smaller in magnitude than the vertical velocity itself. Assuming, specifically, that

\[
\frac{\hat{D}_i}{\hat{D}_2} = O(\delta^{1/2}) \quad i = 1, 3
\]

(1.31)
where \( \hat{D} \) is the scale of the constrained modulus of the soil matrix, we then obtain, from the solid momentum equations,

\[
\frac{\Delta \hat{w}_2}{\hat{w}_i} = O(\delta^{1/2}) \quad i = 1, 3
\]  

(1.32)

indicating that the vertical strain in the aquifer is small relative to that in the confining layers.

### 1.4.4 Consolidation Time

Owing to the large contrast in permeability, the vertical consolidation of the aquifer occurs much faster than that of the semipervious layers. Large ground subsidence of the strata is therefore dominated by the consolidation of the highly compressible semipervious layers. As is well known from the one-dimensional theory of Terzaghi, the consolidation time scale is

\[
\hat{t} = \frac{S_i \hat{b}}{K_i} \quad i = 1, 3
\]

(1.33)

where \( S_i \) is the storage coefficient for the semipervious layers given by

\[
S_i = \frac{\rho_w g \hat{b}}{\hat{D}_i} \quad i = 1, 3
\]

(1.34)

which is not small if \( \hat{b} \) is large enough or if \( \hat{D} \) is sufficiently small. For instance, a 20 m thick layer of soft clay with a typical constrained modulus \( \hat{D} \sim 0.5 \) MPa and hydraulic conductivity \( K \sim 10^{-8} \) m/s will have a finite storage coefficient \( S \sim 0.4 \).

We shall therefore assume that \( S_i (i = 1, 3) \) for the semipervious layers are of order unity and the gravity term must be retained. This time scale should remain the same even if nonlinear effects are significant. From this result an estimate may also be made for the scale of change in porosity. From the conservation law of solid mass
(1.4), we obtain from (1.33)

\begin{equation}
\frac{\hat{n}_i'}{1 - \hat{n}_i} \sim \frac{\hat{\Delta} \hat{\omega}_i}{\hat{b}} \sim S_i \quad i = 1, 3.
\end{equation}

(1.35)

Natural soils have porosity \( \hat{n} \sim 0.5 \), hence \( \hat{n}' = O(S) \). We comment also that in (1.11), the ratio of the gravity term to the pore pressure gradient is

\begin{equation}
\hat{n}'_i(\rho_s/\rho_w - 1) = O(\hat{n}'_i) = O(S_i) \quad i = 1, 3.
\end{equation}

(1.36)

Therefore the scale of porosity variation is also of order unity.

### 1.4.5 Stresses in Soil

From (1.7) and (1.11), one can readily infer that the changes in the vertical normal component of the total and effective stresses in soil are scaled by the change in pore pressure

\begin{equation}
\hat{\tau}'_{zz} \sim \hat{\sigma}'_{zz} = O(\rho wg \hat{s}) = O(\rho wg \hat{b})
\end{equation}

(1.37)

and

\begin{equation}
\frac{\hat{\tau}'_{rz}}{\hat{\tau}'_{zz}} \sim \frac{\hat{\sigma}'_{rz}}{\hat{\sigma}'_{zz}} = O(\delta^{\frac{1}{2}}).
\end{equation}

(1.38)

A 20 m thick soil layer will therefore have a vertical stress scale of 200 kPa, which can result in a significant strain if the soil is soft with, say, a constrained modulus of \( \hat{D} = 0.5 \) MPa. The smallness of \( \tau'_{rz} \) means that, to leading order, the boundary conditions on the tangential stress on the ground surface are ineffective. Hence they are omitted in our first order analysis.

Finally we summarize all the normalization scales in Table 1.1 including the Lagrangian variables to be introduced in the next section, and the compressibility coefficient \( a_v \) to be introduced in (1.78). The two semipervious layers share the same set of scales, which are distinguished in Table 1.1 by the subscript 1. All normalized quantities as introduced in the following sections will be distinguished by an overhead tilde.
Table 1.1: Summary of normalization scales.

<table>
<thead>
<tr>
<th>variable or parameter</th>
<th>normalization scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q)</td>
<td>(2\pi b^2 \hat{K}_2)</td>
</tr>
<tr>
<td>(s', z', z, Z)</td>
<td>(\hat{b})</td>
</tr>
<tr>
<td>(r', r, R)</td>
<td>(\delta^{-1/2} \hat{b})</td>
</tr>
<tr>
<td>(t)</td>
<td>(S_1 \hat{b} \hat{K}_1^{-1})</td>
</tr>
<tr>
<td>(p', \sigma_{zz}, \sigma'<em>{zz}, \tau'</em>{zz})</td>
<td>(\rho_w \hat{g} \hat{b})</td>
</tr>
<tr>
<td>(\sigma'<em>{rz}, \tau'</em>{rz})</td>
<td>(\delta^{1/2} \rho_w \hat{g} \hat{b})</td>
</tr>
<tr>
<td>(u', \Delta w_2)</td>
<td>(\delta^{1/2} \hat{K}_1)</td>
</tr>
<tr>
<td>(w', \Delta w_1, \Delta w_2)</td>
<td>(\hat{K}_1)</td>
</tr>
<tr>
<td>(a_v)</td>
<td>(S_1 (\rho_w \hat{g} \hat{b})^{-1})</td>
</tr>
<tr>
<td>(\hat{K}_2)</td>
<td>(\hat{K}_2 = \delta^{-1} \hat{K}_1)</td>
</tr>
<tr>
<td>(K_1, K_3)</td>
<td>(\hat{K}_1)</td>
</tr>
</tbody>
</table>

1.5 Lagrangian Coordinates

As the ground surface and the interfaces displace with time, their current positions are functions of time and the initial positions, and are not known \textit{a priori}. To circumvent the difficulty of imposing boundary conditions along these unknown surfaces, we shall resort to the Lagrangian approach used before by Cooper (1966), Gibson \textit{et al.} (1967), Philip (1968) and by Lee \textit{et al.} (1992).

Let the Lagrangian coordinates \((R, Z)\) represent the initial radial and vertical positions for a solid particle. The Eulerian coordinates are related to the Lagrangian coordinates by

\[
r(R, Z, t) = R + r'(R, Z, t); \quad z(R, Z, t) = Z + z'(R, Z, t) \tag{1.39}
\]

where \(r'\) and \(z'\) are the solid displacements in the radial and the vertical directions respectively. Normalizing according to Table 1.1, we get

\[
\tilde{r} = \tilde{R} + \delta \tilde{r}'(\tilde{R}, \tilde{Z}, \tilde{t}); \quad \tilde{z} = \tilde{Z} + \delta \tilde{z}'(\tilde{R}, \tilde{Z}, \tilde{t}). \tag{1.40}
\]

The first of (1.40) indicates that the radial displacement is of the order \(\delta \ll 1\) relative
to that in the vertical direction. The Jacobian of transformation, or the determinant of the deformation gradient matrix is

\[ J = \frac{\partial (r, z)}{\partial (R, Z)} = 1 + \frac{\partial z'}{\partial Z} + O(\delta). \]  \hspace{1cm} (1.41)

Physically the Jacobian represents the ratio of the current volume to the initial volume for the same piece of solid material. Therefore

\[ J = \frac{1 - \tilde{n}}{1 - n} = \frac{1 + e}{1 + \tilde{e}} \]  \hspace{1cm} (1.42)

where \( e \) is void ratio related to \( n \) by

\[ e = \frac{n}{(1 - n)}, \quad \text{or} \quad n = \frac{e}{(1 + e)}. \]  \hspace{1cm} (1.43)

It follows from (1.41) and (1.42) that to the leading order

\[ \frac{\partial z'}{\partial Z} = \frac{n - \tilde{n}}{1 - n} = \frac{e - \tilde{e}}{1 + \tilde{e}}. \]  \hspace{1cm} (1.44)

While (1.41) implies physically that the bulk volumetric strain is dominated by the vertical strain which is of the order unity, (1.44) is of mathematical importance for changing spatial derivatives from Eulerian to Lagrangian forms. Specifically, for any function \( F(\tilde{r}(\tilde{R}, \tilde{Z}, t), \tilde{z}(\tilde{R}, \tilde{Z}, t), t) \), the chain rule of differentiation gives:

\[ \frac{\partial \tilde{F}}{\partial \tilde{r}} \rightarrow \frac{\partial \tilde{F}}{\partial \tilde{R}} - \frac{\partial z'}{\partial \tilde{R}} \left( \frac{\partial z}{\partial \tilde{Z}} \right)^{-1} \frac{\partial \tilde{F}}{\partial \tilde{Z}} + O(\delta), \]  \hspace{1cm} (1.45)

\[ \frac{\partial \tilde{F}}{\partial \tilde{z}} \rightarrow \left( \frac{\partial \tilde{z}}{\partial \tilde{Z}} \right)^{-1} \frac{\partial \tilde{F}}{\partial \tilde{Z}} + O(\delta) = \frac{1 - n}{1 - \tilde{n}} \frac{\partial \tilde{F}}{\partial \tilde{Z}} + O(\delta) = \frac{1 + \tilde{e}}{1 + e} \frac{\partial \tilde{F}}{\partial \tilde{Z}} + O(\delta), \]  \hspace{1cm} (1.46)

\[ \frac{\partial \tilde{F}}{\partial \tilde{t}} \bigg|_{(\tilde{R}, \tilde{Z})} \rightarrow \frac{\partial \tilde{F}}{\partial \tilde{t}} \bigg|_{(\tilde{R}, \tilde{Z})} + S_1 \tilde{w} \frac{\partial \tilde{F}}{\partial \tilde{z}} + O(\delta). \]  \hspace{1cm} (1.47)
In deriving (1.47) use has been made of

$$\frac{\partial \tilde{z}'}{\partial \tilde{t}} = S_1 \tilde{w}'$$

(1.48)

according to the scaling law of Table 1.1. Finally we may obtain the Lagrangian expression for the drawdown \(s'(\hat{R}, \hat{Z}, \hat{t})\) in terms of \(p'(\hat{R}, \hat{Z}, \hat{t})\),

$$s'(\hat{R}, \hat{Z}, \hat{t}) = s'(\hat{r}(\hat{R}, \hat{Z}, t), \hat{z}(\hat{R}, \hat{Z}, t), t)$$

$$= \hat{p}(\hat{R}, \hat{Z}, \hat{t}) - \hat{p}(\hat{z}(\hat{R}, \hat{Z}, \hat{t}))$$

$$= \hat{p}(\hat{R}, \hat{Z}, \hat{t}) - \hat{p}(\hat{Z} + \hat{z}')$$

$$= \hat{p}(\hat{R}, \hat{Z}, \hat{t}) - \hat{p}(\hat{R}, \hat{Z}, 0) + \hat{z}'$$

$$= p'(\hat{R}, \hat{Z}, \hat{t}) + \hat{z}'(\hat{R}, \hat{Z}, \hat{t})$$

(1.49)

Equation (1.49) holds for any moving solid particle. On the ground surface \(\hat{p}' = 0\), hence \(s' = \hat{z}'\) which has been deduced in (1.21). We point out that the corresponding Eulerian relation given by the last of (1.10) is different in form.

1.6 Asymptotic Analysis

1.6.1 Solid Equilibrium

For all three layers, the normalized equation for the solid equilibrium in the \(z\) direction is obtained from (1.8)

$$\frac{\partial(\tilde{\sigma}_{zz} + \delta'_{zz})}{\partial \tilde{z}} + \frac{\delta}{\hat{r}} \frac{\partial}{\partial \hat{r}} (\hat{r} \delta_{rz}) = \frac{\partial s'}{\partial \tilde{z}} + (1 - n) \left( \frac{\rho_s}{\rho_w} - 1 \right).$$

(1.50)

The following perturbation expansion

$$\tilde{f}' = \tilde{f}^{(0)} + \delta \tilde{f}^{(1)} + \cdots$$

(1.51)
where $f$ stands for $\sigma_{zz}, \sigma_{rz}$, and $s$, will be substituted into (1.50). Transforming to Lagrangian derivatives according to (1.46), we get

$$\frac{\partial (\tilde{\sigma}_{zz} + \tilde{\sigma}_{zz}^{(0)})}{\partial \tilde{Z}} = \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{Z}} + (1 - \tilde{n}) \left( \frac{\rho_s}{\rho_w} - 1 \right) + O(\delta). \quad (1.52)$$

Since the initial state is given by

$$\frac{\partial \tilde{\sigma}_{zz}}{\partial \tilde{Z}} = (1 - \tilde{n}) \left( \frac{\rho_s}{\rho_w} - 1 \right) \quad (1.53)$$

the difference of (1.52) and (1.53) is

$$\frac{\partial \tilde{\sigma}_{zz}^{(0)}}{\partial \tilde{Z}} = \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{Z}} + O(\delta). \quad (1.54)$$

We emphasize that the disappearance of the gravity term in this Lagrangian relation does not imply the constancy in depth of the total stress variation in Eulerian coordinates, as is often assumed in the literature. The Eulerian counterpart of (1.54) is obtainable by subtracting the initial state equation (1.53) from (1.50)

$$\frac{\partial \tilde{\sigma}^{(0)}_{zz}}{\partial \tilde{z}} = \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{z}} + (\tilde{n} - n) \left( \frac{\rho_s}{\rho_w} - 1 \right) + O(\delta). \quad (1.55)$$

Use has been made of the fact that (1.53) also holds in Eulerian form since $\tilde{Z} = \tilde{z}(\tilde{R}, \tilde{Z}, 0)$. As already shown in (1.36), the change in porosity has the same order of magnitude as the storage coefficient of the semipervious layers which is assumed to be of order unity. Therefore on the right-hand side of (1.55) the second term which represents the gravity effect is as important as the first term. Clearly the departure of the total stress from the initial state is not constant in $\tilde{z}$.

Integrating (1.54) from the top surface $\Gamma_i : \tilde{Z} = \tilde{Z}_i$ for each layer gives

$$\tilde{\sigma}_{zz}^{(0)}(\tilde{R}, \tilde{Z}, \tilde{t}) - \tilde{\sigma}_{zz}^{(0)} \bigg|_{\Gamma_i} = \tilde{s}_i^{(0)}(\tilde{R}, \tilde{Z}, \tilde{t}) - \tilde{s}_i^{(0)} \bigg|_{\Gamma_i} + O(\delta) \quad i = 1, 2, 3. \quad (1.56)$$

From the normalized form of (1.7) and (1.49) and expanding $\tilde{r}_{zz}'$ and $\tilde{z}'$ according to
(1.51), we obtain along the ground surface $\Gamma_3$:

$$
\sigma^{(0)}_{3zz}\big|_{\Gamma_3} - \delta^{(0)}_{3zz}\big|_{\Gamma_3} = \tau^{(0)}_{3zz}\big|_{\Gamma_3} - \delta^{(0)}_{3zz}\big|_{\Gamma_3}.
$$

(1.57)

Therefore, in the upper semipervious layer, $\tilde{B}_1 + \tilde{B}_2 < \tilde{Z} < \tilde{B}_1 + \tilde{B}_2 + \tilde{B}_3$, we get by substituting (1.57) into (1.56)

$$
\tilde{\sigma}^{(0)}_{3zz}(\tilde{R}, \tilde{Z}, \tilde{t}) = \tilde{\delta}^{(0)}_{3zz}(\tilde{R}, \tilde{Z}, \tilde{t}) - \tilde{\delta}^{(0)}_{3zz}\big|_{\Gamma_3} + \tilde{\tau}^{(0)}_{3zz}\big|_{\Gamma_3}.
$$

(1.58)

To obtain the boundary stress and drawdown at the other two interfaces $\Gamma_1$ and $\Gamma_2$, we make use of the stress continuity given by (1.17) and (1.18) where the unit normal vectors along the two interfaces are given respectively by

$$
n_1 = \left(1 - \frac{1}{2} \delta \left(\frac{\partial \tilde{b}_1}{\partial \tilde{r}}\right)^2\right)e_z - \delta \frac{1}{2} \frac{\partial \tilde{b}_1}{\partial \tilde{r}} e_r + O(\delta^{\frac{3}{2}}),
$$

(1.59)

$$
n_2 = \left(1 - \frac{1}{2} \delta \left(\frac{\partial \tilde{b}_2}{\partial \tilde{r}}\right)^2\right)e_z - \left(\delta \frac{1}{2} \frac{\partial \tilde{b}_1}{\partial \tilde{r}} + \delta \frac{1}{2} \frac{\partial \tilde{b}_2}{\partial \tilde{r}}\right)e_r + O(\delta^{\frac{3}{2}}).
$$

(1.60)

To the leading order, $n_1 \sim n_2 \sim e_z$, and continuity of the vertical normal stresses and the drawdowns across the interfaces imply that

$$
\tilde{\sigma}^{(0)}_{1zz}\big|_{\Gamma_1} = \tilde{\sigma}^{(0)}_{2zz}\big|_{\Gamma_1}; \quad \tilde{\sigma}^{(0)}_{2zz}\big|_{\Gamma_2} = \tilde{\sigma}^{(0)}_{3zz}\big|_{\Gamma_2}.
$$

(1.61)

and

$$
\tilde{\sigma}^{(0)}_{1zz}\big|_{\Gamma_1} = \tilde{\sigma}^{(0)}_{2zz}\big|_{\Gamma_1}; \quad \tilde{\sigma}^{(0)}_{2zz}\big|_{\Gamma_2} = \tilde{\sigma}^{(0)}_{3zz}\big|_{\Gamma_2}.
$$

(1.62)

Therefore in the middle aquifer, $\tilde{B}_1 < \tilde{Z} < \tilde{B}_1 + \tilde{B}_2$, (1.56) and (1.6) give the second equations in (1.61) and (1.62) give

$$
\tilde{\sigma}^{(0)}_{2zz}(\tilde{R}, \tilde{Z}, \tilde{t}) - \tilde{\sigma}^{(0)}_{3zz}\big|_{\Gamma_2} = \tilde{s}^{(0)}_{2zz}(\tilde{R}, \tilde{Z}, \tilde{t}) - \tilde{s}^{(0)}_{3zz}\big|_{\Gamma_2}.
$$

(1.63)
Then adding (1.58) evaluated at the interface $\bar{\Gamma}_2$ to (1.63) gives

$$\tilde{\sigma}_{zz}^{(0)}(\bar{R}, \bar{Z}, \tilde{t}) = \tilde{s}_2^{(0)}(\bar{R}, \bar{Z}, \tilde{t}) - \tilde{z}_3^{(0)} \big|_{\Gamma_3} + \tilde{\tau}_{3zz}^{(0)} \big|_{\Gamma_3}. \quad (1.64)$$

By similar arguments and using (1.56), the first equations in (1.61) and (1.62), and (1.64), we can also derive for the lower semipervious layer $0 < \bar{Z} < \bar{B}_1$

$$\tilde{\sigma}_{zz}^{(0)}(\bar{R}, \bar{Z}, \tilde{t}) = \tilde{s}_1^{(0)}(\bar{R}, \bar{Z}, \tilde{t}) - \tilde{z}_3^{(0)} \big|_{\Gamma_3} + \tilde{\tau}_{3zz}^{(0)} \big|_{\Gamma_3}. \quad (1.65)$$

In summary we have obtained the following relation for each of the three layers:

$$\tilde{\sigma}_{zz}^{(0)}(\bar{R}, \bar{Z}, \tilde{t}) = \tilde{s}_i^{(0)}(\bar{R}, \bar{Z}, \tilde{t}) - \tilde{z}_3^{(0)} \big|_{\Gamma_3} + \tilde{\tau}_{3zz}^{(0)} \big|_{\Gamma_3}. \quad i = 1, 2, 3 \quad (1.66)$$

Note that so far no specific boundary conditions on $\bar{\Gamma}_3$ have been used to derive (1.66), and therefore the relation is valid in general. Note also that the gravity effect emerges again in the boundary term $\tilde{z}_3^{(0)} \big|_{\Gamma_3}(\bar{R}, \tilde{t})$, which is the ground surface displacement due to the accumulative effect of the change in porosity across all the layers. The other boundary term $\tilde{\tau}_{3zz}^{(0)} \big|_{\Gamma_3}(\bar{R}, \tilde{t})$ is the surface stress, which is either zero on a free surface, or equal to the contact stress on the base of a foundation.

Before pumping and surface loading begin, all soil layers and the interfaces are assumed to be horizontal and the initial values of the soil parameters are functions of depth only. The initial state void ratio $\bar{e}(Z)$ is determined as in Fallou et al. (1992) and Lee et al. (1992). Briefly, the variation of the initial void ratio is assumed to be resulted from a one-dimensional vertical compression due to initial geostatic effective stress given by (1.9). Based on constitutive laws to be stated in §1.6.3, we prescribe reference values (see end of §1.8) of void ratio at the top of each soil layer to obtain the initial values of $\bar{e}(Z)$, $\bar{\sigma}_{zz}(Z)$, and $\bar{K}(Z)$. Initially the contact stress between the ground surface and the foundation is uniformly distributed and the resultant thrust balances the total building weight.
1.6.2 The Fluid Phase

Middle Aquifer

In Eulerian coordinates, the normalized form of the storage equation (1.6) reads

\[
\frac{\partial}{\partial \tilde{z}} \left( \tilde{K}_2 \frac{\partial \tilde{s}_2^\prime}{\partial \tilde{z}} \right) + \frac{\delta}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \tilde{K}_2 \frac{\partial \tilde{s}_2^\prime}{\partial \tilde{r}} \right) = \frac{\delta^2}{\tilde{r}} \frac{\partial (\tilde{r} \tilde{u}_1^\prime)}{\partial \tilde{r}} + \frac{\delta^2}{\tilde{z}} \frac{\partial \tilde{w}_2^\prime}{\partial \tilde{z}}.
\] (1.67)

Substituting (1.59) and (1.60) for the two unit normal vectors into the boundary condition (1.16), we get on \( \tilde{\Gamma}_1 \)

\[
\delta \tilde{K}_1 \frac{\partial \tilde{s}_1}{\partial \tilde{z}} = -\delta \tilde{K}_2 \left( \frac{\partial \tilde{b}_1}{\partial \tilde{r}} \right) \frac{\partial \tilde{s}_2}{\partial \tilde{r}} + \tilde{K}_2 \frac{\partial \tilde{s}_2}{\partial \tilde{z}} \left( 1 - \frac{1}{2} \delta \left( \frac{\partial \tilde{b}_1}{\partial \tilde{r}} \right)^2 \right) + O(\delta^2),
\] (1.68)

while on \( \tilde{\Gamma}_2 \)

\[
\delta \tilde{K}_3 \frac{\partial \tilde{s}_3}{\partial \tilde{z}} = -\delta \tilde{K}_2 \left( \frac{\partial \tilde{b}_1}{\partial \tilde{r}} \right) \frac{\partial \tilde{s}_2}{\partial \tilde{r}} + \tilde{K}_2 \frac{\partial \tilde{s}_2}{\partial \tilde{z}} \left( 1 - \frac{1}{2} \delta \left( \frac{\partial \tilde{b}_1}{\partial \tilde{r}} \right)^2 \right) + O(\delta^2).
\] (1.69)

Let us now introduce into (1.67) – (1.69) the perturbation expansion (1.51) for the drawdown. At the leading order \( O(\delta^0) \), \( \tilde{s}_2^{(0)} \) is independent of depth, hence

\[
\tilde{s}_2^{(0)}(\tilde{r}, \tilde{t}) = \tilde{s}_1^{(0)}(\tilde{r}, \tilde{b}_1, \tilde{t}) = \tilde{s}_3^{(0)}(\tilde{r}, \tilde{b}_1 + \tilde{b}_2, \tilde{t}).
\] (1.70)

This result implies that the seepage flow in the highly permeable aquifer is essentially horizontal. At the order \( O(\delta) \) we have from (1.67)

\[
\frac{\partial}{\partial \tilde{z}} \left( \tilde{K}_2 \frac{\partial \tilde{s}_2^{(1)}}{\partial \tilde{z}} \right) = -\frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \tilde{K}_2 \frac{\partial \tilde{s}_2^{(0)}}{\partial \tilde{r}} \right),
\] (1.71)

while the boundary conditions (1.68) and (1.69) give

\[
\tilde{K}_2 \frac{\partial \tilde{s}_2^{(1)}}{\partial \tilde{z}} = \tilde{K}_1 \frac{\partial \tilde{s}_1^{(0)}}{\partial \tilde{z}} + \tilde{K}_2 \left( \frac{\partial \tilde{b}_1}{\partial \tilde{r}} \right) \frac{\partial \tilde{s}_2^{(0)}}{\partial \tilde{r}} + \frac{1}{2} \tilde{K}_2 \left( \frac{\partial \tilde{b}_1}{\partial \tilde{r}} \right)^2 \frac{\partial \tilde{s}_2^{(0)}}{\partial \tilde{z}} \quad \text{on } \Gamma_1,
\] (1.72)
\[ \tilde{K}_2 \frac{\partial \tilde{s}^{(1)}_2}{\partial \tilde{z}} = \tilde{K}_3 \frac{\partial \tilde{s}^{(0)}_3}{\partial \tilde{z}} + \tilde{K}_2 \left( \frac{\partial \tilde{b}_1}{\partial \tilde{r}} \right) \frac{\partial \tilde{s}^{(0)}_2}{\partial \tilde{r}} + \frac{1}{2} \tilde{K}_2 \left( \frac{\partial \tilde{b}_1}{\partial \tilde{r}} \right)^2 \frac{\partial \tilde{s}^{(0)}_2}{\partial \tilde{z}} \quad \text{on } \Gamma_2. \]  

Integrating (1.71) with respect to \( \tilde{z} \) across the aquifer and using the boundary conditions (1.72) and (1.73), we can obtain an equation for \( \tilde{s}^{(0)}_2 \) which, when transformed to Lagrangian coordinates according to (1.45) and (1.46), becomes

\[ \tilde{K}_3 \left( \frac{1 + \tilde{e}_3}{1 + e_3} \right) \frac{\partial \tilde{s}^{(0)}_3}{\partial \tilde{Z}} \bigg|_{\Gamma_2} - \tilde{K}_1 \left( \frac{1 + e_1}{1 + e_1} \right) \frac{\partial \tilde{s}^{(0)}_1}{\partial Z} \bigg|_{\Gamma_1} = -\frac{\tilde{B}_2 \tilde{K}_2}{\tilde{R}} \frac{\partial}{\partial \tilde{R}} \left( \tilde{R} \frac{\partial \tilde{s}^{(0)}_2}{\partial \tilde{R}} \right). \]  

This is simply the mass conservation equation in the aquifer, since the left-hand side gives the vertical leakage from the semipervious confining layers, while the right-hand side gives the net radial flux. Note that the flow in the aquifer is quasi-steady, a consequence from its much higher hydraulic diffusivity than the confining layers.

**Upper Semipervious Layer**

For the upper semipervious layer, the normalized storage equation is

\[ \frac{\partial}{\partial \tilde{Z}} \left( \tilde{K}_3 \frac{\partial \tilde{z}^{(0)}_3}{\partial \tilde{Z}} \right) + \frac{\delta}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \tilde{K}_3 \frac{\partial \tilde{z}^{(0)}_3}{\partial \tilde{r}} \right) = \frac{\partial \tilde{w}^{(0)}_3}{\partial \tilde{Z}} + \frac{\delta}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} (\tilde{r} \tilde{u}^{(0)}_3). \]  

As before, on expanding the drawdown and the velocities and converting from Euclidean to the Lagrangian derivatives, we get from the leading order of (1.75):

\[ \frac{\partial}{\partial \tilde{Z}} \left( \tilde{K}_3 \frac{1 + \tilde{e}_3}{1 + e_3} \frac{\partial \tilde{z}^{(0)}_3}{\partial \tilde{Z}} \right) = \frac{\partial \tilde{w}^{(0)}_3}{\partial \tilde{Z}} + O(\delta). \]  

The right-hand side is equal to the rate of normal strain in the vertical direction and can be manipulated as follows:

\[ \frac{\partial \tilde{w}^{(0)}_3}{\partial \tilde{Z}} = \frac{\partial}{\partial \tilde{Z}} \frac{\partial \tilde{z}^{(0)}_3}{\partial \tilde{Z}} \approx \frac{1}{S_1} \frac{\partial}{\partial \tilde{t}} \frac{\partial \tilde{z}^{(0)}_3}{\partial \tilde{Z}} = \frac{1}{S_1} \frac{\partial}{\partial \tilde{t}} \left( \frac{e_3 - \tilde{e}_3}{1 + e_3} \right) \]

\[ = \frac{1}{S_1(1 + e_3)} \frac{\partial e_3}{\partial \tilde{t}} = \frac{1}{S_1(1 + e_3)} \frac{\partial e_3}{\partial \tilde{t}} \frac{\partial \tilde{z}^{(0)}_3}{\partial \tilde{Z}} \frac{\partial \tilde{z}^{(0)}_3}{\partial \tilde{Z}} \frac{\partial \tilde{w}^{(0)}_3}{\partial \tilde{Z}} = \frac{\tilde{a}_v}{1 + e_3} \frac{\partial \tilde{z}^{(0)}_3}{\partial \tilde{Z}}. \]  

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In the final step of (1.77), we have introduced the coefficient of one-dimensional compressibility

\[ a_v = \left( \frac{S_1}{\rho_w g b} \right) \tilde{a}_v \equiv \frac{de}{d\sigma_{zz}} \quad (1.78) \]

Putting (1.77) back into (1.76) and making use of (1.66), we finally get for the upper confining layer,

\[
\frac{\partial}{\partial \tilde{Z}} \left( \tilde{K}_1 \frac{1 + \tilde{e}_3}{1 + e_3} \frac{\partial \tilde{s}_3^{(0)}}{\partial \tilde{Z}} \right) = \frac{\tilde{a}_v}{1 + \tilde{e}_3} \frac{\partial}{\partial t} \left( \tilde{s}_3^{(0)} - \tilde{z}_3^{(0)} \right|_{\tilde{f}_3} + \tilde{\tau}_{3zz}^{(0)} \right|_{\tilde{f}_3},
\]

\[ \tilde{B}_1 + \tilde{B}_2 < \tilde{Z} < \tilde{B}_1 + \tilde{B}_2 + \tilde{B}_3. \quad (1.79) \]

**Lower Semipervious Layer**

Following the same steps as in the upper semipervious layer, one finds that the resulting governing equation is formally the same as for the upper semipervious layer. That is, for \( 0 < \tilde{Z} < \tilde{B}_1 \):

\[
\frac{\partial}{\partial \tilde{Z}} \left( \tilde{K}_1 \frac{1 + \tilde{e}_1}{1 + e_1} \frac{\partial \tilde{s}_1^{(0)}}{\partial \tilde{Z}} \right) = \frac{\tilde{a}_v}{1 + \tilde{e}_1} \frac{\partial}{\partial t} \left( \tilde{s}_1^{(0)} - \tilde{z}_1^{(0)} \right|_{\tilde{f}_3} + \tilde{\tau}_{1zz}^{(0)} \right|_{\tilde{f}_3}. \quad (1.80) \]

### 1.6.3 Constitutive Relations

From the results obtained in the previous subsections, it is clear that information on the constitutive relation between stress and deformation is needed only for the soft semipervious layers, and only in the vertical direction. We shall adopt the following empirical law obtained from one-dimensional compression tests:

\[ e - \bar{e} = -C_c \log_{10} \left( \frac{\tilde{\sigma}_{zz} + \tilde{\sigma}'_{zz}}{\tilde{\sigma}_{zz}} \right). \quad (1.81) \]

Here \( C_c \) is the compression index of the soil. Equation (1.81) also implies a relation for the coefficient of compressibility

\[ \tilde{a}_v = - \left( \frac{C_c}{S_1 \ln 10} \right) \frac{1}{(\tilde{\sigma}_{zz} + \tilde{\sigma}'_{zz})}. \quad (1.82) \]
Figure 1-2: Simplified constitutive relations between void ratio and effective stress under virgin compression and unloading.

For many soils the compression index $C_c$ is practically a constant within a stress range when the soil is normally consolidated. However when the soil is unloaded or reloaded when overconsolidated, $C_c$ takes on a smaller value. In short $C_c$ depends on the stress history and the direction of stress change. We shall follow a simplified model for (1.81), as used by Lee et al. (1992), in which virgin compression follows a straight line with slope $C_c$, and unloading or recompression before reaching normal consolidation will follow another straight line with a smaller slope $C_s$, or the swelling index. Such a scheme of stress-deformation relation is shown in Figure 1-2. In natural soils, $C_s$ is in the range of 10–20% of $C_c$.

Finally we assume that the soil permeability varies with the void ratio according to the Kozeny-Carman relation which may be written as

$$\tilde{K} = \tilde{K}_0 \frac{1 + \bar{e}}{\bar{e}^3} \frac{e^3}{1 + e}. \quad (1.83)$$

In some cases, more refined constitutive laws may be needed. For example, based on the field data at Pixley, California, Helm (1976) has found that during the unloading/recompression stage $a_v$ is constant instead, and that the vertical permeability is a certain function of effective stress. Therefore, to apply the present theory to any
specific site, empirical constitutive laws from local tests should be incorporated. This can be done without modifying the principles of our theory.

1.7 Initial-Boundary-Value Problem

Since the drawdown \( \hat{s}^{(0)}_2 \) in the aquifer is uniform in depth, continuity of pressure across the interface gives (1.70) or, in Lagrangian coordinates,

\[
\left. \hat{s}^{(0)}_1 \right|_{\Gamma_1} (\hat{R}, \hat{t}) = \left. \hat{s}^{(0)}_2 \right|_{\Gamma_2} (\hat{R}, \hat{t}) = \left. \hat{s}^{(0)}_3 \right|_{\Gamma_3} (\hat{R}, \hat{t}). \tag{1.84}
\]

In view of the fact that the governing equations for \( \hat{s}^{(0)}_1 \) and \( \hat{s}^{(0)}_3 \) in the two semipermeable layers are of the same form, we may drop the subscripts distinguishing the two layers and consider the following equivalent boundary value problem for a single drawdown \( \hat{s}^{(0)}(\hat{R}, \hat{Z}, \hat{t}) \) in the vertical region \( 0 < \hat{Z} < \hat{B}_1 + \hat{B}_3 \). The governing equation is

\[
\frac{\partial}{\partial \hat{Z}} \left( \hat{K} \frac{1 + \varepsilon \partial \hat{s}^{(0)}}{1 + \varepsilon} \right) = \frac{\tilde{a}_w}{1 + \delta} \frac{\partial}{\partial \hat{t}} \left( \hat{s}^{(0)} - \hat{z}^{(0)} \right) \left|_{\Gamma_3} + \tilde{\tau}^{(0)}_{zz} \right|_{\Gamma_3} \tag{1.85}
\]

\[0 < \hat{Z} < \hat{B}_1 + \hat{B}_3, \quad \hat{t} > 0.\]

The boundary condition on the bed rock is

\[
\frac{\partial \hat{s}^{(0)}}{\partial \hat{Z}} = 0 \quad \hat{Z} = 0. \tag{1.86}
\]

The seepage boundary condition on the ground surface is

\[
\frac{\partial \hat{s}^{(0)}}{\partial \hat{Z}} = 0, \quad \text{if sealed;} \tag{1.87}
\]

\[
\hat{s}^{(0)} = \hat{z}^{(0)}, \quad \text{if unsealed.} \tag{1.88}
\]

On the uncovered part \( \Gamma_3^U \) of the ground surface

\[
\tilde{\tau}^{(0)}_{zz} = 0 \tag{1.89}
\]
On the covered ground surface $\tilde{R}_3^L$, we have either

$$\tilde{\tau}^{(0)}_{zz} = \frac{-\tilde{W}}{\pi (\tilde{R}_0^2 - \tilde{R}_w^2)} \quad (1.90)$$

if the foundation is soft, or

$$\tilde{\varepsilon}^{(0)} = \text{undetermined constant}, \quad (1.91)$$

with

$$\int_{\tilde{R}_w}^{\tilde{R}_o} 2\pi \tilde{R} \tilde{\tau}^{(0)}_{zz} d\tilde{R} = -\tilde{W} \quad (1.92)$$

if the foundation is rigid. At the interface $\tilde{Z} = \tilde{B}_1$ we must satisfy

$$\left[ \tilde{K} \left( \frac{1 + \tilde{e}}{1 + e} \right) \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{Z}} \right]_{\tilde{B}_1}^{\tilde{B}_1^+} = -\frac{\tilde{K}_2 \tilde{B}_2}{\tilde{R}} \frac{\partial}{\partial \tilde{R}} \left( \tilde{R} \frac{\partial \tilde{\varepsilon}^{(0)}}{\partial \tilde{R}} \right) \quad \tilde{R} > \tilde{R}_w, \quad \tilde{Z} = \tilde{B}_1, \quad (1.93)$$

and

$$\tilde{K}_2 \tilde{B}_2 \tilde{R} \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{R}} = \tilde{Q}(\tilde{T}) \quad \tilde{R} = \tilde{R}_w, \quad \tilde{Z} = \tilde{B}_1. \quad (1.94)$$

In addition we require that

$$\tilde{s}^{(0)} \rightarrow 0 \quad \tilde{R} \rightarrow \infty, \quad (1.95)$$

and

$$\tilde{s}^{(0)}(\tilde{R}, \tilde{Z}, 0) = 0. \quad (1.96)$$

Because the vertical uniformity in the aquifer the three layered system can be alternatively regarded as one soil layer with the aquifer being a plane of discontinuity. The only property of the aquifer is the transmissivity $\tilde{K}_2 \tilde{B}_2$ which will be assumed to be constant. The well becomes a sink at the center of that plane. The governing equation for the drawdown $(1.76)$ holds above and below the plane

$$\frac{\partial}{\partial \tilde{Z}} \left( \tilde{K} \frac{1 + \tilde{e}}{1 + e} \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{Z}} \right) = \frac{\partial \tilde{w}^{(0)}}{\partial \tilde{Z}}. \quad (1.97)$$
To calculate the vertical settlement (cf. (1.85), (1.88), and (1.91)), we integrate (1.97) with respect to \( \tilde{Z} \) from 0 to \( \tilde{B}_1 + \tilde{B}_3 \), recall that both the velocity and the flux are zero at the bottom and \( \tilde{w}^{(0)} = (1/S_1)(\partial \tilde{z}^{(0)}/\partial \tilde{t}) \), and obtain

\[
\frac{\partial \tilde{z}^{(0)}}{\partial \tilde{t}} \bigg|_{\tilde{B}_3} = S_1 \left\{ \tilde{K} \left( \frac{1 + \tilde{e}}{1 + e} \right) \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{Z}} \bigg|_{\tilde{B}_3} - \tilde{K} \left( \frac{1 + \tilde{e}}{1 + e} \right) \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{Z}} \bigg|_{\tilde{B}_i} \right\}. \quad (1.98)
\]

Hence the settling velocity of the ground surface is related to the net vertical water fluxes across the interfaces, i.e., the subsidence rate is equal to the rate of change of water storage in the semipervious layers, in order to conserve water mass.

Equations (1.85) and (1.98) are the governing equations for the variables \( \tilde{s}^{(0)} \) and \( \tilde{z}^{(0)} \big|_{\tilde{B}_3} \). The contact stress \( \tilde{r}_{zz}^{(0)} \big|_{\tilde{B}_3} \) may also be an unknown if the foundation is rigid. The soil parameters \( e(\tilde{R}, \tilde{Z}, \tilde{t}), \tilde{K}(e) \) and \( \tilde{a}_v(e) \), also unknown, are related to the effective stress and therefore the solution of \( \tilde{s}^{(0)} \), by empirical constitutive laws, as described in §1.6.3.

In summary our initial-boundary-value problem consists of six governing equations (1.85), (1.98), (1.66), (1.81), (1.82) and (1.83) for six variables \( \tilde{s}^{(0)}, \tilde{z}^{(0)} \big|_{\tilde{B}_3}, \tilde{r}_{zz}^{(0)}, e, \tilde{a}_v \) and \( \tilde{K} \).

### 1.7.1 Extension to More Layers

Although the mathematical problem has so far been described only for a three-layer system with one aquifer, extension to more layers is straightforward. In particular the entire stratum is described by the same equation (1.85) with different coefficients in different semipervious layers. For each aquifer there is a pair of conditions (1.93) and (1.94) applied at the interface. Finally the ground settlement rate equation (1.98) is modified by including the net water fluxes across all the interfaces. That is, for \( N \) layers of aquifers,

\[
\frac{\partial \tilde{z}^{(0)}}{\partial \tilde{t}} \bigg|_{\tilde{B}_3} = S_1 \left\{ \tilde{K} \left( \frac{1 + \tilde{e}}{1 + e} \right) \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{Z}} \bigg|_{\tilde{B}_3} - \sum_{i=1}^{N} \tilde{K} \left( \frac{1 + \tilde{e}}{1 + e} \right) \frac{\partial \tilde{s}^{(0)}}{\partial \tilde{Z}} \bigg|_{\tilde{B}_i} \right\}. \quad (1.99)
\]
1.7.2 Limiting Case of Small Strain

In the limit of infinitesimal strain, there is no distinction between the Eulerian and the Lagrangian coordinates, and the soil properties become invariant with time. The surface displacement \( \tilde{z}^{(0)} |_{t_3} \) is also infinitesimally small. Therefore if the surface load does not vary with time, (1.85) becomes, in the limit of small strain,

\[
\frac{\partial}{\partial z} \left( \hat{K} \frac{\partial \tilde{z}^{(0)}}{\partial z} \right) = \frac{\tilde{\alpha}_v}{1 + \tilde{\varepsilon}} \frac{\partial \tilde{z}^{(0)}}{\partial t}.
\]  

(1.100)

Now the coefficients do not depend on the unknowns. Expressed in physical variables, the above equation becomes

\[
\frac{\partial}{\partial z} \left( K \frac{\partial s^{(0)}}{\partial z} \right) = \frac{\rho_g g}{D} \frac{\partial s^{(0)}}{\partial t},
\]  

(1.101)

where the constrained modulus \( D \equiv (1 + e)/a_v \) and the hydraulic conductivity \( K \) are known functions of space only. Hence for small strain we have recovered the well-known linear storage equation, which is decoupled from the soil deformation.

1.8 Numerical Solution

For simplicity we shall drop the overhead tilde and the superscript (0) from here on and introduce the following symbols:

\[
\kappa \equiv \frac{K}{1 + e}; \quad \beta \equiv \frac{a_v}{1 + \tilde{\varepsilon}}.
\]  

(1.102)

For computational convenience, we further introduce the following change of variable:

\[
s^*(R, Z, t) \equiv s(R, Z, t) - z'|_{t_3}(R, t).
\]  

(1.103)

In view of (1.88), \( s^* = 0 \) vanishes on the unsealed part of the ground surface.

In order that numerical resolution is adequate near the well where rapid variations
are expected, we introduce a mapping from \( R \) to \( Y \) by

\[
Y = \ln \left( \frac{R}{R_w} \right) \quad \text{or} \quad R = R_w e^Y. \tag{1.104}
\]

Hence uniform grids in \( Y \) will lead to nonuniform grids increasing in size with \( R \) so that the resolution is higher near the well. The initial-boundary-value problem is now changed to:

\[
\frac{\partial}{\partial Z} \left( \kappa \frac{\partial s^*}{\partial Z} \right) = \beta \frac{\partial}{\partial t} \left( s^* + \tau_{zz} |_{\Gamma_3} \right) \quad 0 < Z < B_1 + B_3, \quad t > 0, \tag{1.105}
\]

\[
\frac{\partial s^*}{\partial Z} = 0 \quad Z = 0, \tag{1.106}
\]

sealed surface: \( \frac{\partial s^*}{\partial Z} = 0, \tag{1.107} \)

unsealed surface: \( s^* = 0, \tag{1.108} \)

On uncovered surface:

\[
\tau_{zz} = 0, \tag{1.109}
\]

while on covered surface:

\[
\tau_{zz} = \frac{-W}{\pi (R_0^2 - R_w^2)} \tag{1.110}
\]

beneath a soft foundation, and

\[
z' = \text{undetermined constant}, \tag{1.111}
\]

with

\[
\int_{Y_w}^{Y_0} 2\pi R_w^2 e^{2Y} \tau_{zz} dY = -W \tag{1.112}
\]

beneath a hard foundation.

Across the line \( Z = B_1 \) we have

\[
\left[ \frac{\partial s^*}{\partial Z} \right]_{B_1}^{B_1^*} = -\frac{K_2 B_2}{R^2} \frac{\partial^2}{\partial Y^2} (s^* + z'|_{\Gamma_3}) \quad Y > 0 \quad Z = B_1, \tag{1.113}
\]

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and
\[ K_2 B_2 \frac{\partial (s^* + z'|_{\Gamma_3})}{\partial Y} = Q(t) \quad Y = 0 \quad Z = B_1. \quad (1.114) \]

In addition we must have
\[ s^* \rightarrow 0 \quad Y \rightarrow \infty, \quad (1.115) \]
\[ s^*(Y, Z, 0) = 0. \quad (1.116) \]

Finally the ground subsidence is found from
\[ \frac{\partial z'}{\partial t} \bigg|_{\Gamma_3} = S_1 \left\{ \kappa \left( \frac{\partial s^*}{\partial Z} \right)_{\Gamma_3} - \kappa \left( \frac{\partial s^*}{\partial Z} \right)_{B_1^+} \right\}. \quad (1.117) \]

The boundary term \( z'|_{\Gamma_3} \) is now shifted to the interface conditions (1.113) and (1.114). 

\( Q \) and \( W \) are the only forcing terms.

The initial-boundary-value problem is solved by an ADI (alternating-direction implicit) scheme of finite differences, details of which are given in Appendix A.

In our numerical examples the following input data are used:

**Geometry**
\[ R_w = 0.05, \quad B_1 = B_2 = B_3 = 1. \]

**Soil properties**
\[ \bar{e}(\bar{\Gamma}_1^-) = 5.0, \quad \bar{e}(\bar{\Gamma}_3) = 8.0, \quad \bar{K}(\bar{\Gamma}_1^-) = 1.0, \quad \bar{K}(\bar{\Gamma}_3) = 2.7, \]
\[ C_e = 5.0, \quad C_s = 0.5, \quad \rho_s/\rho_w = 2.67. \]

**Initial geostatic stress**
\[ \bar{\sigma}_{zz}(\bar{\Gamma}_3) = -0.2, \quad \bar{\sigma}_{zz}(\bar{\Gamma}_1) = -1.2. \]

**Computational steps**
\[ \Delta T = 0.0001, \quad \Delta Y = 0.1, \quad \Delta Z = 0.02, \]
The computational domain in $Y$ is 5.

The input data regarding soil geometry and properties are typical of those in Mexico City. The computational steps are so chosen based on numerical experiments that convergence of solutions is ensured.

Taking the depth scale to be $\hat{b} = 30$ m, the corresponding scale for the vertical stress is $\rho_w g \hat{b} = 300$ kPa. The allowable bearing stress for very soft clay, according to the foundation design practice (e.g., NAVFAC DM-7, 1971) is 50 kPa, or a normalized value of 0.17. A typical hydraulic conductivity for an aquifer is $5 \times 10^{-5}$ m/s giving a scale of $\hat{Q} = 0.3$ m$^3$/s for the pumping rate. Also if we assume that for the semipervious layers

$$\hat{D} = 0.5 \text{ MPa}, \quad \hat{K} = 10^{-8} \text{ m/s},$$

the storage coefficient is then $S = 0.6$ and the time scale of consolidation is $\hat{t} = 60$ years.

To interpret the physical radial gradient of ground subsidence from the following results, one has to multiply the computed one by $\delta^{1/2}$, which is the ratio of the length scalings (see §1.4.2). We caution that very near the well our results may need local refinements since the horizontal scale of variation is no longer much greater than the layer depth, as has been assumed in the approximation. A locally two-dimensional solution is needed to describe the physics very close to the well. This is, however, a prohibitively complicated task and will not be pursued in this thesis.

1.9 Results and Discussions

1.9.1 Comparison with Small Strain Theory

In Figure 1-3 we show a comparison of ground settlements, due to pumping only, obtained by the present nonlinear theory and the linear equation (1.100). In the linear theory, $\kappa$ and $\beta$ are kept constant at their initial values, where $a_v$ is calculated from (1.82), using the above input data. The pumping rate is $\hat{Q} = 0.1$, and the surface is uncovered. For the small time $t = 0.1$, the predictions by the two theories
Figure 1-3: Comparison of ground settlements due to pumping only obtained by the nonlinear and the linear theories, $Q = 0.1$; —— nonlinear theory; - - - - linear theory.

are close to each other when the displacements are still small. However at the large time $t = 4.0$, the linear theory gives about 60% larger settlement near the well than the nonlinear theory. This prediction of larger settlement contradicts the assumption of small strain of the linear theory. The overestimation is essentially a result of the ignorance of the finite ground surface displacement, and the finite changes of the soil parameters. From this example, we can infer that it is both mathematically inconsistent and numerically inaccurate to use the linear theory when finite strain is expected.
1.9.2 Subsidence of Ground Surface

From here on, we shall focus on results obtained by the nonlinear theory only. We first discuss the computed results for a circular foundation with outer radius \( R_o = 0.25 \). The normalized pumping rate is fixed at \( \dot{Q} = 0.1 \), while the averaged weight of the building per unit area is \( \bar{\tau}_3 = -0.1 \). Three types of boundary conditions beneath the foundation are considered: (a) rigid footing with perfect sealing; (b) soft footing with perfect sealing; (c) soft footing without sealing. For comparison, results of the simple case (d) of pure pumping without surface load will also be presented.

Pumping without Delay

Let the surface loading and pumping begin at the same time. In Figure 1-4, the radial variations of the ground settlement \( z'_3 \) are shown for three different \( t \). The depressed portion in each of the solid curves corresponds to the loaded surface. The dashed curve gives the result due to pumping only. The effect of the surface loading is clearly to cause a drastic increase in settlement directly underneath the loading, for both the rigid and the soft foundations, confirming the observation in Pingtung County which motivated this study. Among the three loaded cases the rigid foundation (Figure 1-4a) gives the greatest settlement at the outer edge, and relatively small settlement near the well. On the other hand, a sealed and soft foundation (Figure 1-4b) settles the most near the well. The foundation without sealing (Figure 1-4c) settles more during small time, but less at large time than the one with perfect sealing (Figure 1-4b). This is because the drainage beneath the foundation allows a more rapid consolidation initially, and recharging helps to compensate for the depletion of water stored in the semipervious layers.

In Figure 1-5 we compare the time variations of the settlement directly beneath the foundation at \( R = 0.2 \). Additional results for pure pumping without loading, and for pure loading without pumping, are also included for comparison. In any case, the ground displacement takes place rapidly when \( 0 < t < 0.5 \), and slowly when \( t > 1.0 \). As noted above, among the three cases with loading, an unsealed surface (c) settles
Figure 1-4: Radial variations of ground settlement as a function of time; —— pumping $Q = 0.1$ and loading $\bar{\sigma}_3 = -0.1$, (a) rigid and sealed foundation, (b) soft and sealed foundation, (c) soft and unsealed foundation; —— pumping $Q = 0.1$ without loading.
Figure 1-5: Time variations of ground settlement at $R = 0.2$ (beneath the loading); --- pumping $Q = 0.1$ and loading $\bar{\tau}_3 = -0.1$, (a) rigid and sealed foundation, (b) soft and sealed foundation, (c) soft and unsealed foundation; --- pumping $Q = 0.1$ without loading; ---- loading $\bar{\tau}_3 = -0.1$ on rigid sealed foundation without pumping.

faster initially but more slowly ultimately. At $t = 1$, the settlement of the loading-only case is 0.052, while that of the pumping-only case is 0.06. The algebraic sum of these two values gives 0.112 which is smaller than the result for the three cases with both pumping and loading: (a) 0.155, (b) 0.141 and (c) 0.127. This suggests the importance of non-linearity; i.e., addition of the separate results of pure pumping and pure loading would underestimate the combined effect of both pumping and loading.
Delayed Pumping

Sometimes pumping takes place long after the building has been erected. In this situation consolidation due to the surface loading has become steady when the pumping begins. To find out the effects of delayed pumping, we repeat the above computations but the pumping does not start until the building has been in existence for a period of \( t = 4.0 \), long enough for the loading induced consolidation to complete. The corresponding results are shown in Figure 1-6. The solid curves represent the ground displacement since the start of the pumping (i.e., excluding the building settlement prior to pumping) while the dashes are still for the pure pumping without loading history. We are therefore comparing the ground displacements due to pumping only, with and without loading history, and with various foundation rigidity and surface sealing. Contrasting graphs (a), (b) and (c), we can infer that only the foundations which seal the surface will eventually subside more than its surrounding ground surface. Settlement due to delayed pumping in a soft and unsealed foundation turns out to be much the same as the pure pumping without any loading. In the two cases with sealing, the rigid foundation gives a greater differential settlement across its outer edge at all time than the soft one. Hence both the foundation rigidity and the surface sealing contribute to cause larger building settlement than its surrounding ground surface.

To further illustrate the effects of foundation rigidity and surface sealing in delayed pumping, we also show in Figure 1-7 the time variations of the settlement at \( R = 0.2 \), including the case of pure pumping. At large time, the settlements of the rigid foundation and the soft foundation with surface sealing are respectively 0.103 and 0.085 which are about 70% and 40% higher than the settlement due to pure pumping. The soft foundation with recharge/discharge, on the other hand, settles even slightly less than that due to pure pumping without loading history, as a result of the fact that the soil compressibility decreases with increase in effective stress. Also, if the loading settlement prior to pumping, which is 0.052 as shown in Figure 1-5, is included, the ultimate combined settlements at this radius are very close to those resulted from
Figure 1-6: Radial variations of ground settlement as a function of time for delayed pumping; —— pumping $Q = 0.1$ with loading history $\tau_3 = -0.1$, (a) rigid and sealed foundation, (b) soft and sealed foundation, (c) soft and unsealed foundation; —— pumping $Q = 0.1$ without loading history.
Figure 1-7: Time variations of ground settlement at $R = 0.2$ (beneath the loading) due to delayed pumping; —— pumping $Q = 0.1$ with loading history $\tau_3 = -0.1$, (a) rigid and sealed foundation, (b) soft and sealed foundation, (c) soft and unsealed foundation; —— pumping $Q = 0.1$ without loading history.

pumping without delay: (a) 0.155, (b) 0.137 and (c) 0.11. This suggests that as far as long term ground subsidence is concerned, the occurrence sequence of loading and pumping is relatively unimportant.

1.9.3 Physics of Subsidence

From here on, we shall focus only on the case of pumping without delay. The main effects of surface loading are to accelerate the consolidation by increasing the effective stress while it may also seal off the covered ground surface. Since subsidence is caused by the changes of void ratio and pore pressure, we now examine their details in order
to understand better the underlying physics.

**Change in Void Ratio**

In Figure 1-8 we show the depth variation of void ratio in the semipervious layers, at $R = 0.2$, which is directly beneath the foundation. Again results for the three types of foundation, and that due to pure pumping are plotted for comparison. Note that the aquifer corresponds to the horizontal line $Z = 1.0$, and therefore a discontinuity in void ratio exists there for all time. At small time, the change in void ratio is limited to soils immediately below and above the aquifer for all cases. The soft foundation without sealing allows drainage underneath, therefore causing an instantaneous increase in effective stress and an early decrease in void ratio beneath the foundation. This explains the larger initial settlement of the foundation. At large time, the decrease in void ratio is almost uniform in the bottom semipervious layer, but increases with elevation in the upper one. The maximum decrease in void ratio, at the ground surface, is more than 1.2 for the rigid foundation, and 1.1 and 0.8 for the soft foundations with and without sealing respectively. These large variations near the ground surface are of course responsible for the large settlement of ground surface directly beneath the foundation. In contrast when the ground surface is load free, the void ratio remains unchanged at the ground surface because of the constant pore pressure boundary condition. Therefore settlement is greatly enhanced by both the weight and the sealing effect of the foundation.

In Figure 1-9 we show a similar plot for a radial distance $R = 0.5$, which is outside the building foundation. On the unsealed and unloaded ground surface, the boundary conditions are the same for all cases. As expected, the difference in void ratios is small. The maximum decrease in void ratio at the bottom of the upper semipervious layer is less than 0.4. The average decrease in void ratio, which is less than 0.2, is clearly much smaller than that directly underneath the foundation. This is consistent with the relatively small vertical settlement.
Figure 1-8: Depth variations of void ratio at $R = 0.2$ (beneath the loading) at small and large times; ——— pumping $Q = 0.1$ and loading $\bar{\tau}_3 = -0.1$ on rigid and sealed foundation; ----- ditto but on soft and sealed foundation; ······· ditto but on soft and unsealed foundation; ——— pumping $Q = 0.1$ without loading.
Figure 1-9: Depth variations of void ratio at $R = 0.5$ (outside the loading) at small and large times; —— pumping $Q = 0.1$ and loading $\bar{\tau}_3 = -0.1$ on rigid and sealed foundation; —— pumping $Q = 0.1$ without loading.
Change in Pore Pressure

The void ratio changes in direct response to a change in pore pressure. This is seen in Figure 1-10a,b,c where the depth variations of drawdown at $R = 0.2$ is shown as a function of time, for the three types of foundation conditions, and in Figure 1-10d for the case of pure pumping only. Recall that the initial drawdown is zero in all cases.

Consider first the three cases with surface load (Figure 1-10a,b,c). At very small time the drawdown throughout most of the semipervious layers increases to a positive value, signifying the building up of pore pressure, in response to the building weight. Across the interface there are however drops in drawdown caused by pumping. The discontinuity in the drawdown gradient at the interface is associated with leakage from the semipervious layers towards the aquifer. The foundation without sealing (Figure 1-10c) also discharges water at the top, resulting in a more rapid reduction of pore pressure. As time increases, the pore pressure build-up is gradually dissipated through drainage at the interface (and at the top of an unsealed foundation). Eventually the drawdown becomes negative at all depth in all cases. The discontinuity in drawdown gradient at the interface decreases with time, implying that the total mass flux of water into the aquifer diminishes with time. Owing to the no-flux boundary condition along both sealing at the top and the bottom of the lower semipervious layer, the drawdown distributions at large time for the sealed foundations gradually approach a vertical line (Figure 1-10a,b), implying that the vertical flow diminishes. When the drawdown becomes uniform in depth, further pumping is solely supplied by the radial flow in the aquifer. The foundation without sealing however maintains a finite drawdown gradient in the upper semipervious layer at large time (Figure 1-10c), when the flow is mainly supplied by the recharge.

In the case with pure pumping without surface loading (Figure 1-10d), the drawdown variation is qualitatively the same during early times when the response has not yet reached the boundaries away from the well. In this stage, water is taken from the storage of the semipervious layers, resulting in a decrease in void ratio near the aquifer. However when the response reaches the top boundary where free drainage

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is allowed, water is then supplied from above the ground surface and is transmitted through the upper semipervious layer into the aquifer. Consequently, the drawdown gradient in the upper semipervious layer eventually approaches a finite constant as seepage continues. When this equilibrium state is approached, extraction of water from storage in the upper semipervious layer is gradually replaced by recharging from the top. This mechanism explains the smaller final change in void ratio and the smaller settlement. Note in Figure 1-9d that the final drawdown at the top, which is equal to the local ground displacement at \( R = 0.2 \), is about -0.06 while the maximum drawdown is -0.16. This result is another evidence that the gravity term in (cf. (1.66)) is not negligible.

Figure 1-11 gives results at a radial distance \( R = 0.5 \) (outside the foundation) for the rigid foundation. At a very small time, the drawdown is slightly positive near the interface and causes an outward flow along the interface. This is because water is squeezed out by the surface load while on the other hand the effects of pumping are still weak. This increase in pore pressure while the total stress remains unchanged implies a decrease in the effective stress and therefore the soil becomes overconsolidated. Subsequent consolidation of the soil follows the flatter branch of \( \sigma \sim e \) curve and is computed with the much lower swelling index \( (C_s = 0.1 \times C_c = 0.5) \) until the preconsolidation stress level is exceeded (see §1.6.3). This explains that during small times, the drawdown with both pumping and surface loading is smaller than that without surface loading.

Combining the insights of this and the last subsection, we conclude that beneath the foundation with perfect sealing, drainage of pore water contributes most significantly to consolidation. Without recharge the void ratio in the entire top semipervious layer diminishes quickly, leading directly to large subsidence.

**1.9.4 Interior Soil Deformation**

The depth variations of soil vertical displacement, which is the accumulated effect of the change in void ratio, are plotted in Figures 1-12 and 1-13 also for \( R = 0.2 \) and \( R = 0.5 \) respectively. Only the sealed rigid foundation (Case a) is considered. At
Figure 1-10: Depth variations of drawdown at $R = 0.2$ (beneath the loading) as a function of time; (a) pumping $Q = 0.1$ and loading $\bar{r}_3 = -0.1$ on rigid and sealed foundation; (b) ditto but on soft and sealed foundation; (c) ditto but on soft and unsealed foundation; (d) pumping $Q = 0.1$ without loading.
Figure 1-11: Depth variations of drawdown at $R = 0.5$ (outside the loading) as a function of time; ——— pumping $Q = 0.1$ and loading $\tilde{\tau}_3 = -0.1$ on rigid and sealed foundation; —— pumping $Q = 0.1$ without loading.
Figure 1-12: Depth variations of soil displacement at $R = 0.2$ (beneath the loading) as a function of time; —— pumping $Q = 0.1$ and loading $\bar{r}_3 = -0.1$ on rigid and sealed foundation; —— pumping $Q = 0.1$ without loading.

$R = 0.2$, contributions by the two semipervious layers to the overall ground settlement are approximately the same if the foundation is absent (Case d). However with both pumping and loading, the settlement contribution due to the upper semipervious layer is more than twice as much as due to the lower semipervious layer. As expected, the difference between the two cases is modest at $R = 0.5$, outside the foundation. At a small time, the soil displacement for the case of pure pumping is larger than that with both pumping and loading because of overconsolidation, as discussed above.
Figure 1-13: Depth variations of soil displacement at $R = 0.5$ (outside the loading) as a function of time; —— pumping $Q = 0.1$ and loading $\tilde{\tau}_3 = -0.1$ on rigid and sealed foundation; —— pumping $Q = 0.1$ without loading.
1.9.5 Contact Stress Beneath a Rigid Footing

We show in Figure 1-14 the radial variation of the contact stress as a function of time. The initial contact stress is uniformly distributed at -0.1, equal to the applied weight per unit area. As soon as pumping starts, the contact stress varies radially. The minimum and the maximum stress occur respectively at the center and at the outer edge of the foundation. The minimum stress drops rapidly while the maximum stress rises slowly during early times. As time passes, the stress distribution approaches a steady state where the minimum stress stays at a very low value of about 5% of the initial stress while the maximum stress is more than 120% of the initial stress.

This change of contact stress with time is essentially a consequence of the rigidity of the foundation which can neither bend nor tilt in order to accommodate itself to the larger tendency of subsidence nearer the well caused by pumping. As a result, the foundation is more supported at its edge, but less at its center. The phenomenon of change in support from bearing soil is expected to happen to any foundation if over the span of the foundation the differential settlement due to pumping is significant. The shift of bearing support could mean a change in the loads applied to local structural members built directly upon the foundation. If the design limit for a member is exceeded, structural damages may be resulted. Common examples are the shear cracks on a wall, as often observed in Mexico City (Zeevaert, 1991).

How soon after the start of pumping a foundation will lose full support from the bearing soil depends on both the pumping rate and the weight of the building. In Figure 1-15, we present the threshold time of losing support as a function of pumping rate and building weight, where the foundation is still rigid and has a size $R_o = 0.25$. The threshold time $t_c$ is the time at which the absolute value of the minimum contact stress drops below a prescribed small value $10^{-4}$ in the computations. Three initial unit building weights $\bar{\tau}_3$: 0.05, 0.10 and 0.15 are considered. For a particular building weight, when the pumping rate is less than a certain threshold value, the loss of full support will not happen in a finite period of time. However when the threshold pumping rate is exceeded, the loss of full support problem will occur very soon. For
Figure 1-14: Radial variation of contact stress as a function of time ($Q = 0.1, \tau_3 = -0.1$).
Figure 1-15: Threshold time of losing full bearing support as a function of pumping rate and initial unit building weight.

very large pumping rates and a light building, the problem can even happen right after the pumping starts. Therefore increase in building weight can substantially lengthen the threshold time if the pumping rate is relatively low, but has little effect when the pumping rate is high.

1.10 Conclusions

We have investigated the combined and simultaneous effects of water pumping and surface loads on the ground subsidence of a system comprised of an aquifer confined by two semipervious layers. An asymptotic analysis has been made for the case where there is a large contrast of permeabilities between the semipervious layers and an aquifer. The seepage flow in the soil layers becomes quasi-three-dimensional, being primarily horizontal in the highly porous aquifer and vertical in the highly impervious semipervious layers. Also, the deformation in the soft semipervious layers is primarily
vertical, allowing the use of empirically established, one-dimensional laws for finite soil strain. Although the law used here is in its simplest form, refinements for any given soil can be trivially incorporated in the present theory.

For the simple case with radial symmetry, we have compared several types of foundations: (a) rigid and sealed; (b) soft and sealed; (c) soft and unsealed. In the 'rigid' case the foundation can only settle uniformly and the contact stress varies with time and space, while in the 'soft' cases the settlement is non-uniform with the contact stress remains constant in time. In any case, the settlement of the foundation at large time is much larger than its immediate ground surface, and the settlement is also larger than the algebraic sum of the settlement due solely to pumping and that due solely to loading. From the depth variations of void ratio and drawdown beneath and outside the foundation, we find that large soil compaction beneath a sealed cover is the consequence of water depletion without recharge. The contact stress underneath a rigid foundation may change as a result of pumping; this could lead to local structural damages.
Part II

Transport Theories for Soil Vapor Extraction in Aggregated Soils
Chapter 2

Macroscale Soil Vapor Extraction
Equations by Homogenization Theory

2.1 Applications of Soil Vapor Extraction

Organic substances such as gasoline inadvertently spilled or leaked into the subsurface can pose a long-term threat to the quality of groundwater (Figure 2-1a). These compounds are often sufficiently soluble to render the groundwater undrinkable. In addition, many of these hydrocarbons have significant vapor pressures. While the liquid phases may be held back in the soil by capillary forces, their vapors can migrate in the unsaturated zone to affect a far greater extent than the original spill site. Fire and explosion threats are posed when these vapors get into building basements. If the vapors are denser than air, they may eventually sink down to the capillary fringe to further contaminate the groundwater. The migration mechanisms of organic fluids in the unsaturated zone are further discussed by Schwille (1984).

The partitioning of the organic chemicals into various phases often makes their complete removal a difficult task. With so many technologies now available for site remediation, soil vapor extraction (SVE) is the major physical treatment applicable
Figure 2-1: Schematic diagram of: (a) leakage of volatile organic compounds from an underground storage tank; (b) remediation of the vadose zone by soil vapor extraction with air flow induced by an air suction well.
to cleaning up unsaturated soils (vadose zone) contaminated with volatile organic compounds (VOC) (Pedersen and Curtis, 1991; Long, 1993). An SVE system (Figure 2-1b) consists primarily of a vacuum pump (with or without the help of blowers) which draws air through the contaminated zone. As the contaminated air is withdrawn, the local chemical equilibrium is upset, inducing the transfer of contaminant from the dissolved phase, the non-aqueous phase liquid (NAPL) and the sorbed phase, into the gaseous phase. The contaminated gas is then extracted through wells for release into the atmosphere or for further treatment. The air extraction rate is typically in the range 15–150 liter/sec per well (Massmann, 1989). Pressure vacuum within an extraction well is generally 20–50% of the atmosphere, with the radius of influence comparable to the horizontal dimension of the spill site. Further practical details about SVE systems are described by Pedersen and Curtis (1991), Long (1993), Wilson et al. (1988), Johnson et al. (1990b), Noonan et al. (1993), and Bedient et al. (1994).

There are numerous reports of success on the applications of SVE in real cases. For example, Kasbohm et al. (1991) reported that a soil ventilation system was installed to augment the remediation at a leaky gasoline service station on Cape Cod. The system was found more efficient and cheaper than the traditional pump-and-treat and bailing methods. According to another report (ILT Report, 1993), a dual vacuum extraction (one for gas, the other for liquid) system was able to lower the total petroleum hydrocarbons concentration from 2,800 ppm to 30 ppm in five weeks. Baehr et al. (1989) also reported that an SVE system helped to speed up a remediation by recovering 80% of the total spill over a period of three months. The free product layer on the groundwater table was also diminished at the end of the operation. More SVE case reports can be found in the proceedings of the National Outdoor Action Conference (1989, 1990, 1991), and in the proceedings of the NWWA/API Conference (1984, 1986, 1990).
2.2 Existing Analyses

2.2.1 Mathematical Framework

To guide the design of SVE systems, mathematical modeling is necessary to predict the time and space variation of VOC concentration as a function of the characteristics of the chemicals, the soil, the pumping rate, the well spacing, and so on. In a multicomponent system, the macroscale effective transport equations for a nonreactive $\alpha$-component in the various phases, can be written in general form as follows (Abriola and Pinder, 1985; Corapcioglu and Baehr, 1987; Kaluarachchi and Parker, 1990). If the subscripts $g, w, o$ and $s$ represent the vapor, aqueous, NAPL and solid phases respectively, $\theta$ the porosity, $S$ the degree of saturation, $C_j$ the mass of the solute per unit volume of fluid $j$, $C_s$ mass sorbed per unit soil mass, $\rho_b$ the bulk soil density, $\bar{u}$ the mass-average velocity, $\bar{J}$ the dispersive flux, and $I_{ji}$ the net rate of interphase mass transfer from phase $i$ to phase $j$ per unit bulk volume, then the laws of mass conservation are:

Fluid phases (vapor, aqueous, NAPL; $j = g, w, o$):

$$\frac{\partial}{\partial t} \left( \theta S_j C^\alpha_j \right) = -\nabla \cdot \left[ \theta S_j \left( C^\alpha_j \bar{u}_j + \bar{J}^\alpha_j \right) \right] + \sum_{i \neq j} I^\alpha_{ji}, \quad i = g, w, o, s; \quad (2.1)$$

Solid phase:

$$\frac{\partial}{\partial t} \left( \rho_b C^\alpha_s \right) = \sum_i I^\alpha_{si}, \quad i = g, w, o. \quad (2.2)$$

All quantities are averaged over the microscale of pores. In addition, we have

$$I_{ji} = -I_{ij} \quad \text{and} \quad S_g + S_w + S_o = 1. \quad (2.3)$$

To these mass conservation laws additional hypotheses are required. The dispersive fluxes are usually assumed to be of Fickian form, and the advection velocity is related to pore pressure by Darcy's law. For unsaturated flows, it is common to assume that one or both of the liquid (aqueous, NAPL) phases are immobile (Rathfelder et al., 1991). Since most subsurface environments are humid, direct sorptive exchange
between vapor and solid may also be ignored (Chiou and Shoup, 1985). The above interphase mass transfer processes are illustrated with the schematic diagram in Figure 2-2.

### 2.2.2 Models for Vapor Flow Only

There are a few SVE models which focus only on the vapor flow, but not on the interphase mass transfer. Wilson et al. (1987) presented a solute transport model for the miscible displacement of soil vapor by clean air in the absence of soil moisture and residual NAPL. Therefore the key processes such as volatilization and sorption were not considered. Massmann (1989) modified the groundwater flow equations for confined and leaky aquifers to study the transient gas flow field in a vented unsaturated zone. Similar analysis but for steady gas flow in a site with open ground surface was presented by Shan et al. (1992). Gamliel and Abdul (1993) carried out numerical studies on the effects of several design parameters of air venting: well spacing, screen length ratio and sealing of surface.
2.2.3 Local Equilibrium Models

In many early works (e.g., Wilson et al., 1988; Baehr et al., 1989; Johnson et al., 1990a; Rathfelder et al., 1991) one assumes that kinetics of mass transfer between phases is unimportant and local equilibrium exists among all phases. Specifically, the partition ratio between air and water is given by Henry’s law, that between the air and NAPL by Raoult’s law, and that between sorbed solid and water by the sorption isotherm relationship. Hence

$$C_w^\alpha = C_g^\alpha / H^\alpha, \quad C_o^\alpha = C_g^\alpha / K_{og}^\alpha, \quad C_s^\alpha = C_w^\alpha K_d^\alpha,$$  \hspace{1cm} (2.4)

where

$$K_{og}^\alpha = P_o^\alpha / \left( R_g \Theta \sum_{\alpha=1}^{N} \frac{c_\alpha^\alpha}{M_\alpha} \right),$$  \hspace{1cm} (2.5)

and $H$ is the Henry’s law constant, $R_g$ is the universal gas constant, $\Theta$ is the temperature, $M$ is the molecular weight, $P_o^\alpha$ is the vapor pressure for pure liquid, and $K_d$ is the solid-water partition coefficient (for linear sorption isotherm), and vapor and organic liquid sorptions are ignored. On relating all the concentrations with the laws of partition, the four transport equations (2.1) and (2.2) can be summed to eliminate the interphase mass transfer terms to give a single equation for the concentration in one phase.

The adoption of the local equilibrium assumption was motivated in part by some experimental evidence and in part by its extensive use in the oil industry (Abriola and Pinder, 1985). However the experimental evidence (Van der Waarden et al., 1971; Kappeler and Wuhrmann, 1978; Fried et al., 1979), as cited by Abriola and Pinder (1985), only suggests equilibrium of soluble hydrocarbons between the aqueous and nonaqueous phases in groundwater pollution, while the oil industry applies the assumption for reservoir oil and gas phases. In both situations, the partition takes place only between two phases in the absence of strong advective flux of either phase.

Mathematical models for use in evaluating the feasibility of site clean-up by air venting were developed by Wilson et al. (1988). Local equilibrium between vapor and
dissolved phases is assumed. While they emphasized on the estimations of Henry’s Law constant, they have not justified the rationale for the use of the local equilibrium assumption.

Baehr et al. (1989) presented a 1-D local equilibrium model to describe gasoline transport in a steady advective air flow column experiment (Marley and Hoag, 1984). On calibrating the constituent vapor pressures, their model was able to fit data on the early time variations of effluent vapor flux. They found that the effluent concentration flux is not sensitive to the partitions to aqueous and adsorbed phases and therefore ignored these two partitions in their modeling. However, as later pointed out by Armstrong et al. (1994), since effluent concentration flux is indeed insensitive to local transfer kinetics, monitoring the effluent flux only is not adequate to judge what happens locally. It is likely that while the effluent vapor concentration has dropped and leveled off at a low value, the concentrations retained in the dissolved and sorbed phases may still be very high.

Predictive screening models for three design issues of SVE system: the vapor flow-rate, the composition of the residual contamination, and the location of contamination relative to air flow path, were described by Johnson et al. (1990a). They used a box-model to simulate compositional changes in various phases. They justified the local equilibrium assumption by estimating the distance in which clean air would become saturated on passing through a contaminated region. Considering only molecular diffusion in air, they found a typical distance of 0.2 cm which is very small compared with contaminated zone sizes. Their analysis however overlooks the fact that the interphase mass transfers are usually rate-limited by diffusion in the aqueous phase, especially when retarded by sorption. Diffusivity in aqueous solution with sorption retardation can be five to ten orders of magnitude less than in the air. Therefore a rapid saturation of air does not necessarily indicate a local equilibrium situation. Another predictive model for initial feasibility studies, based on crude approximations for gas flow and phase exchanges, was developed by Falta et al. (1993).

A more comprehensive numerical model for field-scale SVE operations has been developed by Rathfelder et al. (1991). They found by sensitivity analysis that equi-
librium partitioning is a good assumption in modeling organic liquid volatilization in field venting operations, while mass transfers from aqueous phase and solid desorption are potentially rate-limiting. They verified their model by comparing results with experimental data. In the experiments a 3-component organic was emplaced at residual level in a dry column of non-adsorbing porous medium. The column was vented with nitrogen gas and effluent vapor concentrations of individual components were measured. Based on local equilibrium partitioning, their model predicts fairly well with the measured effluent vapor concentrations. However, as they have commented, the experimental results did not provide information about the rate at which equilibrium concentrations were established and accordingly, predictions of effluent vapor concentration did not provide model validation for spatial and compositional changes in the organic phases. Moreover, the medium in the experiment was dry and non-adsorbing, so the possible causes of local kinetics in SVE – transfers from the dissolved and sorbed phases – were non-existent in the experiment.

There are also works emphasizing computational capabilities and efficiencies on simulating SVE problems, such as Benson et al. (1993), and Sleep and Sykes (1993). Ho and Udell (1991, 1992, 1993) conducted experimental investigations on the air venting of a pool of organics from dry homogeneous and heterogeneous sand packings. The geometrical pool evolutions were recorded and the effluent vapor concentrations were measured. Results for heterogeneous packings were compared with calculations by a transfer model which assumes the existence of a concentration boundary layer in the high permeability zone. It should be noted that they have used rather high air velocities, as much as 70 mm/sec, for their experiment. Typical air velocity induced by an SVE vacuum in field applications is, except very near the well, not greater than the order of 1 mm/sec (Bachr et al., 1989; Johnson et al., 1990a).

There are also many vapor extraction experiments which indicate that in the absence of liquid organic phase, the effluent concentration often show very long tailing behavior (Gierke et al., 1992; Grathwohl and Reinhard, 1993). Vapor concentrations usually drop rapidly to a low level in the early stage of vapor extraction, but during a temporary shutdown, they are often found to increase again (DiGiulio, 1992; Arm-
Figure 2-3: Generic breakthrough curves of a local equilibrium situation (dashes), and a kinetic situation (solid line) featuring tailing and rebound during a temporary shutdown.

strong et al., 1994). Such rebound in vapor concentration indicates the slower decay in concentrations of other phases, or the importance of kinetics in the transfer of solutes into the air stream. Figure 2-3 shows a contrast between typical breakthrough curves exhibited by local equilibrium and kinetic situations.

2.2.4 First-Order Kinetic Model

Application of classical mass transfer theories for a multi-phase flow in porous media is difficult because of the variability of the interphase area of contact, the geometry of the interfaces and the distribution of the phases within the pores. In view of these difficulties, a simplified approach – an “overall” first-order kinetic theory – is used by many authors. By this theory, the transfer rate per bulk volume is proportional to the difference between the equilibrium and the actual concentrations, where the proportionality constant is an overall mass transfer coefficient reflecting all pore-level physical and chemical factors in the corresponding process. The adoption of the first-order kinetics is largely motivated by its extensive use in chemical engineering. Sleep and Sykes (1989) proposed the following first-order kinetic expressions for the
volumetric rates of dissolution $I_{wo}$, volatilization $I_{go}$, and air-water partition $I_{gw}$:

$$I_{wo} = \theta S_w \lambda_d (C_{wm} - C_w),$$  \hspace{1cm} (2.6)  

$$I_{go} = \theta S_g \lambda_v (C_{gm} - C_g),$$  \hspace{1cm} (2.7)  

$$I_{gw} = \theta S_g \lambda_h (HC_w - C_g),$$  \hspace{1cm} (2.8)  

where $\theta$ is the total porosity, $\lambda_d$, $\lambda_v$ and $\lambda_h$ are the respective rate constants, $H$ is the Henry's Law constant, $C_w$ and $C_g$ are the actual concentrations, while $C_{wm}$ and $C_{gm}$ are the equilibrium concentrations in the two phases. Similar first-order kinetic expressions have also been used by Cho and Jaffé (1990), Rathfelder et al. (1991), Gierke et al. (1992), Armstrong et al. (1994), and Szatkowski et al. (1995). An obvious shortcoming in the above expressions is that each rate is directly proportional to the degree of saturation of only one phase, despite two phases being involved in each process.

As in many chemical engineering applications, the first-order kinetic theory is often difficult to apply because of lack of reliable estimates for the transfer coefficients. Sleep and Sykes (1989) found in their numerical simulations a greater spread of a contaminant plume would be resulted from a mild increase in the values of the transfer coefficients from 0.1 day$^{-1}$ to 0.5 day$^{-1}$. These values are purely hypothetical. They also suggested that the transfer coefficients might be identified by an inverse modeling approach.

Only very scarce measurements giving relevant estimations for these first-order coefficients have been reported in the literature. Moreover, these reported values vary over a wide range of orders of magnitude. For example, Cho and Jaffé (1990) obtained fitted values of $6 \times 10^{-7}$ s$^{-1}$ to 0.02 s$^{-1}$ for the air-water mass transfer coefficient from their column experiment in which organic vapor diffuses in the presence of a counter-flow of infiltrating water. The coefficient was found sensitive to the water infiltrating rate and the parameters for tortuosity and transfer between mobile and immobile water regions. Rathfelder et al. (1991) made use of the data by Petrovic and
Thodos (1968) to obtain relations for transfer coefficient for pure liquid volatilization. The experiment measured mass transfers for vaporization of water and some heavy hydrocarbons into an air stream in packed beds of randomly distributed spheres saturated with the liquid. The transfer coefficient was found to vary with different liquids and different sphere sizes, though in all cases the coefficient increases with the gas flux. Apparently, all these transfer coefficients must have a strong dependence on the flow kinematics and the porous medium structures.

More recently, Fischer et al. (1996) have found experimentally that the transfer coefficients are not constant, but changing in values over a long enough period of air venting. Such time variability of the transfer coefficients suggests the inadequacy of the first-order relations to describe the microscopic phase exchange processes.

2.2.5 Diffusion Model for Aggregated Soils

Soil Aggregation

In most soils the individual particles do not exist as discrete entities but are grouped into aggregates or peds with fairly distinctive shapes and sizes. This is found most often in horizons of medium texture. In the two extremes, soils that are composed predominantly of coarse sand are loose and without well-formed aggregates, while those composed mainly of clay tend to be coherent or massive and to form fewer larger aggregates. It is also found that in soils with well-formed aggregates, the individual units may have only a few points of contact but generally are surrounded by a continuous pore phase.

Soils aggregates occur in various sizes and shapes. They can be smaller than 1 mm as very fine soil crumbs, or larger than 100 mm as coarse columnar structures (FitzPatrick, 1980). Emerson (1959) provided a model of the internal bonding forms which can constitute a soil aggregate (Figure 2-4). In his model, quartz particles and domains of oriented clay are bonded together by electrostatic forces. Stability of the aggregate is enhanced by linkage of organic polymers between the quartz grains and the faces or edges of clay domains. The intra-aggregate pores (or micropores), having
the same size as the parent particles of the aggregates (say, < 0.06 mm for silt), are therefore much smaller than the inter-aggregate pores (or macropores) which are comparable in size to the aggregates. Soil physicists (e.g., Fong et al., 1980) sometimes define inter-aggregate pores as being water-filled at water potential greater than -100 mbar (the field capacity) which roughly corresponds to a pore radius greater than 0.014 mm. Unsaturated soils with a potential less than -100 mbar may therefore be assumed to be wet only in the micropores. On the other hand, some definitions of macropores and macroporosity, as summarized in Table 2.1, have been reviewed by Beven and Germann (1982).

Solute transports in aggregated soils are often modeled by assuming that micropore fluid velocity is negligible as compared to that in the macropores. Fluids in these two regions are accordingly referred to as in immobile (or stagnant) and mobile (or dynamic) status. Solute movement in the immobile region is dominated by molecular diffusion, while that in the mobile region is carried out by advection and dispersion. In the unsaturated zone where the moisture content is at the irreducible
Table 2.1: Some definitions of macropores and macroporosity (after Beven and Germann, 1982).

<table>
<thead>
<tr>
<th>reference</th>
<th>capillary potential (kPa)</th>
<th>equivalent diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nelson and Baver (1940)</td>
<td>&gt; −3.0</td>
<td></td>
</tr>
<tr>
<td>Marshall (1959)</td>
<td>&gt; −10.0</td>
<td>&gt; 30</td>
</tr>
<tr>
<td>Brewer (1964)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coarse macropores</td>
<td></td>
<td>&gt; 5,000</td>
</tr>
<tr>
<td>medium macropores</td>
<td></td>
<td>2,000–5,000</td>
</tr>
<tr>
<td>fine macropores</td>
<td></td>
<td>1,000–2,000</td>
</tr>
<tr>
<td>very fine macropores</td>
<td></td>
<td>75–1,000</td>
</tr>
<tr>
<td>McDonald (1967)</td>
<td></td>
<td>&gt; −6.0</td>
</tr>
<tr>
<td>Webster (1974)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(quoted in Mosley, 1979)</td>
<td>&gt; −5.0</td>
<td></td>
</tr>
<tr>
<td>Ranken (1974)</td>
<td>&gt; −1.0</td>
<td></td>
</tr>
<tr>
<td>Bullock and Thomasson (1979)</td>
<td>&gt; −5.0</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>Reeves (1980)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>enlarged macrofissures</td>
<td></td>
<td>2,000–10,000</td>
</tr>
<tr>
<td>macrofissures</td>
<td></td>
<td>200–2,000</td>
</tr>
<tr>
<td>Luxmoore (1981)</td>
<td>&gt; −0.3</td>
<td>&gt; 1,000</td>
</tr>
<tr>
<td>Beven and Germann (1981)</td>
<td>&gt; −0.1</td>
<td>&gt; 3,000</td>
</tr>
</tbody>
</table>
Figure 2-5: Microscopic phase distributions in a soil aggregate in the unsaturated zone.

level, we can assume that the water is held stationary by capillary forces within the micropores while the mobile air occupies the macropores. Accordingly the aqueous and the sorbed phases will be distributed inside an aggregate, while the vapor phase resides in the intra-aggregate space. A schematic diagram for the phase distributions is shown in Figure 2-5.

**Non-volatile Solute Transport in Aggregated Soils**

Before we review on the subject of vapor transport in aggregated soils, let us first broaden our scope to review the much more studied problems of non-volatile solute transport in aggregated media.

The sorption kinetics of organic compounds to soils and sediments in a *saturated* environment is a most extensively studied problem. The often observed early breakthrough and tailing of effluent breakthrough curves (BTC) are signs of the sorptive exchange kinetics. For aggregated soils, the mobile/immobile-region (or 2-region) model has been able to describe these asymmetric traits of BTCs (e.g., van Genuchten and Wierenga 1976; Rao *et al.*, 1980a,b). In the case of linear sorption and one sorption-site, the model by van Genuchten and Wierenga (1976) can be described
as follows:

\[
\theta_m \frac{\partial C_m}{\partial t} + (\theta_{im} + \rho K_d) \frac{\partial \bar{C}_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial z^2} - v_m \theta_m \frac{\partial C_m}{\partial z}, \tag{2.9}
\]

\[
(\theta_{im} + \rho K_d) \frac{\partial \bar{C}_{im}}{\partial t} = \chi (C_m - \bar{C}_{im}). \tag{2.10}
\]

where the subscripts \( m \) and \( im \) refer to mobile and immobile regions, \( C \) is solute concentration, \( \bar{C} \) is volume average concentration, \( \theta \) is bulk void ratio, \( \rho \) is the solid bulk density, \( K_d \) is the sorption partition coefficient, \( D \) is the dispersion coefficient, \( v \) is the advection velocity, and \( \chi \) is the mass transfer coefficient. It has been assumed that the adsorption to solid is instantaneous, and transfer between mobile and immobile water is governed by a first-order relation as in (2.10).

For a few specific aggregate geometries, the solute diffusion in the immobile region can be determined analytically. One commonly assumed geometry is a sphere (e.g., Rao et al., 1980a,b; van Genuchten, 1985; Goltz and Roberts, 1986a). Assuming dependence only on \( r \), the local radial position in a sphere, the diffusion in a spherical aggregate is given by

\[
\frac{\partial C_{im}}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_{im}}{\partial r} \right), \tag{2.11}
\]

with the boundary condition

\[
C_{im}(a, z, t) = C_m(z, t), \tag{2.12}
\]

where \( D_e \) is the effective diffusion in aggregates, and \( a \) is the aggregate radius. Analytical solutions for the radial diffusion equation (2.11) under various boundary and initial conditions are readily available (e.g., Carslaw and Jaeger, 1959; Crank, 1975). The mass exchange rate between mobile and immobile water can then be determined from \( \partial \bar{C}_{im} / \partial t \) where \( \bar{C}_{im} = (3/a^3) \int_0^a r^2 C_{im} \, dr \). This approach avoids the use of the empirical first-order relation (2.10). The direct coupling of (2.11), which is a microscopic diffusion equation, with the macro-transport equation (2.9) is however a heuristic approach. In the boundary condition (2.12), \( C_{im}(a, z, t) \) is a local concen-
tration while $C_m(z,t)$ is a macroscopic quantity obtained by averaging the mobile concentration over an elementary volume. The validity of this boundary condition has to be justified before the solution can be relied on. Piquemal (1993) developed some conditions under which the boundary condition may be realized.

The radial diffusion model was originally developed in chemical process industries for problems of mass and heat transfer during saturated flow through a packed-bed consisting of spherical porous particles. Analytical solutions for one-dimensional solute transport by advection and dispersion in a semi-infinite domain have been given by, among others, Rosen (1952), Babcock et al. (1966), Pellett (1966) and Rasmuson and Neretnieks (1980). They all assume a film resistance near the surface of a sphere, and an empirical film transfer coefficient has to be included to describe mass flux in/out of a sphere.

For a closed batch system with aggregates immersed in a well-stirred solution, Rao et al. (1980a) correlated the analytical results for the diffusion equation (2.11) and the first-order model. They obtained an expression for the mass transfer coefficient $\chi$ in terms of the aggregate parameters. Among other dependence, $\chi$ decreases with time. They therefore proposed the use of a time-averaged coefficient $\bar{\chi}$ based on the length of time of the problem. They further used both the diffusion model and the first-order model to study solute transport in a miscible displacement column test (Rao et al., 1980b). Predictions from either model were found in close agreement with experimental data, as long as they adopted the mean column residence time as the time period over which the transfer coefficient $\chi$ was averaged. Consequently $\bar{\chi}$ depends on the pore fluid velocity. In a further study using batch experiments (Rao et al., 1982), they demonstrated by the diffusion model that solute diffusion from nonspherical aggregates could be approximated by diffusion in equivalent spheres. The radius of the equivalent sphere was chosen such that the sphere volume was the same as that of the nonspherical aggregate.

Wu and Gschwend (1986, 1988) further studied sorption kinetics using the spherical diffusion model in a closed batch system. Using hydrophobic organic compounds, their experiment provided evidence for intraparticle diffusion, and the diffusivity was
found to be four to seven orders of magnitude smaller than that in bulk water. The first-order model was found unable to fit well the data for concentration changes. Nevertheless, they correlated the first-order model with the diffusion model by matching solutions of the two models at half-equilibrium points. Simulation results given by the correlated transfer coefficient were found satisfactory only when the concentration fluctuation time scale was close to the half-equilibrium time. Furthermore, it is unclear whether these transfer coefficients, correlated for closed systems, are still reliable in an open system with bulk flow.

Very few works have studied multi-dimensional solute transport in aggregated soils. Carnahan and Remer (1984) and Goltz and Roberts (1986b) presented analytical solutions for 3-dimensional transport due to an instantaneous point source in a uniform groundwater flow.

Hassanizadeh (1988) developed governing equations for the transport of a low concentration species by concentrated brine through an aggregated medium. In order to close the problem, he introduced constitutive relations, in the form of first-order expression, for the mass exchange rates between the macropores and the micropores. Piquemal (1992) used the method of volume averaging to derive basic transport equation in a system containing stagnant fluid. For closure, he also assumed a first-order phenomenological relation for the cross-region mass exchange rate. Furthermore, Piquemal fails to account for the fact that the diffusivity in the macropore fluid is usually much higher than that in the stagnant fluid in micropores.

**Vapor Transport in Aggregated Soils**

A comprehensive spherical diffusion model for vapor transport in a unidirectional flow has been proposed by Gierke et al. (1990, 1992) who have allowed nonlinear sorption isotherm, film resistance and the presence of mobile water in the macropores. Separate transport equations are set up for the chemical in the air and in the mobile water, with first-order kinetic terms for exchange between air and mobile water, and between mobile and immobile water. The resulting equations contain 10 dimensionless parameters involving many transfer coefficients which are not easily measured.
directly but are introduced to curve-fit the final results. They performed experiments in which organic vapor was advected through an initially uncontaminated soil column. Breakthrough curves under various conditions were obtained. However their experimental results did not provide any information on the validity of the first-order model.

Brusseau (1991) suggested a two-region/two-site conceptual model for soil venting problems with soil heterogeneity and rate-limited sorption. In his model, a first-order relation is also assumed for the mass transfer between mobile gas phase and immobile water phase. His model however involves a large number of field and sorbent/sorbate parameters and rate constants, many of which are difficult to evaluate and estimate in practical situations.

Rasmuson et al. (1990) studied the uptaking of hydrolyzable gases (SO₂ and CO₂) in macropores by immobile soil moisture. They used a linear diffusion model for the mass exchange rate. Their emphases were on the factors of absorption of such gases, such as the pH of the solution and the soil structure.

Similar first-order kinetic relations have also been used by McCoy and Rolston (1992) who, with four different models of soil aggregates, studied the effects of chemical partitioning and aggregate diffusion on the convective transport of gases in moist porous media.

2.3 Present Work

Mathematical modeling of solute transport in natural soils is an immensely difficult problem due to the complexity in geometrical structure of, and physical and chemical processes in the soil (Brusseau and Rao, 1990). To improve our capability for practical prediction the component processes that a model purports to describe should be carefully examined both separately and collectively. Based on the preceding discussions, we may summarize the three models commonly used to describe the phase exchange on the macroscale:
local equilibrium – fails to describe tailing, rebound etc.

\begin{itemize}
\item empirical transfer coefficients
\item first-order – which are difficult to estimate
\item and not constant in time
\item kinetic
\item appropriate model if mass transfer is rate-limited by aqueous diffusion in micropores
\end{itemize}

Despite the many idealizations regarding the simple aggregate structure, the aggregate-diffusion model is based more on physical processes involving the most fundamental coefficients, and less on curve-fitting hypotheses, than other models. In the present work we shall take the minimalist’s approach and employ a theory accounting only for effects and parameters which can be reliably estimated or measured. In this chapter we shall formally derive by the homogenization theory the governing equations for soil vapor extraction in aggregated soils, previously obtained by heuristic arguments.

The theory of homogenization, introduced by Sanchez-Palencia (1974) and summarized in the books by Bensoussan et al. (1978) and Sanchez-Palencia (1980), is a formalism for deducing both the macroscale equations and the effective constitutive coefficients for many mechanics problems (e.g., seepage flow, deformation, heat and mass transfer) in composite media. An assumption central to the theory is that there exist two disparate length scales: the microscale \( l \) and the macroscale \( L \) where \( l/L = \epsilon \ll 1 \). It is also assumed that the microstructure is periodic so that averages can be taken over a periodic cell. In sharp contrast to many other averaging techniques, the homogenization theory derives phenomenological equations on the basis of
micromechanics by the multiple-scale asymptotic method, in a general and rigorous manner without any closure hypotheses. All constitutive coefficients are definable by a sets of canonical boundary-value problems in a unit-cell, whose solutions can in principle be found numerically. Some applications of the homogenization theory have been recently reviewed by Mei et al. (1996).

To apply the homogenization theory to the present problem, we first make the following qualitative assumptions for the model soil system:

1. Soils exist as spherical aggregates. Water with dissolved and sorbed chemicals is held immobilized in the aggregates, while only air with chemical vapors can flow in the inter-aggregate pore space. This assumption implies the neglect of mobile water in the macropores, and avoids the difficulty of dealing with a multiphase flow. This is true when the soil is well above the groundwater table where the residual moisture forms a discontinuous phase retained only in the micropores by capillary forces.

2. As a first problem, we assume that residual NAPL is not present in the soil matrix, or has already been volatilized into vapor phase. The case in which residual NAPL is present will be studied in Chapter 5.

3. Sorptive exchange between solid and aqueous phases may occur inside an aggregate, but is fast relative to aqueous diffusion. This is usually true for non-polar or hydrophobic compounds (e.g., benzene, toluene). To describe sorption of VOC to wet soils, a linear sorption isotherm is usually adequate and will be assumed here.

4. There are two vastly different length scales; on the microscale (aggregate) the soil structure is periodic.

For simplicity, the micro-structure is here assumed to be a periodic array of spherical aggregates whose size can vary only slowly over the macroscale (Figure 2-6). Therefore there is only one aggregate in each cell. This geometrical assumption can be relaxed by considering microcells consisting of many aggregates of varying sizes and
Figure 2-6: A cubic periodic array of spherical aggregates where $\Omega = \text{unit cell}$, $\Omega_g = \text{air-filled pore space}$, $\Omega_a = \text{water-saturated aggregate}$, $\Gamma_{ga} = \text{air/aggregate interface}$. Shapes. Modification of the present theory can \textit{in principle} be made by augmenting the numerical effort in solving the type of cell problems to be described.

### 2.4 Scales Estimates and Physical Parameters

For the idealized model just described, we wish to establish first the practical relevance of certain scaling assumptions before proceeding with the procedure of homogenization. Let $l$ and $L$ be the microscopic and macroscopic length scales respectively; their ratio $l/L = \epsilon \ll 1$ will be the small ordering parameter. Further let $U_g$, $\nu$, $D_g$ and $D_w$ be the characteristic air velocity, air kinematic viscosity, molecular diffusivity in air and molecular diffusivity in the aggregate aqueous solution respectively. Note that $D_w$ is the effective diffusivity of the water/grain mixture, and not of pure water. After estimating typical orders of magnitude of the physical parameters, quantitative assumptions are made in terms of the ratio $\epsilon$, as shown below.
(a) Pore Reynolds number \( Re = U_g l / \nu \)

Typical air velocity in SVE operations is in the order of 0.1 mm/sec. Assuming an aggregate size of \( O(1 - 10) \) mm, and using \( \nu = 0.15 \) cm\(^2\)/sec, we get \( Re = O(10^{-2} - 10^{-3}) \). Specifically we shall assume that

\[
Re = O(\epsilon). \tag{2.13}
\]

(b) Pore Péclet number \( Pe = U_g l / D_g = Re(\nu / D_g) \)

Typical diffusivity in air \( D_g \) is in the order of 0.1 cm\(^2\)/sec, which is comparable to kinematic viscosity of air. Hence we shall take

\[
Pe = O(Re) = O(\epsilon). \tag{2.14}
\]

(c) Ratio of diffusivities \( D_w / D_g \)

Typical diffusivity of chemical compounds in pure water is in the order of \( 10^{-5} \) cm\(^2\)/sec. Solely because of impedance (tortuosity, constrictivity) by solid grains, the effective value in aggregate solution, \( D_w \), can be as low as \( O(10^{-7}) \) cm\(^2\)/sec where the retardation due to sorption is yet to be included (Wu and Gschwend, 1986). Therefore the ratio of diffusivities \( D_w / D_g \) is \( O(10^{-4} - 10^{-6}) \), and we shall make the important assumption that

\[
\frac{D_w}{D_g} = O(\epsilon^2). \tag{2.15}
\]

(d) Time scales

On dimensional grounds there are three time scales in this transport problem: (i) time for diffusion through an aggregate, \( t^2 / D_w \); (ii) time for diffusion in air over the global length scale, \( L^2 / D_g \); (iii) convection time over the global length scale, \( L / U_g \). However the assumptions (2.14) and (2.15) imply that all these
time scales are comparable. We first let

$$T = \frac{l^2}{D_w}. \quad (2.16)$$

Then by $l = \epsilon L$ and the assumption (2.15) it follows immediately that $T = O(L^2/D_g)$. Furthermore

$$\frac{L^2}{D_g} = \frac{L}{U_g} \frac{L}{l} \frac{D}{U_g} = \frac{Pe}{\epsilon} \frac{L}{U_g}. \quad (2.17)$$

Therefore by the condition (2.14) we also have $T = O(L/U_g)$. As numerical estimates, we take $D_w = 10^{-7}$ cm$^2$/sec, then $T \sim 1$ day for $l = 1$ mm, and $T \sim 100$ days for $l = 1$ cm.

Assuming cubic packing, a micro-cell $\Omega$ is of cubic shape and linear dimension $l$ (Figure 2-6). Centered in each cell is a spherical aggregate of radius $a$ which may vary slowly in space. Let the surface of the aggregate be $\Gamma_g$ and be described mathematically by $F(x_i) = 0$. Also the aggregate domain $\Omega_a$ corresponds to $F(x_i) > 0$, and the gas domain $\Omega_g$ corresponds to $F(x_i) < 0$. Then the gradient of the function $F$ will give the normal vector to $\Gamma_g$ directing into the aggregate. The volume ratios $\theta_g = |\Omega_g|/|\Omega|$ and $\theta_a = |\Omega_a|/|\Omega| = 1 - \theta_g$ are respectively the macroporosity and the aggregate volume fraction; both are assumed to be slowly varying on the global scale. The average over $\Omega$ of a quantity $f$ in $\Omega_g$ or $\Omega_a$, is defined respectively by

$$\langle f \rangle_g \equiv \frac{1}{|\Omega|} \iiint_{\Omega_g} f d\Omega, \quad \text{and} \quad \langle f \rangle_a \equiv \frac{1}{|\Omega|} \iiint_{\Omega_a} f d\Omega. \quad (2.18)$$

Properties in an aggregate, such as microporosity $\phi$, sorption coefficient $K_d$, and effective diffusivity $D_w$ are also assumed to be slowly varying on the global scale.
2.5 Air Flow

Let us start from governing equations on the microscale. For the steady flow of a compressible gas, the continuity equation is

\[
\frac{\partial \rho u_i}{\partial x_i} = 0, \quad (2.19)
\]

and the momentum equation is

\[
\rho u_j \frac{\partial u_i}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \mu \frac{\partial^2 u_i}{\partial x_j \partial x_j} + \frac{\mu}{3} \frac{\partial^2 u_j}{\partial x_i \partial x_j}, \quad (2.20)
\]

where gravity has been ignored and the bulk viscosity is assumed to be zero. Assuming an ideal gas, the equation of state is

\[
\frac{p M}{R_g \Theta} = \rho. \quad (2.21)
\]

In the preceding equations, \( u_i \) are the velocity components, \( p \) is the absolute air pressure, \( \rho \) is the air density, \( \mu \) is the dynamic viscosity, \( M \) is the molecular weight of air mixture, \( R_g \) is the universal gas constant and \( \Theta \) is the absolute temperature. Since the pressure variation in an SVE well can be in the order of 0.1 to 0.5 atm, the compressibility of air can be important. Isothermal conditions will be assumed and therefore the dynamic viscosity will be taken as a constant owing to its insensitivity to pressure change.

As discussed in Mei (1992), the scale of pressure variation \( P \) is characterized by \( \mu L U_g / l^2 \) over the global length scale \( L \). In terms of the normalized variables (distinguished by a hat):

\[
x_i = l \hat{x}_i, \quad p = P \hat{p}, \quad u_i = U_g \hat{u}_i, \quad \rho = \frac{PM}{R_g \Theta} \hat{\rho}, \quad (2.22)
\]

the dimensionless Navier-Stokes equations are

\[
\frac{\partial \hat{p} \hat{u}_i}{\partial \hat{x}_i} = 0, \quad (2.23)
\]
\[
\frac{\partial \hat{p}}{\partial \hat{x}_i} = \epsilon \left( \frac{\partial^2 \hat{u}_i}{\partial \hat{x}_j \partial \hat{x}_j} + \frac{1}{3} \frac{\partial^2 \hat{u}_j}{\partial \hat{x}_i \partial \hat{x}_j} \right) - \epsilon \text{Re} \hat{u}_j \frac{\partial \hat{u}_i}{\partial \hat{x}_j}.
\] (2.24)

Use has been made of (2.21) and the isothermal assumption so that \( p \sim \rho \). Since \( \text{Re} \) has been assumed to be of order \( \epsilon \), the last term in (2.24) is of order \( \epsilon^2 \).

From here on let us return to physical variables but keep the ordering parameter for identification,

\[
\frac{\partial pu_i}{\partial x_i} = 0,
\] (2.25)

\[
\frac{\partial p}{\partial x_i} = \epsilon \mu \left( \frac{\partial^2 u_i}{\partial x_j \partial x_j} + \frac{1}{3} \frac{\partial^2 u_j}{\partial x_i \partial x_j} \right) - \epsilon^2 \rho u_j \frac{\partial u_i}{\partial x_j}.
\] (2.26)

Let us introduce the local and global coordinates \( x_i \) and \( X_i = \epsilon x_i \), and the multiple-scale expansions

\[
u_i = u_i^{(0)} + \epsilon u_i^{(1)} + \cdots, \quad p = p^{(0)} + \epsilon p^{(1)} + \cdots,
\] (2.27)

where \( u_i^{(m)}, p^{(m)} \) \( (m = 0, 1, \cdots) \) depend on \( x_i \) and \( X_i = \epsilon x_i \). By the standard procedure of multiple scales (e.g., Nayfeh, 1973), one gets at the leading order \( O(\epsilon^0) \),

\[
p^{(0)} = p^{(0)}(X_i),
\] (2.28)

and

\[
\frac{\partial u_i^{(0)}}{\partial x_i} = 0.
\] (2.29)

That is, to the leading order the pressure depends only on the global coordinates and the air flow is incompressible locally.

At the next order \( O(\epsilon) \), the boundary value problem for \( u_i^{(0)} \) and \( p^{(1)} \) is linear, and the second term inside the parentheses of (2.26) vanishes by virtue of (2.29). The resulting problem can be represented in terms of the global pressure gradient by

\[
u_i^{(0)} = -\frac{K_{ij}}{\mu} \frac{\partial p^{(0)}}{\partial X_j},
\] (2.30)

\[
p^{(1)} = -A_j \frac{\partial p^{(0)}}{\partial X_j} + \bar{p}^{(1)},
\] (2.31)
where $K_{ij}(x_k, X_k), A(x_k, X_k)$ must satisfy the canonical cell problem which is the same as that for incompressible fluid (Ene and Sanchez-Palencia, 1975):

$$\frac{\partial K_{ij}}{\partial x_i} = 0 \quad \text{in} \quad \Omega_g, \quad (2.32)$$

$$- \frac{\partial A_j}{\partial x_i} + \frac{\partial^2 K_{ij}}{\partial x_k \partial x_k} = -\delta_{ij} \quad \text{in} \quad \Omega_g, \quad (2.33)$$

with the boundary conditions

$$K_{ij} = 0 \quad \text{on} \quad \Gamma_{ga}, \quad (2.34)$$

$$K_{ij} \text{ and } A_j \text{ are } \Omega \text{-periodic}, \quad (2.35)$$

where $\delta_{ij}$ is the Kronecker delta. Once the tensor $K_{ij}$ is solved from the above cell boundary value problem, the cell $\Omega$-average of (2.30) gives Darcy's law

$$\langle u_i^{(0)} \rangle_g = - \frac{\langle K_{ij} \rangle_g}{\mu} \frac{\partial p^{(0)}}{\partial X_j}. \quad (2.36)$$

On averaging the $O(\epsilon)$ continuity equation and using Gauss theorem, we get the leading order global continuity equation

$$\frac{\partial}{\partial X_i} \left( p^{(0)} \langle u_i^{(0)} \rangle_g \right) = 0. \quad (2.37)$$

Equations (2.36) and (2.37) are the effective flow equations for air on the global scale. In particular when the soil matrix is isotropic, $\langle K_{ij} \rangle_g = K \delta_{ij}$ and we may combine (2.36) and (2.37) to yield the nonlinear equation for $p^{(0)}$,

$$\frac{\partial}{\partial X_i} \left( \frac{K}{\mu} p^{(0)} \frac{\partial p^{(0)}}{\partial X_i} \right) = 0. \quad (2.38)$$

So far $K$ can still be a function of $X_i$. If we further assume a homogeneous soil, $K$
reduces to a constant and (2.38) can be simplified as

\[
\frac{\partial^2 (p^{(0)})^2}{\partial X_i \partial X_i} = 0.
\]  

(2.39)

Hence for a steady air flow in an isotropic and homogeneous porous medium, the leading order pressure \( p^{(0)} \) may readily be determined from (2.39) with appropriate global boundary conditions; the leading order specific discharge \( \langle u_i^{(0)} \rangle_g \) is then found from (2.36).

Strictly speaking, in SVE operations, air flow must start from a static condition before approaching the steady-state. This transient period must be relatively short in order to justify our assumption of steady-state air flow. For an unsteady air flow, the continuity equation (2.37) would be replaced by

\[
\frac{\partial (\theta_g p^{(0)})}{\partial t} + \frac{\partial}{\partial X_i} \left( p^{(0)} \langle u_i^{(0)} \rangle_g \right) = 0.
\]  

(2.40)

With the help of (2.36), the time scale required to approach steadiness is readily seen to be

\[
T_t = O \left( \frac{\theta_g \mu L^2}{KP} \right).
\]  

(2.41)

For a site of \( L \sim 10 \text{ m} \) with soil properties \( \theta_g = 0.5, K = 10^{-11} \text{ m}^2 \) (coarse sand), air viscosity \( \mu = 1.8 \times 10^{-5} \text{ Pa s} \) and a pressure variation of 0.2 atm, we can estimate that \( T_t \sim 1 \text{ hour} \). This is much shorter than the usual clean-up time, which is in the order of weeks or months, as estimated after (2.17). Thus the steady air flow assumption is justified.
2.6 Solute Transport

2.6.1 Solute Transport in Air

We begin with the microscopic vapor transport equation

$$\frac{\partial C_g}{\partial t} + \frac{\partial}{\partial x_i} (u_i C_g) = \frac{\partial^2 C_g}{\partial x_i \partial x_i}.$$  \hspace{1cm} (2.42)

Normalizing $x_i$ and $u_i$ according to (2.22), and

$$C_g = C_{g0} \hat{C}_g, \hspace{1cm} t = (L/U_g) \hat{t},$$ \hspace{1cm} (2.43)

where $C_{g0}$ is a characteristic value for the vapor concentration, we may write (2.42) as

$$\epsilon \frac{\partial \hat{C}_g}{\partial \hat{t}} + \frac{\partial}{\partial \hat{x}_i} (\hat{u}_i \hat{C}_g) = \frac{1}{Pe} \frac{\partial^2 \hat{C}_g}{\partial \hat{x}_i \partial \hat{x}_i}.$$  \hspace{1cm} (2.44)

Recall that the pore Péclet number $Pe = O(\epsilon)$ as estimated in (2.14). We may now return to physical variables but retain $\epsilon$ for ordering identification:

$$\epsilon^2 \frac{\partial C_g}{\partial t} + \epsilon \frac{\partial}{\partial x_i} (u_i C_g) = \frac{\partial^2 C_g}{\partial x_i \partial x_i}.$$  \hspace{1cm} (2.45)

Expanding $C_g = C_g^{(0)} + \epsilon C_g^{(1)} + \epsilon^2 C_g^{(2)} + \cdots$ with $C_g^{(m)}$ depending on $(x_i, X_i)$, we obtain:

$$0 = D_g \frac{\partial^2 C_g^{(0)}}{\partial x_i \partial x_i},$$  \hspace{1cm} (2.46)

$$\frac{\partial}{\partial x_i} (u_i^{(0)} C_g^{(0)}) = D_g \left( \frac{\partial^2 C_g^{(1)}}{\partial x_i \partial x_i} + 2 \frac{\partial^2 C_g^{(0)}}{\partial X_i \partial x_i} \right),$$  \hspace{1cm} (2.47)

$$\frac{\partial C_g^{(0)}}{\partial t} + \frac{\partial}{\partial x_i} \left( u_i^{(0)} C_g^{(1)} + u_i^{(1)} C_g^{(0)} \right) + \frac{\partial}{\partial X_i} (u_i^{(0)} C_g^{(0)})$$

$$= D_g \frac{\partial}{\partial x_i} \left( \frac{\partial C_g^{(2)}}{\partial x_i} + \frac{\partial C_g^{(1)}}{\partial X_i} \right) + D_g \frac{\partial}{\partial X_i} \left( \frac{\partial C_g^{(1)}}{\partial x_i} + \frac{\partial C_g^{(0)}}{\partial X_i} \right).$$  \hspace{1cm} (2.48)
2.6.2 Diffusion in an Aggregate

Solute in an aggregate is partitioned between the aqueous phase and the sorbed phase. Therefore the total mass per unit aggregate volume \( C_a \) is given by

\[
C_a = (1 - \phi) \rho_s C_s + \phi C_w, \tag{2.49}
\]

where \( \phi \) is the porosity of the aggregate (or microporosity), \( \rho_s \) is the aggregate solid density, \( C_s \) is the mass sorbed per unit mass of solid, and \( C_w \) is the mass of solute per unit volume of aqueous solution. On the microscale of the aggregate, sorption is fast compared to the aqueous diffusion so that local equilibrium prevails between the aqueous and the sorbed phases within each aggregate. Further we assume the sorbate-sorbent follows a linear isotherm

\[
C_s = K_d C_w, \tag{2.50}
\]

where \( K_d \) is the sorption partition coefficient. Then (2.49) may be written as

\[
C_a = [K_d(1 - \phi) \rho_s + \phi] C_w. \tag{2.51}
\]

We stress that these assumptions of equilibrium partition are made only on the microscale.

Mass transfer in the aggregates is solely due to molecular diffusion in the immobile aqueous solution, hence

\[
\frac{\partial C_a}{\partial t} = \phi D_w \frac{\partial^2 C_w}{\partial x_i \partial x_i}. \tag{2.52}
\]

Substituting (2.51) for \( C_a \), the diffusion equation becomes

\[
\frac{\partial C_w}{\partial t} = D_e \frac{\partial^2 C_w}{\partial x_i \partial x_i}, \tag{2.53}
\]
where $D_e$ is the diffusivity in an aggregate effectively retarded by sorptive exchange:

$$D_e = \frac{\phi D_w}{K_d(1 - \phi) \rho_s + \phi}. \quad (2.54)$$

If the fraction of organic matter $f_{om}$ in a soil is greater than 0.002 kg om/kg solid, the organic matter will be the dominant site for the sorption (Schwarzenbach et al., 1993). If this is true,

$$K_d = K_{om} f_{om} \quad (2.55)$$

where $K_{om}$ is the organic matter-water partition coefficient and is a chemical property. Because of hydrophobicity, VOCs usually have a high value of $K_{om}$. For example, $K_{om}$ of toluene at 25°C is approximately 100 (mol·kg⁻¹·om)/(mol·L⁻¹·water). On the other hand, $f_{om}$ is a property of the aggregate material, and can be as high as 0.05 kg om/kg solid for aquifer sand. Therefore, in the case of toluene, $K_d$ will range from a negligible value to 5 (mol·kg⁻¹·solid)/(mol·L⁻¹·water) when the organic matter content varies between 0 and 0.05 kg om/kg solid. As $\rho_s \approx 2.65$ kg/L and $\phi < 1$, it is clear from (2.54) that $D_e \leq O(D_w^*)$. Therefore the diffusion in an aggregate can be greatly reduced when the organic matter content, or the sorptivity, is high.

By (2.15), it follows that

$$\frac{D_e}{D_g} \leq O(\epsilon^2). \quad (2.56)$$

Following similar normalization procedures as for the vapor transport equation, we may show that both sides of (2.53) are of the same order, as expected. Introducing multiple-scale expansions $C_w = C_w^{(0)} + \cdots$, the leading order equation is clearly

$$\frac{\partial C_w^{(0)}}{\partial t} = D_e \frac{\partial^2 C_w^{(0)}}{\partial x_i \partial x_i}. \quad (2.57)$$

### 2.6.3 Microscale Boundary Conditions

Boundary conditions on gas-aggregate interface $\Gamma_{ga}$:
(a) Continuity of flux:

In terms of physical variables,

$$D_g \frac{\partial C_g}{\partial x_i} n_i = \phi D_w \frac{\partial C_w}{\partial x_i} n_i, \quad (2.58)$$

where

$$n_i = \frac{\partial F}{\partial x_i} \left| \frac{\partial F}{\partial x_i} \right|^{-1} \quad (2.59)$$

is the unit normal vector to \( \Gamma_{ga} \) directing into the aggregate. Note that by (2.15) the right-hand side of (2.58) is of order \( \epsilon^2 \) relative to the left-hand side. To allow the cell geometry to vary on the global scale we express the interface \( \Gamma_{ga} \) by \( F(x_i, X_i) = 0 \). Thus the macro-porosity is allowed to vary slowly in space. After expanding for \( C_g, C_w \) and \( x_i \), we obtain the following boundary conditions

$$D_g \frac{\partial C_g^{(0)}}{\partial x_i} \frac{\partial F}{\partial x_i} = 0, \quad (2.60)$$

$$D_g \left( \frac{\partial C_g^{(1)}}{\partial x_i} + \frac{\partial C_g^{(0)}}{\partial X_i} \right) \frac{\partial F}{\partial x_i} + D_g \frac{\partial C_g^{(0)}}{\partial x_i} \frac{\partial F}{\partial X_i} = 0, \quad (2.61)$$

$$D_g \left( \frac{\partial C_g^{(2)}}{\partial x_i} + \frac{\partial C_g^{(1)}}{\partial X_i} \right) \frac{\partial F}{\partial x_i} + D_g \left( \frac{\partial C_g^{(1)}}{\partial x_i} + \frac{\partial C_g^{(0)}}{\partial X_i} \right) \frac{\partial F}{\partial X_i} = \phi D_w \frac{\partial C_w^{(0)}}{\partial x_i} \frac{\partial F}{\partial x_i}. \quad (2.62)$$

(b) Partition:

On the aggregate level, local equilibrium dominates along the gas-water interface as a result of the high gas molecular velocity (Schwarzenbach et al., 1993). We therefore assume that partition of solute along \( \Gamma_{ga} \) follows Henry's law: \( H = C_g/C_w \) where \( H \) is Henry's law constant. Thus, on expanding,

$$H = \frac{C_g^{(m)}}{C_w^{(m)}} \quad (m = 0, 1, 2, \cdots) \quad \text{on} \quad \Gamma_{ga}. \quad (2.63)$$

It should be emphasized that this is a local assumption on the aggregate scale and differs from the usual assumption of local equilibrium on the global scale.

Along the cell boundaries, \( C_g^{(m)} \) \((m = 0, 1, \cdots)\) are \( \Omega \)-periodic.
2.6.4 Effective Transport Equations on the Macroscale

The effective transport equation may now be derived from these perturbation equations.

\( O(1) \):

From (2.46) and (2.60), it is obvious that

\[
C^{(0)}_g = C^{(0)}_g(X_i, t). \tag{2.64}
\]

That is, the leading order vapor concentration is independent of the local scale.

\( O(\varepsilon) \):

By (2.64) and (2.29), (2.47) now becomes

\[
0 = D_g \frac{\partial^2 C^{(1)}_g}{\partial x_i \partial x_i}. \tag{2.65}
\]

Since \( C^{(1)}_g \) satisfies the linear boundary condition (2.61), we let

\[
C^{(1)}_g = -N_l \frac{\partial C^{(0)}_g}{\partial X_i}, \tag{2.66}
\]

which implies a canonical boundary value cell problem for \( N_l(x_i, X_i) \):

\[
\frac{\partial^2 N_l}{\partial x_i \partial x_i} = 0, \tag{2.67}
\]

subject to the boundary conditions

\[
\frac{\partial N_l}{\partial x_i} \frac{\partial F}{\partial x_i} = \frac{\partial F}{\partial x_i} \quad \text{along } \Gamma_{ga}. \tag{2.68}
\]

Furthermore \( N_l \) must be \( \Omega \)-periodic along the cell boundaries. Once \( N_l \) are solved, the first-order correction \( C^{(1)}_g \) may be determined in terms of \( \partial C^{(0)}_g / \partial X_i \) from (2.66).

\( O(\varepsilon^2) \):

We first find \( \Omega \)-average of (2.48). In doing so, we need to interchange the operations of cell averaging and global differentiation. The interchange rule can be obtained by
extending the Leibniz rule to a three-dimensional geometry with two spatial scales (Mei et al., 1996):

\[
\left< \frac{\partial f_i}{\partial X_i} \right> \bigg|_g = \frac{\partial}{\partial X_i} \left< f_i \right> \bigg|_g + \frac{1}{|\Omega|} \int_{\Gamma_{ga}} f_i \frac{\partial F/\partial X_i}{|\partial F/\partial x_i|} \, d\Gamma.
\]

(2.69)

where \( f_i \) is any vector in \( \Omega_g \). The derivation of the above spatial averaging rule is also given in Appendix B. This result is essentially the same as the spatial averaging theorem in the method of volume averaging (Whitaker, 1985; Gray and Lee, 1977). In particular for all convection-related terms which are proportional to \( u_i \), the surface integral on the right-hand side of (2.69) vanishes because of zero velocity at the aggregate boundary. For these terms microscale averaging and macroscale differentiation can be interchanged. With (2.69), we average (2.48) over the \( \Omega \)-cell and obtain after using Gauss theorem and substituting (2.66),

\[
\theta_g \frac{\partial C_g^{(0)}}{\partial t} + \frac{\partial}{\partial X_i} \left( \left< u_i^{(0)} \right> C_g^{(0)} \right) = \frac{\partial}{\partial X_i} \left[ D_g \left( -\left< \frac{\partial N_i}{\partial x_i} \right> \bigg|_g + \theta_g \delta_{il} \right) \frac{\partial C_g^{(0)}}{\partial X_i} \right] + I_{ga},
\]

(2.70)

where \( \theta_g = |\Omega_g|/|\Omega| \) is the macroporosity, \( \delta_{il} \) is the Kronecker delta, and

\[
I_{ga} = \frac{1}{|\Omega|} \int_{\Gamma_{ga}} D_g \left[ \left( \frac{\partial C_g^{(2)}}{\partial x_i} + \frac{\partial C_g^{(1)}}{\partial X_i} \right) \frac{\partial F/\partial x_i}{|\partial F/\partial x_i|} \right. + \left. \left( \frac{\partial C_g^{(1)}}{\partial x_i} + \frac{\partial C_g^{(0)}}{\partial X_i} \right) \frac{\partial F/\partial X_i}{|\partial F/\partial x_i|} \right] \, d\Gamma.
\]

(2.71)

amounts to an apparent source, representing the total influx from the aggregate \( \Omega_a \).

We next take \( \Omega \)-average of (2.57) and use also Gauss theorem to obtain

\[
\frac{\partial \left< C_w^{(0)} \right>}{\partial t} = -\frac{1}{|\Omega|} \int_{\Gamma_{ga}} D_e \frac{\partial C_w^{(0)}}{\partial x_i} \frac{\partial F/\partial x_i}{|\partial F/\partial x_i|} \, d\Gamma.
\]

(2.72)

Since \( D_e, D_w \) and \( \phi \) are independent of microscale coordinates, the right-hand side of (2.72) is equal to \(-(D_e/\phi D_w)I_{ga}\) by virtue of the boundary condition (2.62). Therefore the source term can be expressed as

\[
I_{ga} = -\frac{\phi D_w \theta_a \partial \bar{C}_w^{(0)}}{D_e} \frac{\partial}{\partial t},
\]

(2.73)
where $\tilde{C}_w^{(0)} = \langle C_w^{(0)} \rangle_{a}/\theta_a$ denotes the average of $C_w^{(0)}$ over $\Omega_a$, and $\theta_a = |\Omega_a|/|\Omega| = 1 - \theta_g$ is the volume fraction of aggregates.

Substituting $I_{ga}$ from (2.73) into (2.70), we obtain

$$
\theta_g \frac{\partial C_g^{(0)}}{\partial t} + \frac{\partial}{\partial X_i} \left( \theta_g \tilde{u}_i^{(0)} C_g^{(0)} \right) - \frac{\partial}{\partial X_i} \left( \theta_g (D_g^{*})_{iil} \frac{\partial C_g^{(0)}}{\partial X_l} \right) = -\frac{\phi D_w \theta_a}{D_e} \frac{\partial \tilde{C}_w^{(0)}}{\partial t},
$$

(2.74)

where

$$
\tilde{u}_i^{(0)} = \langle u_i^{(0)} \rangle_{g}/\theta_g
$$

(2.75)

is the effective air seepage velocity in which $\langle u_i^{(0)} \rangle_{g}$ can be found from Darcy’s law (2.36), and

$$
(D_g^{*})_{iil} = -\frac{D_g}{\theta_g} \left\langle \frac{\partial N_i}{\partial x_l} \right\rangle_{g} + D_g \delta_{iil}
$$

(2.76)

is the effective air diffusivity in the unsaturated soil matrix. It can be shown that the tensor $(D_g^{*})_{iil}$ is symmetric and positive definite for any microstructure (Brenner, 1980). A proof is also given in Appendix C. Note from the cell problem (2.67)–(2.68) that $N_i$ depends only on the cell geometry, but not the flow. It follows that $(D_g^{*})_{iil}$ is a function of the aggregate structure only but not the flow. In other words the hydrodynamical dispersion is relatively unimportant by virtue of (2.14). This has been pointed out previously by Johnson et al. (1990a), Gierke et al. (1992), and Brusseau (1991).

To find the source term on the right-hand side of (2.74), we first find $C_w^{(0)}(x_i, X_i, t)$ from (2.57) and (2.63) where $C_g^{(0)}$ is uniform in a local cell. For the simple geometry of spherical aggregates, the problem reduces to

$$
\frac{\partial C_w^{(0)}}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_w^{(0)}}{\partial r} \right),
$$

(2.77)

with the boundary condition

$$
C_w^{(0)}(r = a, X_i, t) = C_g^{(0)}(X_i, t)/H,
$$

(2.78)
and the initial concentration is a function of global coordinates only

$$C_w^{(0)}(r, X_i, t = 0) = C_w(0, X_i).$$ (2.79)

Solution for (2.77)–(2.79) can be found from Carslaw and Jaeger (1959):

$$C_w^{(0)} = -\frac{2}{a\pi} \sum_{n=1}^{\infty} (-1)^n \exp(-\lambda_n t) \sin \left( \frac{n\pi r}{a} \right) \left\{ \frac{a^2}{n\pi} C_w(0) + \frac{n\pi D_e}{H} \int_0^t \exp(\lambda_n \tau) C_g^{(0)} d\tau \right\},$$ (2.80)

where

$$\lambda_n = \frac{n^2 \pi^2 D_e}{a^2}.$$ (2.81)

The $\Omega_a$-average of $C_w^{(0)}$ is

$$\bar{C}_w^{(0)} = \frac{3}{a^3} \int_0^a r^2 C_w^{(0)} dr$$

$$= \frac{6D_e}{a^2} \sum_{n=1}^{\infty} \exp(-\lambda_n t) \left[ \frac{C_w(0)}{\lambda_n} + \int_0^t \exp(\lambda_n \tau) \frac{C_g^{(0)}}{H} d\tau \right].$$ (2.82)

Differentiating (2.82) with respect to time, and integrating by part, we get

$$\frac{\partial \bar{C}_w^{(0)}}{\partial t} = \frac{6D_e}{a^2} \sum_{n=1}^{\infty} \exp(-\lambda_n t) \left[ \left( \frac{C_g(0)}{H} - C_w(0) \right) + \int_0^t \exp(\lambda_n \tau) \frac{\partial C_g^{(0)}}{\partial \tau} d\tau \right],$$ (2.83)

where $C_g(0)(X_i) = C_g^{(0)}(X_i, t = 0)$ is the initial vapor concentration. We shall suppose that before air venting begins the chemical has resided long enough in the soils so that locally the two phases are in equilibrium. Then $C_w(0) = C_g(0)/H$ and the two terms inside the parentheses in (2.83) cancel each other. Finally substitution of (2.83) into (2.74) gives the macro-transport equation for the vapor phase solute:

$$\theta_g \frac{\partial C_g^{(0)}}{\partial t} + \frac{\partial}{\partial X_i} \left( \theta_g \tilde{u}_i^{(0)} C_g^{(0)} \right) - \frac{\partial}{\partial X_i} \left( \theta_g (D_g^*)_{il} \frac{\partial C_g^{(0)}}{\partial X_l} \right)$$

$$= -\frac{6\phi D_w \theta_g}{a^2 H} \sum_{n=1}^{\infty} \int_0^t \exp[-\lambda_n (t - \tau)] \frac{\partial C_g^{(0)}}{\partial \tau} d\tau.$$ (2.84)

In summary, one first finds $p^{(0)}$ from (2.38) or (2.39), $\langle u_i^{(0)} \rangle_g$ from (2.36), and
then solves for $C_g^{(0)}$ from (2.84) and $\tilde{C}_w^{(0)}$ from (2.82). The present theory does not depend on the assumption of first-order kinetics and empirical transfer coefficients, and justifies the heuristic derivations by Rao et al. (1980a,b) and others cited before. Theoretically it is an extension of Hornung (1991) for diffusion of nonvolatile solute in saturated porous media.

So far, we have completed the formal derivations of the effective transport equations for SVE in an unsaturated soil. Upon hindsight of the results, we may also derive the same equations using heuristic arguments without the multiple-scale analysis. Such an heuristic derivation of the above effective transport equations is presented in Appendix D.

### 2.6.5 Normalization and Dimensionless Parameters

Let us further assume that the soil matrix is isotropic and homogeneous so that $(D_g^*)_{ij}$ reduces to $D_g^* \delta_{ij}$ and all the soil properties $\theta_g$, $\theta_a$, $\phi$, $a$, $D_w$ are independent of space. Introducing the following normalized variables (distinguished by a hat):

$$
C_g^{(0)} = C_{g0} \hat{C}_g, \quad \tilde{C}_w^{(0)} = (C_{g0}/H)\hat{C}_w, \quad X_i = L \hat{X}_i, \quad t = (L/U_g)\hat{t}, \quad \hat{u}_i^{(0)} = U_g \hat{u}_i,
$$

the normalized forms of (2.84) and (2.82) are

$$
\frac{\partial \hat{C}_g}{\partial \hat{t}} + \frac{\partial (\hat{u}_i \hat{C}_g)}{\partial \hat{X}_i} - \frac{1}{Pe} \frac{\partial^2 \hat{C}_g}{\partial \hat{X}_i^2} = -6\xi \sigma \sum_{n=1}^{\infty} \int_0^\hat{t} \exp[-\lambda_n(\hat{t} - \hat{\tau})] \frac{\partial \hat{C}_g}{\partial \hat{\tau}} d\hat{\tau},
$$

(2.85)

$$
\hat{C}_w = 6\sigma \sum_{n=1}^{\infty} \left[ \frac{\exp(-\lambda_n \hat{t})}{\lambda_n} + \int_0^\hat{t} \exp[-\lambda_n(\hat{t} - \hat{\tau})] \hat{C}_g d\hat{\tau} \right] = \hat{C}_g - 6\sigma \sum_{n=1}^{\infty} \frac{1}{\lambda_n} \int_0^\hat{t} \exp[-\lambda_n(\hat{t} - \hat{\tau})] \frac{\partial \hat{C}_g}{\partial \hat{\tau}} d\hat{\tau},
$$

(2.87)

where

$$
P e = \frac{LU_g}{D_g},
$$

(2.88)
\[
\xi = \frac{\phi D_w \theta_a}{H D_e \theta_g} = \frac{[K_d(1 - \phi)\rho_s + \phi] \theta_a}{H \theta_g},
\]
(2.89)
\[
\sigma = \frac{D_e L}{a^2 U_g},
\]
(2.90)
and
\[
\lambda_n = n^2 \pi^2 \sigma.
\]
(2.91)

Physically \(\overline{Pe}\) is the global Péclet number which indicates the significance of advection over diffusion in air transport, while \(\sigma\) is a ratio of global advection time to the aggregate diffusion time which characterizes the speed of depletion of chemicals from aggregates. Note that \(\sigma\) is small when the aggregate radius \(a\) is large. The parameter \(\xi\) is a function of chemical and soil properties and is related to the chemical partitioning:
\[
\frac{C_{a0} \theta_a}{C_{g0} \theta_g} = \frac{(\phi D_w / D_e) (C_{g0} / H) \theta_a}{C_{g0} \theta_g} = \frac{\phi D_w \theta_a}{H D_e \theta_g} = \xi,
\]
(2.92)

where in the first step use has been made of (2.51) and Henry’s law. Thus \(\xi\) is the ratio of initial mass of the species partitioned in aggregates to that in the vapor phase per bulk volume of soil.

### 2.7 Limiting Cases

#### 2.7.1 Local Equilibrium

Although the derived equations cover cases where kinetics is important, let us rederive, as a check, the limiting case of local equilibrium. From the radial diffusion equation (2.77) for \(C_w\), the aggregate effective diffusion time scale can be estimated:
\[
T_a = O \left( \frac{a^2}{D_e} \right) = O \left( \frac{a^2 [K_d(1 - \phi)\rho_s + \phi]}{\phi D_w} \right).
\]
(2.93)

The vapor concentration \(C_g\) varies according to the global time scale \(T_g = L/U_g\). When the vapor concentration varies sufficiently slowly in the aggregate diffusion
time, or $T_g \gg T_a$ which is equivalent to

$$\sigma \gg 1,$$

(2.94)

the aggregate diffusion reaches the steady state almost instantly compared to vapor transport. Then the condition (2.78) holds not only on the boundary but throughout an aggregate, i.e.,

$$C_w^{(0)}(r, X_i, t) = \bar{C}_w = C_g^{(0)}(X_i, t)/H, \quad 0 \leq r \leq a, \quad t \geq 0,$$

(2.95)

which implies local equilibrium between $C_w^{(0)}$ and $C_g^{(0)}$ macroscopically. When this is true, (2.74) can be simplified as

$$R \frac{\partial C_g^{(0)}}{\partial t} + \frac{\partial}{\partial X_i} \left( \bar{u}_i^{(0)} C_g^{(0)} \right) - \frac{\partial}{\partial X_i} \left( (D_i^*) \frac{\partial C_g^{(0)}}{\partial X_i} \right) = 0,$$

(2.96)

where $R$ is the retardation factor

$$R = 1 + \frac{\phi D_w \theta_a}{HT e \theta_g} = 1 + \xi.$$  

(2.97)

Obviously $\xi$ is the contribution due to mass partitioned in aggregates.

As a mathematical confirmation, we note that $\hat{\lambda}_n = n^2 \pi^2 \sigma \gg 1$ when $\sigma \gg 1$. The integral on the right-hand side of (2.86) may be approximated by considering contributions from the neighborhood of $\hat{\tau} = \hat{t}$, according to Laplace’s method. Thus

$$\text{RHS}(2.86) = -6\sigma \sum_{n=1}^{\infty} \int_0^t \exp[-\hat{\lambda}_n(\hat{t} - \hat{\tau})] \frac{\partial \hat{C}_g}{\partial \hat{\tau}} d\hat{\tau}$$

$$\approx -6\sigma \frac{\partial \hat{C}_g}{\partial \hat{t}} \sum_{n=1}^{\infty} \int_0^t \exp[-\hat{\lambda}_n(\hat{t} - \hat{\tau})] d\hat{\tau}$$

$$\approx -6\sigma \frac{\partial \hat{C}_g}{\partial \hat{t}} \sum_{n=1}^{\infty} \frac{1}{\hat{\lambda}_n}$$

$$= -\frac{6\xi}{\pi^2} \frac{\partial \hat{C}_g}{\partial \hat{t}} \sum_{n=1}^{\infty} \frac{1}{n^2} = -\xi \frac{\partial \hat{C}_g}{\partial \hat{t}},$$

(2.98)
which gives (2.96) also.

In brief, local equilibrium can be expected when the effective diffusion in an aggregate is much faster than the travel of vapor over a characteristic global distance. We remark that our theory is capable of dealing with both kinetic and local equilibrium conditions automatically whenever the situation presents itself. This is in sharp contrast to the local equilibrium models which have no mechanism to switch to describing kinetics, and to those first-order models in which artificially high values of transfer coefficients have to be used for the local equilibrium limit.

2.7.2 Small $\xi$ with $\sigma \leq O(1)$

If the Henry's law constant is so large that $\xi \ll 1$, very little amount of VOC is partitioned in the aggregates as relative to the partition in vapor phase. Then the right-hand side of (2.86) becomes negligible as compared to the left-hand side as long as $\sigma \leq O(1)$; the vapor transport equation is reduced to

$$\frac{\partial \hat{C}_g}{\partial t} + \frac{\partial (\hat{u}_i \hat{C}_g)}{\partial X_i} - \frac{1}{Pe} \frac{\partial^2 \hat{C}_g}{\partial X_i \partial X_i} \approx 0,$$

(2.99)

which is independent of $\sigma$. While the normalized aqueous concentration can be calculated from (2.87) and still depends on $\sigma$, the physical value of $C_{w0}^{(0)}$ is small compared to $C_{g0}^{(0)}$, though it may still be unacceptably high to meet the water quality standard.

Another limiting case is when the aggregate diffusion rate is also relatively very small (because of, for example, large aggregates and high pumping rates) so that $\sigma \ll 1$. The vapor concentration, governed by (2.99), will drop rapidly to a small value as a result of air venting in a finite volume of contaminated soil. Then (2.87) reduces to simply a series of exponential decay:

$$\hat{C}_w \approx 6 \sum_{n=1}^{\infty} \frac{\exp(-\lambda_n t)}{n^2 \pi^2} \quad \text{or} \quad \bar{C}_w \approx 6C_{w0} \sum_{n=1}^{\infty} \frac{\exp(-\lambda_n t)}{n^2 \pi^2}$$

(2.100)

which is a function of aggregate properties only. Therefore when both $\xi$ and $\sigma$ are small, the changes of vapor and aqueous concentrations become insensitive to each
other; the vapor phase drops rapidly while the aqueous phase decays slowly. This is a highly non-equilibrium case.

2.8 Concluding Remarks

In this chapter we have reviewed the existing mathematical modelings for soil vapor extraction. As both local equilibrium and first-order kinetic models are not entirely satisfactory, we propose a radial diffusion model to describe the interphase mass transfer kinetics. We have derived systematically the effective equations for the transport of VOC vapor in the vadose zone composed of aggregated soils. Two important assumptions are that (i) the aqueous phase is entirely immobile and trapped in the aggregates and (ii) there is a sharp contrast between diffusivities (cf. (2.15)). The first assumption amounts to assuming that the unsaturated soil is well above the capillary fringe where air is the only mobile fluid. The method of homogenization is used in order to identify the range of validity of the theory. All aggregates are assumed to be spheres whose size can change slowly on the macroscale. The derived effective equations on the macro scale are Darcy's law and the continuity for a compressible gas, and (2.84) for the convection-diffusion transport of a chemical vapor. The latter is an integro-differential equation where the kinetics of phase exchange between vapor and aggregates is described by a convoluted time integral. All physical and chemical parameters in the transport equation can be reliably determined experimentally, in contrast to existing kinetic models which are based on ad hoc first-order relation. Under one of the following two conditions the vapor transport becomes independent of the aggregate diffusion: (i) local equilibrium, or (ii) when the mass initially partitioned in the aggregates is much less than that in the vapor phase.

Applications of the deduced effective equations will be presented in the next chapter. In the first application the theory will be compared to published experiments in a laboratory column where the parameters are either measured or reliably estimated. In the other examples, the model is applied to simulate venting under radial flow fields so that the effects of pumping, soil and chemical properties can be examined.
Chapter 3

Soil Vapor Extraction in Unidirectional and Radial Flows

3.1 Introduction

Applications of the aggregate diffusion model will be presented in this chapter. Let us first briefly review the underlying assumptions of our model derived in Chapter 2. We assume that there is no mobile water or residual NAPL in the unsaturated soil (the effects of residual NAPL will however be studied in Chapter 5). The soil matrix is modeled as a periodic array of spherical aggregates (Figure 2-6), where the intra-aggregate water is immobile, and the diffusivity in the aggregates is much smaller than that in the inter-aggregate air. The film resistance resulting from concentration boundary layer is not pertinent in most SVE operations since the micro Peclet number is typically very small. Since most VOC are hydrophobic, we assume sorptive exchange between solid and aqueous phases inside an aggregate to be in equilibrium, and described by a linear isotherm. Features of the present work in contrast to Gierke et al. (1990, 1992) are summarized in Table 3.1. In §3.2, the transport equations, whose normalized forms contain only three dimensionless parameters, is first applied to the one-dimensional experiments of Gierke et al. (1992), with a view to testing the adequacy and gaining physical insights. The effects of these parameters are then further studied for the problem of air venting from a well along the axis of a
Table 3.1: Comparison of the present work to Gierke et al. (1990, 1992).

<table>
<thead>
<tr>
<th>Features</th>
<th>Present Work</th>
<th>Gierke et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>spherical aggregates</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>mobile water</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>film resistance</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>sorption isotherm</td>
<td>linear</td>
<td>nonlinear</td>
</tr>
<tr>
<td>number of parameters</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>kinetic term</td>
<td>analytical integral</td>
<td>numerical integral</td>
</tr>
</tbody>
</table>

circularly symmetric zone of contamination, for the case of one-dimensional unsteady flow in a confined layer in §3.3, and the case of two-dimensional steady flow in a layer with unsealed ground surface in §3.4.

## 3.2 Unidirectional Flow Through a Column

### 3.2.1 Theory

Gierke et al. (1992) have reported some results of tests of vapor transport in an unsaturated soil column packed with aggregated materials. They filled a 30 cm long, 5 cm ID column with porous materials saturated only in the micropores. In each test, the column was fed steadily with some organic chemical vapor (toluene or methane) for a sufficiently long time after breakthrough, and then the input was switched to some inert gas (air or nitrogen) until elution of the organic chemical vapor was substantially completed. The effluent gaseous concentration was measured as a function of time; the aqueous phase concentration was not. A sketch of their experimental apparatuses is shown in Figure 3-1.

In these tests, the measured pressure difference was below 1%, compressibility effects can be ignored. Our normalization scales in (2.85) are chosen as follows: \( C_{g0} \) is the steady chemical vapor concentration in the pulse input; \( U_g \) is the steady gas seepage velocity; \( L \) is the column length. According to (2.86), the one-dimensional
problem can be stated in normalized form as follows:

$$\frac{\partial C_g}{\partial t} + \frac{\partial C_g}{\partial z} - \frac{1}{Pe} \frac{\partial^2 C_g}{\partial z^2} = -6 \xi \sigma \sum_{n=1}^{\infty} \int_0^t e^{-\lambda_n (t-\tau)} \frac{\partial C_g}{\partial \tau} d\tau,$$

$$C_g - \frac{1}{Pe} \frac{\partial C_g}{\partial z} = \begin{cases} 1, & 0 < t < t_p \\ 0, & t > t_p \end{cases} \quad \text{at } z = 0,$$

$$\frac{\partial C_g}{\partial z} = 0 \quad \text{at } z = 1,$$

$$C_g = C_w = 0 \quad \text{at } t = 0.$$ 

where the hats have been dropped for simplicity and $t_p$ is the duration of the pulse input of chemical vapor. The boundary conditions (3.2) and (3.3) follow from continuity of mass flux across the inlet and the outlet of the column. These boundary conditions are valid when the transport in the connecting end tubes takes place much faster than that in the column. With a zero initial value, the aqueous concentration
in the aggregates is
\[ \tilde{C}_w = 6\sigma \sum_{n=1}^{\infty} \int_0^t e^{-\lambda_n(t-\tau)}C_g \, d\tau. \] (3.5)

Let us denote the Laplace transform of \( C_g \) by \( C_g^*(s) \equiv \mathcal{L}[C_g(t)] \) where \( s \) is the independent variable in the transformed space. Then the Laplace transform of (3.1) gives, with the initial condition (3.4),
\[ \frac{d^2C_g^*}{dz^2} - \frac{dC_g^*}{dz} - G(s)C_g^* = 0, \] (3.6)

where
\[ G(s) = \mathcal{P} \left( s + 6\xi_0 \sum_{n=1}^{\infty} \frac{s}{s + \lambda_n} \right) \]
\[ = \mathcal{P} \left( s + 3\xi_0 \left\{ \sqrt{\frac{s}{\sigma}} \coth \sqrt{\frac{s}{\sigma}} - 1 \right\} \right). \] (3.7)

The last equality is made possible by the partial fraction expansion of the cotangent function (Abramowitz and Stegun, 1972, p75). With the boundary conditions (3.2) and (3.3) also transformed:
\[ C_g^* - \frac{1}{\mathcal{P}e} \frac{dC_g^*}{dz} = \frac{1 - e^{-t_p s}}{s} \quad \text{at} \quad z = 0, \] (3.8)
\[ \frac{dC_g^*}{dz} = 0 \quad \text{at} \quad z = 1, \] (3.9)

the solution to (3.6) is given by
\[ C_g^* = \left( \frac{1 - e^{-t_p s}}{s} \right) e^{\frac{\mathcal{P}e}{s}z} \left\{ \frac{\mathcal{P}e}{z} \sinh[\zeta(1-z)] + \zeta \cosh[\zeta(1-z)] \right\}, \] (3.10)

where
\[ \zeta(s) = \sqrt{\frac{\mathcal{P}e^2}{4} + G(s)}. \] (3.11)

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Table 3.2: Parameters for the three moist column tests reported by Gierke et al. (1992).

<table>
<thead>
<tr>
<th>Column Test</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil Material</td>
<td>APSM</td>
<td>APSM</td>
<td>Sand</td>
</tr>
<tr>
<td>Organic Vapor</td>
<td>Toluene</td>
<td>Methane</td>
<td>Toluene</td>
</tr>
<tr>
<td>$U_g$, cm/s</td>
<td>0.046/0.061*</td>
<td>0.034/0.026*</td>
<td>0.02</td>
</tr>
<tr>
<td>$L$, cm</td>
<td>30.1</td>
<td>30.1</td>
<td>30.1</td>
</tr>
<tr>
<td>$a$, cm</td>
<td>0.035</td>
<td>0.035</td>
<td>0.035</td>
</tr>
<tr>
<td>$K_d$, cm$^3$/gm</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$H$</td>
<td>0.26</td>
<td>26</td>
<td>0.26</td>
</tr>
<tr>
<td>$\theta_g$</td>
<td>0.25</td>
<td>0.25</td>
<td>0.24</td>
</tr>
<tr>
<td>$\theta_a$</td>
<td>0.75</td>
<td>0.75</td>
<td>0.76</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>$t_p$, hr</td>
<td>16</td>
<td>2.4</td>
<td>5.4</td>
</tr>
<tr>
<td>$D_g^*$, cm$^2$/sec</td>
<td>0.02</td>
<td>0.06</td>
<td>0.027</td>
</tr>
<tr>
<td>$D_w$, cm$^2$/sec</td>
<td>8.4 $\times$ 10$^{-8}$</td>
<td>3.4 $\times$ 10$^{-7}$</td>
<td>8 $\times$ 10$^{-8}$</td>
</tr>
<tr>
<td>$\bar{P}$e</td>
<td>69/92*</td>
<td>15/12*</td>
<td>22</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.044/0.032*</td>
<td>0.21/0.28*</td>
<td>9.9</td>
</tr>
<tr>
<td>$\xi$</td>
<td>5.7</td>
<td>0.06</td>
<td>1.2</td>
</tr>
<tr>
<td>$i_p$</td>
<td>88</td>
<td>9</td>
<td>13</td>
</tr>
</tbody>
</table>

* the two figures are for breakthrough and elution respectively.

† Estimated using the methane diffusivity in pure water $3 \times 10^{-8}$ cm$^2$/sec (Schwarzenbach et al., 1993, p. 238) divided by a “tortuosity” factor of 88 obtained experimentally by McKenzie (1990).

Similarly the aqueous concentration may be found, from (3.5),

$$
\bar{C}_w = 6\sigma L^{-1} \left[ \frac{C_g^*}{2s} \left( \frac{\bar{s}}{\sigma} \coth \sqrt{\frac{s}{\sigma}} - 1 \right) \right].
$$

(3.12)

We perform inverse Laplace transforms using the numerical method developed by Crump (1976) whose accuracy has been tested by Davies and Martin (1979).

### 3.2.2 Comparison of Theory and Experiments

In the column experiments by Gierke et al. (1992), two soils were used: a cohesionless sand and a manufactured aggregated porous soil material (APSM). Organic carbon content had been found to be zero in both materials. Three of the tests were run
for moist conditions, and the others were run for dry conditions. In the absence of organic matter, sorption was found to be negligible in the moist runs. However in the dry tests (in the absence of liquid water), they found it necessary to fit their model prediction with rather high sorption coefficient. One possible explanation is that in dry soils chemicals can directly adsorb onto mineral surfaces of solid grains which in the moist cases would have been preempted by the more polar water molecules (Chiou and Shoup, 1985). Such dry sorption isotherms are in general nonlinear and the parameters are more difficult to estimate. In view of insufficient information to estimate independently the sorptivity of the chemicals with the dry soils, we will exclude the dry tests in our comparisons.

The physical parameters for the three moist tests are cited in Table 3.2. In the first two runs, different advection velocities were recorded for the breakthrough and the elution of chemical vapor, which were caused by different pumping pressures during these two stages. We have checked that in each case the pulse length \( t_p \) was long enough to render the aqueous phase to be in equilibrium with the vapor phase before elution was started. This enables us to switch values of \( \bar{Pe} \) and \( \sigma \) for computing the breakthrough and the elution curves. In accordance with their observations, we take \( K_d = 0 \), so that \( D_e = D_w \). The soil parameters \( \theta_g, \theta_s, \phi \) are calculated from the degree of saturation and the total porosity reported by them. The effective gas and water diffusivities were obtained by Gierke et al. by dividing the corresponding value in bulk fluid by the estimated tortuosity of the porous medium (except in test b, where they used an artificially high \( D_w = 0.1 \text{ cm}^2/\text{s} \) for methane; a more realistic value of \( D_w = 3.4 \times 10^{-7} \text{ cm}^2/\text{s} \) is used in the present study). The tortuosity in the packed column was estimated from the porosity by the Millington formula, while the tortuosity in aggregates was measured in a batch experiment. In Table 3.2 we also give values of the dimensionless parameters calculated from (2.88) to (2.89). From the calculated values of \( \sigma \), we can anticipate by (2.94) that tests (a) and (b) correspond to kinetic vapor/aqueous exchange, while test (c) is a case of local equilibrium.

In Figures 3-2 to 3-4, our prediction (solid lines) is compared with the measured data (heavy dots) of effluent vapor concentration for tests (a), (b) and (c) respectively.
Figure 3-2: Comparison of simulation to experimental data of breakthrough and elution of vapor for Column Test (a) in Table 3.2. Solid line denotes spherical diffusion model; short-dashed line denotes local equilibrium theory; dots denote experimental data; long-dashed line denotes aqueous concentration at outlet of the column.
Figure 3-3: Comparison of simulation to experimental data of breakthrough and elution of vapor for Column Test (b) in Table 3.2. Solid line denotes spherical diffusion model; short-dashed line denotes local equilibrium theory; dots denote experimental data; long-dashed line denotes aqueous concentration at outlet of the column.
The results of local equilibrium theory (2.96) are also plotted (short-dashed lines) for tests (a) and (b) in Figures 3-2 and 3-3. Also for comparison, we show for tests (a) and (b) the time variations of aqueous concentration at the column outlet (long-dashed lines) in Figures 3-2 and 3-3, although no measurements were reported. In test (c) the value of $\sigma = 10$ is very large; local equilibrium prevails so that the time variations of dimensionless concentrations in the vapor and aqueous phases are the same, because of the normalization. From Figures 3-2 to 3-4, the following observations can be made:

1. In each case shown in Figures 3-2 to 3-4, there is a close agreement between the prediction and most of the data. Minor discrepancies which occur at some point of the breakthrough curves are probably caused by imperfectly abrupt feeding of the vapor in the experiments. In view of the overall agreement, our three-parameter model appears adequate to describe the data for vapor transport in these column tests. To fit the same experiments, Gierke et al. (1992) used very high values of transfer coefficient for the exchange of solute between the air and the immobile water and concluded that the film transfer resistance was not important in these tests.

2. For test (a), the local equilibrium theory fails to predict closely the time changes of both vapor and aqueous concentrations (Figure 3-2). In particular, the predicted elution assuming equilibrium is much faster than the measured; the difference is more than 35 normalized time units (see the elution curves, i.e., the decaying part of the curves, in Figure 3-2). The kinetic effect in this run can be expected from the relatively small value of $\sigma$ shown in Table 3.2. The difference between the normalized $C_g$ and $C_w$ is substantial, signifying substantial departure from local equilibrium.

3. In test (b), methane has a rather high Henry’s law constant ($H = 26$), and therefore a relatively higher partition in the vapor phase. The source term, due to aggregate diffusion, becomes insignificant in the vapor-phase transport equation. The values of $\sigma$ and $\xi$ are both small so that local equilibrium the-
Figure 3-4: Comparison of simulation to experimental data of breakthrough and elution of vapor for Column Test (c) in Table 3.2. Solid line denotes spherical diffusion model; dots denote experimental data.
Figure 3-5: Problem sketch of soil vapor extraction in a radial flow.

ory should give a good prediction for the effluent vapor concentration (Figure 3-3). However as seen from the calculated results in Figure 3-3, the normalized aqueous concentration is still quite different from the normalized vapor concentration. Hence local equilibrium is not strictly true as far as the entire process is concerned, which is anticipated from the small value of $\sigma$. The absolute amount of chemical partitioned in water is small, but it may still be of concern in practice. In the present example, the physical aqueous concentration of methane is 1.4 ppm before elution.

3.3 One-dimensional Radial Flow into a Well

3.3.1 The Problem

The problem of SVE in a radial flow field has been recently studied by Goltz and Oxley (1994) based on the first-order kinetic model of Brusseau (1991). Air compressibility was ignored.

We consider a confined unsaturated layer of uniform thickness and composed of
homogeneous and isotropic aggregated soil (Figure 3-5). Both the top and the bottom boundaries of the layer are assumed to be impermeable. Initially the soil is clean. At the instant \( t = 0 \) a VOC-contaminated soil column is introduced at the center \( r \leq r_0 \) and fully penetrates the layer. The vapor concentration at the source is constant \( C_g = C_{g0} \), and the vapor diffuses outward into the rest of the soil. At \( t = T > 0 \) the contaminated soil column is replaced by a vacuum well, which withdraws air together with vapor from the soil. The pumping goes on until the maximum vapor and aqueous concentrations in the soil drops to a certain level. The problem is to find the flow, and the vapor transport before and during pumping, as a function of \( r \) and \( t \). Unlike Goltz and Oxley (1994), we allow the air to be compressible; the unsteady air flow problem can be found from the continuity equation and Darcy's law:

\[
\theta_g \frac{\partial p}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left( r k p \frac{\partial p}{\partial r} \right) = 0, \quad (3.13)
\]

subject to the boundary conditions:

\[
p = p_0 \quad r = r_0; \quad p = p_a \quad r \to \infty, \quad t > T, \quad (3.14)
\]

and the initial condition:

\[
p = p_a \quad r_0 < r < \infty, \quad t = T, \quad (3.15)
\]

where \( p(r, t) \) is the absolute air pressure, \( k \) is the medium permeability divided by the air dynamic viscosity, \( p_0 \) is the air pressure at the well and \( p_a \) is the atmosphere pressure. Note that in (3.13) air is modeled as an ideal gas and the gravity effect is ignored as it is usually not important in flows caused by pumping. When \( p \) is solved, the radial seepage velocity can be found from

\[
u_r(r, t) = -\frac{k}{\theta_g} \frac{\partial p}{\partial r}. \quad (3.16)
\]

Let us change from the absolute pressure \( p \) to pressure deviation \( p' \) from the
atmospheric pressure according to

\[ p' \equiv p_a - p. \]  \hspace{1cm} (3.17)

Then the pressure deviation at the pumping well \( p'_0 = p_a - p_0 \) will give the proper scale of pressure change in the soil. It follows from Darcy’s law that the air velocity scale \( U_g \) will be given by

\[ U_g = k p'_0 / (\theta_g L) \]  \hspace{1cm} (3.18)

where \( L \), the characteristic transport length scale, is assumed to be comparable to the radius of influence of the pumping. We now introduce the following normalized variables (distinguished by a hat):

\[ p' = p'_0 \hat{p}', \quad C_g = C_{g0} \hat{C}_g, \quad C_w = (C_{w0}/H) \hat{C}_w, \quad r = L \hat{r}, \quad t = (L/U_g) \hat{t}, \quad u_r = U_g \hat{u}_r. \]  \hspace{1cm} (3.19)

The normalized air flow equation becomes

\[ \frac{\partial \hat{p}'}{\partial \hat{t}} - \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left[ \hat{r} (\hat{p}_a - \hat{p}') \frac{\partial \hat{p}'}{\partial \hat{r}} \right] = 0, \]  \hspace{1cm} (3.20)

where

\[ \hat{p}_a = p_a/p'_0 = 1/(1 - p_0/p_a) \]  \hspace{1cm} (3.21)

is the dimensionless well pressure parameter. The boundary conditions at the well of radius \( \hat{r}_0 \) and at a great radial distance are respectively:

\[ \hat{p}' = 1 \quad \hat{r} = \hat{r}_0; \quad \hat{p}' = 0 \quad \hat{r} \to \infty, \]  \hspace{1cm} (3.22)

and the normalized seepage velocity is given by

\[ \hat{u}_r = \frac{\partial \hat{p}'}{\partial \hat{r}}. \]  \hspace{1cm} (3.23)
For the vapor transport, the normalized problem in radial cylindrical coordinate is

\[ \frac{\partial \hat{C}_g}{\partial \hat{t}} + \frac{1}{\hat{r}} \frac{\partial (\hat{r} \hat{u}_r \hat{C}_g)}{\partial \hat{r}} - \frac{1}{Pe \hat{r}} \frac{\partial}{\partial \hat{r}} \left( \hat{r} \frac{\partial \hat{C}_g}{\partial \hat{r}} \right) = -6 \xi \sigma \sum_{n=1}^{\infty} \int_0^t e^{-\lambda_n (\hat{t} - \hat{t})} \frac{\partial \hat{C}_g}{\partial \hat{r}} d\hat{r}, \]  

(3.24)

\[ \hat{C}_g = 1 \quad 0 < \hat{t} \leq \hat{T}, \quad \hat{r} = \hat{r}_0, \]  

(3.25)

\[ \frac{\partial \hat{C}_g}{\partial \hat{r}} = 0 \quad \hat{t} > \hat{T}, \quad \hat{r} = \hat{r}_0, \]  

(3.26)

\[ \hat{C}_g = 0 \quad \hat{t} > 0, \quad \hat{r} \to \infty. \]  

(3.27)

We do not use the Danckwerts boundary condition at a finite radius. The conditions for validity of the Danckwerts boundary conditions in a radial flow problem are derived in Appendix E.

Note that the seepage velocity scale \( U_g \) is directly proportional to the well pressure deviation \( p'_0 \). To discuss the effects of pumping rate it is more convenient if we normalize time by the constant atmospheric pressure. Hence we introduce the new dimensionless time and parameters which do not depend on the pumping pressure:

\[ \hat{t}' = t \left( k p_a / \theta_g L^2 \right), \quad \sigma' = D_e \theta_g L^2 / a^2 k p_a, \quad Pe' = k p_a / \theta_g D_g^*. \]  

(3.28)

which are related to the old quantities by

\[ \hat{t} = \hat{t}' / \hat{p}_a, \quad \sigma = \sigma' \hat{p}_a, \quad \hat{P}e = Pe' / \hat{p}_a, \quad \text{with} \quad \hat{p}_a = p_a / p'_0 = p_a / (p_a - p_0). \]  

(3.29)

In the computations, values of \( \hat{p}_a \), \( \sigma' \) and \( Pe' \) are independently specified. While others inputs are varied, the following values are fixed for the computations:

\[ \hat{r}_0 = 0.1, \quad Pe' = 100, \quad \hat{T}' = 10. \]  

(3.30)

Using \( p_a \sim 10^8 \text{ Pa} \) and \( D_g^* \sim 0.1 \text{ cm}^2/\text{sec} \), and \( k \sim 10^{-8} \text{ m}^2/\text{Pa s} \) for the air conductivity, we get \( Pe' = 100 \). Then for a characteristic length scale \( L \sim 10 \text{ m} \), the time scale for \( \hat{t}' \) is in the order of one day. \( \hat{T}' = 10 \) then means that the vapor source exists in the soil for about 10 days before it is replaced by the pumping well. For simplicity
we shall omit from now on the overhead hats in all normalized quantities.

### 3.3.2 Numerical Method

Solutions to the flow problem (3.20)–(3.23) and the transport problem (3.24)–(3.27) are obtained numerically by finite differences. While the left-hand side of (3.24) can be approximated by a standard second-order implicit scheme of forward-time centered-space differences, computation of the source term on the right-hand side deserves some care because the series is singular at $t = 0$.

To truncate the exponential infinite series at a finite number $N$ of terms, we make use of the following approximation introduced by Herrera and Yates (1977):

$$
\sum_{n=1}^{\infty} e^{-\lambda_n t} \approx \alpha_N \delta(t) + \sum_{n=1}^{N} e^{-\lambda_n t}, \quad (3.31)
$$

where $\alpha_N$ is chosen so that the time integrals of the two sides from 0 to $\infty$ are equal:

$$
\alpha_N = \sum_{n=1}^{\infty} \frac{1}{\lambda_n} - \sum_{n=1}^{N} \frac{1}{\lambda_n} = \frac{1}{6\sigma} - \sum_{n=1}^{N} \frac{1}{\lambda_n}. \quad (3.32)
$$

The rationale for (3.31) is to use the dirac delta function to account for the singularity of the infinite series at $t = 0$. The larger $N$ is, the better is the above representation. The source term is now approximated as follows:

$$
-6\xi \sigma \int_0^t \left[ \sum_{n=1}^{\infty} e^{-\lambda_n (t-\tau)} \right] \frac{\partial C_g}{\partial \tau} d\tau \\
\approx -6\xi \sigma \int_0^t \left[ \alpha_N \delta(t-\tau) + \sum_{n=1}^{N} e^{-\lambda_n (t-\tau)} \right] \frac{\partial C_g}{\partial \tau} d\tau \\
= -6\xi \sigma \alpha_N \frac{\partial C_g}{\partial t} - 6\xi \sigma \sum_{n=1}^{N} e^{-\lambda_n t} \int_0^t e^{\lambda_n \tau} \frac{\partial C_g}{\partial \tau} d\tau. \quad (3.33)
$$

Now the first term can be added to the unsteady term on the left-hand side of (3.24), while the second series can be computed by using the following scheme. If we know
the integral at \( t = m \Delta t \), i.e.,

\[
E_n^m = e^{-\lambda_n t} \int_0^t e^{\lambda_n \tau} \frac{\partial C_g}{\partial \tau} d\tau = e^{-\lambda_n m \Delta t} \int_0^{m \Delta t} e^{\lambda_n \tau} \frac{\partial C_g}{\partial \tau} d\tau,
\]

(3.34)

then the integral at the next time step is

\[
E_n^{m+1} = e^{-\lambda_n (m+1) \Delta t} \int_0^{(m+1) \Delta t} e^{\lambda_n \tau} \frac{\partial C_g}{\partial \tau} d\tau
\]

\[
= e^{-\lambda_n \Delta t} E_n^m + e^{-\lambda_n (m+1) \Delta t} \int_{m \Delta t}^{(m+1) \Delta t} e^{\lambda_n \tau} \frac{\partial C_g}{\partial \tau} d\tau
\]

\[
\cong e^{-\lambda_n \Delta t} E_n^m + e^{-\lambda_n \Delta t/2} (C_g^{m+1} - C_g^m).
\]

(3.35)

After finding \( C_g^{m+1} \) for the new time level, the aqueous concentration \( \bar{C}_w^{m+1} \) may be computed according to (2.87) and by using the above approximations:

\[
\bar{C}_w^{m+1} \cong C_g^{m+1} - \frac{6 \sigma \alpha'_N}{\Delta t} (C_g^{m+1} - C_g^m) - 6 \sigma \sum_{n=1}^{N} \frac{E_n^{m+1}}{\lambda_n}
\]

(3.36)

where

\[
\alpha'_N = \frac{1}{90 \sigma^2} - \sum_{n=1}^{N} \frac{1}{\lambda_n^2}.
\]

(3.37)

Formula (3.35) avoids the storage of all past values of \( C_g \) for computing the history of gas/water exchange. Only the two most recent levels of \( C_g \) need to be stored. An implicit finite-difference scheme for the above radially one-dimensional transport equation is used and yields a tridiagonal linear system which can be solved by a simple routine. We have checked the accuracy of our program by comparing results for the column case with those generated by Laplace transform as discussed in §3.2.1. This comparison also helps us choose the time step \( \Delta t \), grid interval \( \Delta \tau \) and \( N \) so that the agreement is within four significant figures.
Figure 3-6: Concentrations as a function of $r$ and $t'$, for $\sigma' = 0.1$, $\xi = 1$ and $\overline{Pe} = 50$.

### 3.3.3 Results of Computations

#### Temporal and Spatial Variations of Concentrations

Figure 3-6 shows the radial variations of $C_g$ and $\bar{C}_w$ as a function of time before and during pumping with $\sigma' = 0.1$, $\xi = 1$ and $\bar{\rho}_a = 2$ (or $\overline{Pe} = 50$). Prior to pumping, the vapor diffuses outward. At $t' = 10$ when pumping begins, the vapor and the aqueous concentrations are nearly in local equilibrium. With pumping after $t' = 10$, the vapor concentration drops more rapidly than the aqueous concentration initially. Therefore during the early stage of pumping different phases are not in local equilibrium. After long pumping both concentrations drop more slowly as they reach to lower levels. The concentrations farther away from the well also diminish at a slower rate, as the seepage velocity decreases with radial distance.
Effects of Pumping Strength and Sorptivity on Purge Time

The primary concern of the SVE operation is the time required to remove the contaminant in both vapor and aqueous phases from the soil. For practical reasons, complete elimination is difficult and pumping is usually stopped when the concentrations drop below a certain level as specified by local standards. In our computations, we have examined the various effects on the purge time for a phase which is defined as the time of pumping required to reduce the maximum concentration of that phase to 1% of that released from the original source. Figure 3-7 shows how the vapor phase purge time depends on the pumping strength and the parameter $\xi$, with $\sigma' = 0.1$, $\xi = 1, 10$ and $\hat{p}_a = 2 - 20$. The corresponding range of $Pe$ is from 50 to 5. A larger $Pe$ means a stronger pumping. For a weak pumping $Pe = 5$, the purge time is as long as 80, or 8 times the pre-pumping period. The purge time decreases dramatically to less than 15 when the pumping strength increases to $Pe = 20$. Further decrease in the purge time is however modest when $Pe$ increases further above 30. This suggests that a too strong pumping is not cost-effective for accomplishing the clean-up in a reasonable time.

Also in Figure 3-7, we show the effect of a larger $\xi$, which can be resulted from a larger sorptivity of the chemical to the soil. As noted earlier, the parameter $\xi$ indicates the tendency of the chemical to partition into solid and aqueous phase within aggregates. A larger $\xi$ means a higher retardation to the vapor transport. Clearly from the plot the purge time is more sensitive to the value of $\xi$ when the pumping is weak than when it is strong. In this case when $\xi$ is increased by 10 times, the purge time is almost doubled for $Pe = 5$, but only slightly increased for $Pe = 50$. We conclude that the pumping strength should not be too low or too high in order to achieve a short but economical purge time.

Effects of Aggregate Diffusivity on Purge Time

For fixed pumping strength, the parameter $\sigma$ is proportional to the diffusion rate in an aggregate and determines how fast the chemical is being removed from the aggregates.
Figure 3-7: Vapor phase purge time as a function of $\bar{Pe}$ and $\xi$, for $\sigma' = 0.1$. 
Figure 3-8: Purge times for vapor and aqueous phases as a function of $\sigma$, for $\xi = 1$ and $\overline{Pe} = 50$. 
Figure 3-9: Effluent vapor concentration and maximum aqueous concentration as a function of $\sigma$ and $t'$, for $\xi = 1$ and $Pe = 50$.

Figure 3-8 shows how the parameter $\sigma$ affects the purge times for the vapor phase and the aqueous phase, with $\xi = 1$ and $Pe = 50$. As expected, it always takes less time to purge vapor than aqueous phase; the difference reflects the departure from local equilibrium. The local equilibrium is approached when $\sigma$ becomes large, which is consistent with our theoretical criterion (2.94): $\sigma \gg 1$. It is also clear that while the vapor phase purge time is practically insensitive to change of $\sigma$, the aqueous phase purge time increases dramatically when $\sigma$ becomes small enough. Thus for fine aggregates the various phases are removed at about the same rate, while for very coarse aggregates it takes longer to clean up the aqueous phase than the vapor phase. In nature, soil aggregates tend to increase in size with depth (FitzPatrick, 1980) which may cause the rate of contaminant removal to be nonuniform across the depth.
Figure 3-10: Effluent vapor concentration and maximum aqueous concentration as a function of $\sigma$ and $t'$, with a period of pumping shut-down as indicated, for $\xi = 1$ and $\overline{Pe} = 50$.

**Effluent Concentration**

In SVE applications, the effluent vapor concentration is often measured only at the well. In Figure 3-9 we compare the time variation of the effluent vapor concentration in the well with that of the maximum aqueous concentration in the soil for $\sigma = 2$ and 0.02, $\xi = 1$ and $\overline{Pe} = 50$. For either value of $\sigma$, the effluent vapor concentration initially drops rapidly with time. On the other hand, the decay of the aqueous phase follows closely to that of the vapor phase when $\sigma = 2$, but is much slower when $\sigma = 0.02$. In the first case the remediation can be terminated rather quickly. However, in the second case, which is much more rate-limited by aqueous diffusion, the effluent vapor concentration exhibits the so-called “tailing” effect at large times. Therefore it is inadequate if only the vapor phase concentration is measured for progress monitoring.
Interrupted Pumping

Finally we examine the effects of interrupted pumping, as was also discussed by Wehrle (1993) and Armstrong et al. (1994). We repeat the case shown in Figure 3-9, but now the pumping is shut-down during the period \( t' = 12 \) to 15. The results are shown in Figure 3-10. In the shut-down period, the flow stops and the transport is controlled solely by molecular diffusion. Clearly during the shut-down, the effluent vapor concentration rebounds, but to a different extent depending on \( \sigma \). For \( \sigma = 2 \), the rebound is very small and the concentration soon levels off and drops again before pumping is restarted. On the other hand, for \( \sigma = 0.02 \), the concentration continues to rise until pumping is restarted. The larger rebound in the latter case is due to the larger amount of the chemical yet stored in the aggregates. In a field monitoring program, the different traits of effluent vapor concentration rebound during a pumping shut-down can tell us whether the transport is rate-limited by aqueous diffusion and therefore dominated by kinetics.

### 3.4 Two-dimensional Radial Flow into a Well

In another example of radial flow, we consider an unsaturated layer which is similar to the previous one except that the ground surface is now unsealed, and therefore both concentration and pressure deviation are zero there. The flow and the transport now have dependence on the vertical coordinate \( z \). With an open surface, the vapor diffusion prior to pumping will eventually reach a steady-state which can be found from the following boundary value problem:

\[
\frac{\partial^2 C_g}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_g}{\partial r} \right) = 0 \quad r_0 < r < \infty, \quad 0 < z < z_m, \quad t > 0, \quad (3.38)
\]

\[
C_g = C_{g0} \quad \text{at} \quad r = r_0; \quad C_g = 0 \quad \text{at} \quad r \to \infty, \quad (3.39)
\]

\[
\frac{\partial C_g}{\partial z} = 0 \quad \text{at} \quad z = 0; \quad C_g = 0 \quad \text{at} \quad z = z_m, \quad (3.40)
\]
where \( z = 0 \) is the bottom and \( z = z_m \) is the ground surface. The above problem can readily be solved analytically using finite Fourier transform. Normalizing \( C_g \) with respect to the source concentration \( C_{g0} \), and \( r \) and \( z \) with respect to the layer thickness \( z_m \), we may write the normalized steady-state vapor concentration distribution before pumping as follows:

\[
\hat{C}_g(\hat{r}, \hat{z}, \hat{t} = 0) = 2 \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\cos(\alpha_n \hat{z})}{\alpha_n} \frac{K_0(\alpha_n \hat{r})}{K_0(\alpha_n \hat{r}_0)}, \quad \text{where} \quad \alpha_n = (2n - 1)\pi/2
\]

and \( K_0 \) is the modified Bessel function of the second kind of order zero.

As the ground surface is freely open to the atmosphere, the flow field in the soil can attain the steady-state quickly after the pumping starts. We therefore ignore the flow transient and assume that the air pressure distribution is always in a steady-state, governed by the following boundary value problem:

\[
\frac{\partial^2 p^2}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial p^2}{\partial r} \right) = 0 \quad r_0 < r < \infty, \quad 0 < z < z_m, \quad t > 0,
\]

\[
p = p_0 \quad \text{at} \quad r = r_0; \quad \quad p = p_a \quad \text{at} \quad r \to \infty, \quad (3.43)
\]

\[
\frac{\partial p}{\partial z} = 0 \quad \text{at} \quad z = 0; \quad \quad p = p_a \quad \text{at} \quad z = z_m. \quad (3.44)
\]

This problem resembles that for the initial concentration distribution and can be solved in a similar manner. The solution for the pressure deviation, in terms of normalized quantities, is

\[
\hat{p}'(\hat{r}, \hat{z}) = \hat{p}_a - \left( \hat{p}_a^2 + 2 \left( (\hat{p}_a - 1)^2 - \hat{p}_a^2 \right) \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\cos(\alpha_n \hat{z})}{\alpha_n} \frac{K_0(\alpha_n \hat{r})}{K_0(\alpha_n \hat{r}_0)} \right)^{1/2}. \quad (3.45)
\]

Figure 3-11 shows the contours of vapor concentration as a function of time with \( \sigma' = 0.05, \, \xi = 1 \) and \( Pe = 50 \). The initial vapor concentration distribution and the seepage velocity field, represented by the vectors, are presented in Figure 3-11a. The clean air enters directly from above the contaminated region. Note that the air circuit path is short and the velocity is large in magnitude in the neighborhood of the well near the ground level. The opposite is true for farther and deeper locations.
Figure 3-11: Contours of vapor concentration as a function of $t'$ for $\sigma' = 0.05$, $\xi = 1$ and $Pe = 50$. 

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Consequently, the concentration level drops more rapidly near the ground surface than near the bottom. It takes very long time to extract vapor from the deep and far locations.

We also compare in Figure 3-12 the effluent vapor concentration with the maximum aqueous concentration as a function of \( t \) for \( \sigma' = 0.05 \), \( \xi = 1 \), and \( \overline{Pe} = 5, 50 \). Note that the effluent vapor concentration is given by the depth-average of the concentration in the well which can be small because of the much cleaner air drawn to the top half of the well. On the other hand, the maximum aqueous concentration is always located near the bottom of the layer. As in the last example, the effluent vapor concentration drops rapidly in the early stage, but has an extended profile of low concentration (i.e., the tailing) in the long run. The maximum aqueous concentration always decays at a slower rate. The difference between the decaying speeds of these concentrations is appreciable even in the case of low pumping rate \( (\overline{Pe} = 5) \), and is much more prominent in the case of high pumping rate \( (\overline{Pe} = 50) \). Clearly the local equilibrium is not true in either case. During a period of pumping shut-down from \( t = 1 - 2 \), the effluent vapor concentration exhibits an immediate rebound followed a gradual decrease in the case of \( \overline{Pe} = 5 \). On the other hand, for \( \overline{Pe} = 50 \) the rebound is more salient and lasts throughout the shut-down period.

### 3.5 Concluding Remarks

In this chapter we have applied the aggregate diffusion model to study the chemical vapor transport due to venting in an unsaturated zone. The theory is first tested by comparing with experiments for vapor transport in a short column; the agreement is good and easily explained. We then apply the theory for soil vapor extraction by a vacuum well in a radially symmetric contaminated region. The effects of properties of the soil and the chemical, and pumping on the removal of volatile compounds are examined systematically. In general a higher sorptivity and/or a larger aggregate size can result in a longer SVE operation. For a chemical which tends to partition more in vapor phase than in aggregate, the vapor transport is not sensitive to the
Figure 3-12: Effluent vapor concentration and maximum aqueous concentration as a function of $t$ for $\sigma' = 0.05$, $\zeta = 1$, and (a) $\bar{Pe} = 5$; (b) $\bar{Pe} = 50$; (c) $\bar{Pe} = 5$ with a period of pumping shut-down; (d) $\bar{Pe} = 50$ with a period of pumping shut-down.
vapor/aqueous transfer kinetics. The optimum air velocity is such that the advection time is comparable to the aggregate diffusion time so that the situation is neither highly kinetic nor at the local equilibrium limit. If contaminant removal is rate-limited by aqueous diffusion, the vapor concentration can drop rapidly to a low level while the aqueous concentration is only modestly reduced. In such case, measuring only the effluent vapor concentration will not be adequate to monitor the operation. A temporary pumping shut-down may however be useful to tell how significant the kinetics is by checking the rebound of the vapor concentration.

So far, our focus has been on homogeneous soils whose properties vary only slowly on the macroscale. In the next chapter, we will study the effects of soil heterogeneity – a semipervious lens embedded in a coarse medium – on the vapor transport in soil vapor extraction.
Chapter 4

Effects of a Semipervious Lens on Soil Vapor Extraction

4.1 Introduction

In this chapter we are going to describe a theory for the removal of volatile organic compounds (VOC) from an unsaturated soil stratum consisting of highly porous sand layers sandwiching a thin and semipervious lens. As described in Chapter 2, soil vapor extraction (SVE) is the major technology for the removal of VOC vapor in the unsaturated zone by pumping the vapor-laden air in the pores into suction wells placed in the contaminated vadose zone. As the vapor is removed, the aqueous and the sorbed phases will also be depleted driven by phase change kinetics. Although some authors (e.g., Johnson et al., 1990a; Pedersen and Curtis, 1991) have remarked that SVE is more successful in more permeable soils which allow a faster transport of vapor to the suction point, it is also true that, as an opposing effect, a more permeable soil permits a wider spread of vapor from the contaminant source before treatment, which then demands a longer or stronger venting for the clean-up. The effects of soil properties on the effectiveness of SVE are even more complex in the presence of layered heterogeneity. Very often, unsaturated zones are stratified; layers of semipervious soil, such as clay lenses, are embedded in a medium of more porous or sandy materials. Obviously if SVE is applied in such a heterogeneous system, the
progress of the remediation is likely limited by the slow removal rate of contaminant in the low-permeability layers, which is usually more difficult to evaluate and monitor. To provide guidance for designing SVE in a layered soil, it is necessary to develop an effective vapor transport model which takes into account of the difference in flow and transport capacity of individual layers.

Most existing models on the vapor transport in unsaturated zone are focused on homogeneous soils. In earlier works (e.g., Abriola and Pinder, 1985; Corapcioglu and Baehr, 1987; Kaluarachchi and Parker, 1990), the emphasis is to develop multiphase transport models for groundwater contamination which consider only diffusive vapor transport. The effects of density-driven advection of dense vapor are later studied by Sleep and Sykes (1989), Falta et al. (1989) and Mendoza and Frind (1990). SVE is distinguished by the fact that vapor advection is forced by pumping. Typical works in this category include Wilson et al. (1988), Baehr et al. (1989), Johnson et al. (1990a), Rathfelder et al. (1991), and Falta et al. (1993). These models ignore the kinetics of interphase mass transfer and assume that all phase partitionings are always in local equilibrium. Evidence of the transfer kinetics is nevertheless known in some experimental observations. This motivates the kinetic models by Sleep and Sykes (1989), Brusseau (1991) and Armstrong et al. (1994) who adopt first-order relations to describe the interphase mass transfer rates on the macroscale. The first-order rate constants are essentially empirical; in most cases definite data are not available and are difficult to estimate. A more theoretically satisfactory alternative is the spherical aggregate diffusion model (e.g., Brusseau and Rao, 1990; Gierke et al., 1992) for which the governing equations have been justified rigorously in Chapter 2. With constitutive coefficients known from reliable experimental data, this model has been confirmed by one-dimensional experiments in a packed soil column, as presented in Chapter 3.

Studies on the effects of soil heterogeneity on SVE have been rather limited. Johnson et al. (1990a,b) presented one-dimensional mass-transfer limited models for steady vapor transport on top of a layer of liquid VOC or a layer of low-permeability soil with residual liquid hydrocarbon. Experimental and theoretical investigations of
a similar problem were carried out by Ho and Udell (1991, 1992), who provide visual
evidence of the geometrical evolution of a liquid VOC pool in a low-permeability
layer as a result of overhead air blowing. Contrasting features of air flow and vapor
transport in different layers are however not studied in these works.

The objective of this chapter is to examine theoretically the effects of soil strat-
ification on the flow of pore air and the transport of volatile chemicals in an SVE
operation. Letting each layer be formed by spherical aggregates, we shall derive ap-
proximate equations that capture the essential physics for a shallow soil stratum with
a thin lens of very low permeability. The coarse- and fine-grained layers are assumed
to have sharply contrasting air conductivities and vapor diffusivities. While the con-
taminant source is confined to a small region in the coarse layer above the lens, the
vapor is allowed to spread laterally before pumping to great distances. We assume
that the density-driven advection is not important. This is true for compounds like
toluene and xylene which have a relatively small molecular weight and a low vapor
pressure at soil temperatures (Falta et al., 1989).

In §4.2, we shall give the basic equations and boundary conditions. Scales of
various physical parameters are estimated in §4.3. Based on the small ratio of char-
acteristic length scales which is also related to the permeability ratio, a perturbation
analysis is carried out in §4.4 and yields the leading order governing equations and
boundary conditions. The asymptotic procedure resembles that used previously in
deriving the seepage equation for finite strain consolidation in an aquifer-aquitard-
aquifer system (Fallou et al., 1992; Lee et al., 1992; Chapter 1 of this thesis). It will
be seen that the sharp contrast of material properties helps to simplify the spatial
dependence in both flow and transport problems. Numerical solutions of the asym-
ptotic equations are discussed in §4.5. Attention will be focused on the effects of the
soil properties (conductivity, diffusivity and retardation factor), aggregate diffusion
rate and pumping strength on the vapor distribution as a function of space and time.
4.2 Problem Formulation

As shown in Figure 4-1, the unsaturated zone consists of a confined and horizontal stratum of coarse and highly permeable soil sandwiching a thin lens of much finer and semipervious soil. To study the physics without excessive computation, axial symmetry about the center of the lens is assumed. With its top and bottom surfaces being well-sealed, the unsaturated zone is assumed to extend radially to infinity. Practically a sealed ground surface is desirable for SVE in order to control air flow to pass through the contaminated soils (e.g., Johnson et al., 1990b). The case with an underlying saturated zone is not treated in this study. The moisture content in the unsaturated zone is assumed to be at the irreducible level so that in the absence of surface recharge the pore water is not draining. A cylindrical coordinate system $(r, z)$ is defined as shown in Figure 4-1.

We denote the semipervious lens by $\Omega_f$ (where the subscript $f$ stands for fine grains), its lower surface by $\Gamma_1 : z = F_1(r)$, its upper surface by $\Gamma_2 : z = F_2(r)$, and its maximum radius by $r = r_b$. For convenience of identification the coarse zone is divided into three layers: the inner layers below ($\Omega_1$) and above ($\Omega_2$) the lens, and the outer layer $\Omega_3$. The thicknesses $d_1$, $d_2$ and $d_f$ of $\Omega_1$, $\Omega_2$ and $\Omega_f$ respectively are functions of $r$, while the total thickness $d_3$ of the soil stratum is assumed to be constant. We also assume that within each layer the soil is isotropic, though not necessarily homogeneous.

We suppose that initially ($t < 0$) the soil is clean. At the instant $t = 0$ a VOC-contaminated soil column is introduced at the center and fully penetrates the upper layer $\Omega_2$. The vapor concentration in the soil column is maintained at a constant level for the duration $0 < t < T$, while vapor diffuses continuously into the surrounding soil. At $t = T > 0$, the contaminated soil column is replaced by a vacuum well, in which the pressure is lowered in order to withdraw air from the surrounding soil. Variations of VOC vapor concentration as a function of time and space is to be sought.

On the pore scale, each soil layer is assumed to be packed by uniform spherical aggregates inside which water is held immobilized by capillary forces. Air containing
Figure 4-1: Definition sketch of problem geometry.
the vapor phase of a chemical fills and moves in the pore space between the aggregates. The same chemical is also dissolved in the intra-aggregate water, and adsorbed on the particles constituting the aggregates. We further assume equilibrium chemical partitioning between aqueous and sorbed phases inside an aggregate, and also between vapor and aqueous phases on the air/aggregate interface. Note that these are local assumptions on the aggregate scale and differ from the usual assumption of local equilibrium on the macroscale.

### 4.2.1 Governing Equations

For demonstrating our basic ideas, it suffices to consider the case of axial symmetry. We begin with the exact equations for the air flow and the vapor transport applicable to all layers. Because the externally applied pressure change can be significant, air can be compressible and must satisfy the continuity equation:

$$
\theta_g \frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r \rho u) + \frac{\partial}{\partial z} (\rho w) = 0
$$

(4.1)

where $t$ is the time, $(u, w)$ are the radial and the vertical components of the specific discharge (i.e., flow per unit area of soil matrix), $\rho$ is the air density, and $\theta_g$ is the macroporosity (i.e., the volume fraction of air-filled pore space) of the medium. The specific discharge is related to the pressure gradient according to Darcy's law:

$$
(u, w) = -k \left( \frac{\partial p}{\partial r}, \frac{\partial p}{\partial z} \right)
$$

(4.2)

where $p$ is the absolute air pressure, and $k$ is the air conductivity of the medium divided by the air specific weight. Gravity effect is ignored in (4.2). This is justifiable during pumping since the applied pressure gradient will dominate. Before pumping, buoyancy effect is also negligible as compared to diffusion when the chemical has a relatively small molecular weight and its vapor pressure is much lower than the atmospheric pressure (Falta et al., 1989).
Modeling air as an ideal gas, the equation of state reads:

\[
\frac{pM}{R_g \Theta} = \rho \tag{4.3}
\]

where \( M \) is the molecular weight of the air mixture, \( R_g \) is the universal gas constant, and \( \Theta \) is the absolute air temperature. We assume that both \( \Theta \) and \( M \) are constants so that \( p \) is linearly proportional to \( \rho \). Note that we shall not distinguish the air pressure from the total gas pressure, since the partial pressure due to VOC vapor is assumed to be relatively small. Limiting to these conditions, a nonlinear equation for \( p \) follows by inserting (4.2) into (4.1):

\[
\theta_g \frac{\partial p}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left( r k_p \frac{\partial p}{\partial r} \right) - \frac{\partial}{\partial z} \left( k_p \frac{\partial p}{\partial z} \right) = 0. \tag{4.4}
\]

Note that the above flow equation is independent of chemical vapor transport and can be solved in advance.

We adopt the so-called aggregate-diffusion model where the soil in each layer is composed of a regular array of spherical aggregates of equal radius \( a \). The aqueous diffusivity inside an aggregate \( (D_w) \) is assumed to be very small compared to the vapor diffusivity in the pore air \( (D) \) (e.g., see Brusseau and Rao, 1990; and references cited therein). The equation for the vapor transport is

\[
\theta_g \frac{\partial C_g}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r u C_g) + \frac{\partial}{\partial z} (w C_g) - \frac{1}{r} \frac{\partial}{\partial r} \left( r D \frac{\partial C_g}{\partial r} \right) - \frac{\partial}{\partial z} \left( D \frac{\partial C_g}{\partial z} \right) = -\frac{6 \phi D_w \theta_a}{a^2 H} \sum_{n=1}^{\infty} \int_0^t e^{-\lambda_n (t-\tau)} \frac{\partial C_g}{\partial \tau} d\tau, \tag{4.5}
\]

where the time integral on the right-hand side represents the mass transfer rate from aggregates into pore air per bulk soil volume. In this equation, the vapor concentration \( C_g(r, z, t) \) is defined as the mass of chemical vapor per phase volume, \( \phi \) is the intra-aggregate porosity, \( \theta_a = 1 - \theta_g \) is the volume fraction of aggregates, and \( H \) is Henry's law constant. Also,

\[
\lambda_n = n^2 \pi^2 D_e/a^2 \quad (n = 1, 2, \cdots), \tag{4.6}
\]
where

$$D_e = \frac{\phi D_w}{K_d(1 - \phi)\rho_s + \phi} \quad (4.7)$$

is the sorption-retarded effective diffusivity in an aggregate, in which $K_d$ is the sorption partition coefficient, and $\rho_s$ is the aggregate solid density. The aqueous concentration in aggregates, $C_w$, is in general not in equilibrium with the vapor concentration, and its mean value over an aggregate volume can be found from:

$$\bar{C}_w = \frac{1}{H} \left[ C_g - \frac{6D_e}{a^2} \sum_{n=1}^{\infty} \int_0^t e^{-\lambda_n(t-\tau)} \frac{\partial C_g}{\partial r} \frac{d\tau}{\lambda_n} \right]. \quad (4.8)$$

Equations (4.5) and (4.8) hold for each layer, coarse or fine, and have been derived rigorously by the theory of homogenization in Chapter 2.

### 4.2.2 Boundary Conditions

Referring to Figure 4-1, let us distinguish by the subscripts $i = 1, 2$ quantities for the two coarse layers below and above the lens respectively, and $i = 3$ the coarse layer outside the vertical cylinder containing the lens. The subscript $f$ is used to distinguish the fine-grained semipermeable lens. First, at the center of the bottom coarse layer $\Omega_1$, the pressure and the concentration gradients are zero by axial symmetry:

$$\frac{\partial p_1}{\partial r} = 0, \quad \frac{\partial C_{g1}}{\partial r} = 0 \quad \text{at } r = 0, \quad 0 < z < F_1(r), \quad 0 < t. \quad (4.9)$$

At the outer radius of the center column of radius $r_0$, i.e., the well screen, in the upper coarse layer $\Omega_2$, the boundary condition depends on the stage of operation. During the state of contamination, $0 < t < T$, there is no flow but a constant vapor concentration $C_{g0}$ at $r = r_0$:

$$\frac{\partial p_2}{\partial r} = 0, \quad C_{g2} = C_{g0} \quad \text{at } r = r_0, \quad F_2(r) < z < d_3, \quad 0 < t < T. \quad (4.10)$$

During pumping, $t > T$, the pressure is equal to that in the well, $p_0$, which is below the atmospheric pressure $P_a$. The concentration in the well is uniform so that there
is no concentration gradient. Thus
\[ p_2 = p_0, \quad \frac{\partial C_{g2}}{\partial r} = 0 \quad \text{at } r = r_0, \quad F_2(r) < z < d_3, \quad T < t. \] (4.11)

On the cylindrical interface between the outer coarse zone \( \Omega_3 \) and the two inner coarse zones \( \Omega_1 \) and \( \Omega_2 \), we require the continuity of pressure, concentration, and fluxes of air and vapor:

\[ p_3 = p_1, \quad C_{g3} = C_{g1}, \quad \frac{\partial p_3}{\partial r} = \frac{\partial p_1}{\partial r}, \quad \frac{\partial C_{g3}}{\partial r} = \frac{\partial C_{g1}}{\partial r} \quad \text{at } r = r_b, \quad 0 < z < F_1(r), \] (4.12)

\[ p_3 = p_2, \quad C_{g3} = C_{g2}, \quad \frac{\partial p_3}{\partial r} = \frac{\partial p_2}{\partial r}, \quad \frac{\partial C_{g3}}{\partial r} = \frac{\partial C_{g2}}{\partial r} \quad \text{at } r = r_b, \quad F_2(r) < z < d_3. \] (4.13)

Let the bottom of \( \Omega_1 \) and \( \Omega_3 \) and the top of \( \Omega_2 \) and \( \Omega_3 \) be impermeable; the normal fluxes are then zero there:

\[ \frac{\partial p}{\partial z} = 0, \quad \frac{\partial C_g}{\partial z} = 0 \quad \text{at } z = 0 \text{ and } z = d_3, \quad 0 < r < \infty. \] (4.14)

Along the lens boundaries \( \Gamma_1 \), i.e., \( z = F_1(r), \ r < r_b \) and \( \Gamma_2 \), i.e., \( z = F_2(r), \ r < r_b \), we also require the continuity of pressure, concentration, and normal fluxes of air and vapor:

\[ p_i = p_f, \quad C_{g_i} = C_{gf} \quad \text{on } \Gamma_i (i = 1, 2), \] (4.15)

\[ k_i \frac{\partial p_i}{\partial r} n_r + k_i \frac{\partial p_i}{\partial z} n_z = k_f \frac{\partial p_f}{\partial r} n_r + k_f \frac{\partial p_f}{\partial z} n_z \quad \text{on } \Gamma_i (i = 1, 2), \] (4.16)

\[ \left( u_i C_{g_i} - D_i \frac{\partial C_{g_i}}{\partial r} \right) n_r + \left( w_i C_{g_i} - D_i \frac{\partial C_{g_i}}{\partial z} \right) n_z \]
\[ = \left( u_f C_{gf} - D_f \frac{\partial C_{gf}}{\partial r} \right) n_r + \left( w_f C_{gf} - D_f \frac{\partial C_{gf}}{\partial z} \right) n_z \quad \text{on } \Gamma_i (i = 1, 2). \] (4.17)
where \((n_r, n_z)\) are the radial and the vertical components of the normal vector to the lens surface \(\Gamma_i : z = F_i\) given by

\[
(n_r, n_z) = \left( -\frac{\partial F_i}{\partial r}, 1 \right).
\]  \(\text{(4.18)}\)

Finally, at a large radial distance from the center, the pressure is equal to the atmospheric pressure \(P_a\) and the vapor concentration is zero:

\[
p_3 = P_a, \quad C_{g3} = 0 \quad \text{at} \ r \to \infty, \quad 0 < z < d_3.
\]  \(\text{(4.19)}\)

For heterogeneous soils the three dimensional equations and boundary conditions of this section are however unwieldy for computations and unrevealing for physical understanding. We shall therefore seek approximations for situations emulating some aspects of reality.

### 4.3 Estimate of Scales

To provide a basis of perturbation analysis we first estimate the scales of important physical variables, and the relationship between some dimensionless ratios. All scales will be distinguished by tildes, i.e., the scale of \(f\) is \(\tilde{f}\). For convenience, we summarize in Table 4.1 the scales discussed below which will be used for normalization in later sections.

#### 4.3.1 Geometrical Shallowness

The radial length scale \(\tilde{r}\), characterized by the maximum radius of the semipervious lens, is assumed to be much larger than the vertical length scale \(\tilde{d}\), typical of a layer depth. We define the square of their ratio as the small ordering parameter:

\[
\delta \equiv (\tilde{d}/\tilde{r})^2 \ll 1.
\]  \(\text{(4.20)}\)
4.3.2 Radius of Influence and Conductivity Contrast

Let $\tilde{r}_p$ be the radius of influence which is the radial length scale over which the pressure change in response to air pumping is significant. By balancing the radial flux through the pumping coarse layer and the vertical flux through the semipervious layer, it can be shown that the radius of influence is related to the permeability ratio (Lee et al., 1992):

$$\frac{\tilde{d}}{\tilde{r}_p} = \left(\frac{\tilde{k}_f}{\tilde{k}_c}\right)^{1/2}$$  \hspace{1cm} (4.21)

where $\tilde{k}_f$ and $\tilde{k}_c$ are respectively the scales of the air conductivity of the semipervious lens and the coarse zone. The conductivity of air in soil is known to vary over a wide range of values. Typically for coarse materials $\tilde{k}_c = O(10^{-7} - 10^{-9})$ m$^2$ (Pa s)$^{-1}$ and for fine materials $\tilde{k}_f = O(10^{-11} - 10^{-13})$ m$^2$ (Pa s)$^{-1}$. Thus the ratio $\tilde{k}_f/\tilde{k}_c$ varies over a broad range of small values $10^{-6} - 10^{-2}$. However, we shall for generality assume that the conductivity ratio is such that the radius of influence is comparable to the radial geometrical length scale:

$$\tilde{r}_p = O(\tilde{r}).$$  \hspace{1cm} (4.22)

It then follows from (4.20) and (4.21) that

$$\delta_k \equiv \frac{\tilde{k}_f}{\tilde{k}_c} = O(\delta).$$  \hspace{1cm} (4.23)

4.3.3 Contrast of Effective Diffusivities in Pore Air

The effective diffusivity in pore air ($D$) varies with the air saturation and the total porosity of the medium according to Millington formula (Millington, 1959):

$$D/D_{\text{pure}} = (\text{air saturation})^{10/3}(\text{total porosity})^{4/3}$$  \hspace{1cm} (4.24)

where $D_{\text{pure}}$ is the diffusivity in pure air. Typically both air saturation and total porosity are larger in the coarse medium than the fine medium, and therefore $D$ may differ appreciably in different media. For example, consider an air saturation of 0.8 and a total porosity of 0.5 for a coarse medium, and an air saturation of 0.2 and a
total porosity of 0.2 for a fine medium. Then the above ratio is 0.19 for the coarse medium, but has a much smaller value of $5.5 \times 10^{-4}$ for the fine medium. In this study we assume that the material contrast is sufficiently large such that

$$\delta_D \equiv \tilde{D}_f / \tilde{D}_c = O(\delta), \quad (4.25)$$

where $\tilde{D}_f$ and $\tilde{D}_c$ are respectively the scales of the effective vapor diffusivity in the semipervious lens and in the coarse layers.

### 4.3.4 Air Specific Discharge

By the large conductivity contrast, the air specific discharge will have different scales in the two zones, and in different directions. Let $(\tilde{u}_c, \tilde{w}_c)$ and $(\tilde{u}_f, \tilde{w}_f)$ be respectively the scales of the specific discharge in the coarse layers and in the semipervious lens. From Darcy’s law, we may estimate that the two radial components are given by

$$\tilde{u}_c = -O(\tilde{k}_c \Delta \tilde{p} / \tilde{\tau}_p), \quad (4.26)$$

$$\tilde{u}_f = -O(\tilde{k}_f \Delta \tilde{p} / \tilde{\tau}_p) = O(\delta \tilde{u}_c), \quad (4.27)$$

where $\Delta \tilde{p} = P_a - p_0$ is the scale of pressure drop in the well. While the radial specific discharges of air in the two zones differ by an order of $\delta$, the vertical ones are comparable to each other by virtue of continuity. It is well-known that in a horizontally layered system with a sharp contrast in $k$ the effective vertical conductivity of the composite is dominated by the conductivity of the less pervious layer. Therefore

$$\tilde{w}_c = \tilde{w}_f = -O(\tilde{k}_f \Delta \tilde{p} / \tilde{d}) = O(\delta^{1/2} \tilde{u}_c) \quad (4.28)$$

where the last equality is obtained by (4.20), (4.22) and (4.23). On combination of (4.27) and (4.28) it is clear that the flow is predominantly horizontal in a coarse layer, but almost vertical in the lens. For normalization purpose, the radial velocity scale
is taken to be a positive number defined by

\[ \tilde{u}_c = \tilde{k}_e (P_a - p_0) / \tilde{r}, \quad (4.29) \]

which varies with the well pressure \( p_0 \). We also use the pressure drop in the well \( P_a - p_0 \) as the scale of pressure deviation from the atmospheric pressure.

A dimensionless parameter characterizing the flow rate is the Péclet number in the coarse layers, defined by

\[ Pe \equiv \tilde{u}_c \tilde{r} / \tilde{D}_c = \tilde{k}_e (P_a - p_0) / \tilde{D}_c, \quad (4.30) \]

where the second equality is obtained using (4.29). Assuming \( P_a - p_0 \) is a finite fraction of \( P_a = O(10^5) \) Pa, and using \( \tilde{D}_c = O(0.1) \) cm\(^2\) s\(^{-1}\) and \( \tilde{k}_e = O(10^{-7} - 10^{-9}) \) m\(^2\) (Pa s\(^{-1}\)), we estimate that \( Pe = O(10^{-3}) \). Though the Péclet number can be large, it is desirable for generality to obtain a transport equation in which the diffusion is as important as the advection. Therefore we assume that

\[ Pe \geq O(1). \quad (4.31) \]

### 4.3.5 Time Scale

The advection time over a global distance along a coarse layer is given by \( \tilde{t} = \tilde{r} / \tilde{u}_c \)

which, by virtue of the above assumptions, is also comparable to

(i) the advection time scale across a coarse layer or the lens:

\[ \tilde{t} = (\tilde{r} / \tilde{d})(\tilde{w}_c / \tilde{u}_c)(\tilde{d} / \tilde{w}_c) = O(\tilde{d} / \tilde{w}_c) = O(\tilde{d} / \tilde{w}_f); \quad (4.32) \]

(ii) the diffusion time scale across the lens:

\[ \tilde{t} = (\tilde{r} / \tilde{d})^2(\tilde{D}_c / \tilde{u}_c \tilde{r})(\tilde{D}_f / \tilde{D}_c)(\tilde{d}^2 / \tilde{D}_f) = O(\tilde{d}^2 / \tilde{D}_f); \quad (4.33) \]

and

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(iii) the diffusion time over a global distance along a coarse layer:

\[ \tilde{t} = (\tilde{D}_c/\tilde{u}_c\tilde{r})(\tilde{r}^2/\tilde{D}_c) = O(\tilde{r}^2/\tilde{D}_c). \]  \hspace{1cm} (4.34)

In addition, we assume for generality that \( \tilde{t} \) is also comparable to the diffusion time across an aggregate in the coarse layers:

\[ \tilde{t} = O(a_c^2/D_{wc}) \]  \hspace{1cm} (4.35)

where \( a_c \) denotes the aggregate radius and \( D_{wc} \) is the aqueous diffusivity in an aggregate, both for the coarse layers. In summary only one distinct time scale \( \tilde{t} \) will be pertinent in the present problem.

To facilitate discussions on the evolution of vapor plume prior to pumping, it is however desirable to use a time scale which is independent of the pumping pressure. Therefore we redefine the time scale as

\[ \tilde{t} = \tilde{r}/(\tilde{u}_c\hat{P}_a) = \tilde{r}^2/(\tilde{k}_cP_a) \]  \hspace{1cm} (4.36)

where \( P_a \) is the atmospheric pressure, and

\[ \hat{P}_a = P_a/(P_a-p_0) = 1/(1-p_0/P_a) \]  \hspace{1cm} (4.37)

is the dimensionless parameter characterizing the well pressure, which is assumed to be of order unity. Note that the time scale for the flow to approach steady-state is also given by (4.36), which as shown in (4.32)–(4.34) is comparable to the transport time scales. Therefore in the present transport problem the flow must be considered as transient. This is different from the case of open ground surface in which steady air flow can be established in a much shorter time scale than the transport processes.
Table 4.1: Normalization scales \((i = 1, 2, 3, j = 1, 2)\).

<table>
<thead>
<tr>
<th>variable or parameter</th>
<th>normalization scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r, r_0, r_b)</td>
<td>(\tilde{r})</td>
</tr>
<tr>
<td>(z, d_i, d_f, F_j)</td>
<td>(\tilde{d} = \delta^{1/2} \tilde{r})</td>
</tr>
<tr>
<td>(k_i)</td>
<td>(\tilde{k}_c)</td>
</tr>
<tr>
<td>(k_f)</td>
<td>(\tilde{k}_f = \delta_k \tilde{k}_c)</td>
</tr>
<tr>
<td>(D_i)</td>
<td>(\tilde{D}_c)</td>
</tr>
<tr>
<td>(D_f)</td>
<td>(\tilde{D}_f = \delta_D \tilde{D}_c)</td>
</tr>
<tr>
<td>(u_i)</td>
<td>(\tilde{u}_c = \tilde{k}_c(P_a - p_0)/\tilde{r})</td>
</tr>
<tr>
<td>(u_f)</td>
<td>(\delta \tilde{u}_c)</td>
</tr>
<tr>
<td>(w_i, w_f)</td>
<td>(\delta^{1/2} \tilde{u}_c)</td>
</tr>
<tr>
<td>(t, T)</td>
<td>(\tilde{t} = \tilde{r}/(\tilde{u}_c \tilde{P}_a))</td>
</tr>
<tr>
<td>(C_{g_i}, C_{g_f})</td>
<td>(C_{g_0})</td>
</tr>
<tr>
<td>(C_w)</td>
<td>(C_{g_0}/H)</td>
</tr>
<tr>
<td>(p_i', p_f')</td>
<td>(P_a - p_0)</td>
</tr>
</tbody>
</table>

### 4.4 Perturbation Equations

We shall now deduce asymptotic expansions of the flow and the transport equations. The generic expansion of an unknown variable \(f\) is expanded in a power series of \(\delta\) as follows:

\[
f = f^{(0)} + \delta f^{(1)} + \delta^2 f^{(2)} + \cdots. \tag{4.38}\]

All normalized quantities will be distinguished by overhead hats.

### 4.4.1 Air Flow

Since the pressure drop in the well \(P_a - p_0\) governs the pressure change in the soil layers, let us introduce the pressure deviation \(p'\) by

\[
p'(r, z, t) \equiv P_a - p(r, z, t), \tag{4.39}\]

and define the normalized pressure deviation by

\[
\tilde{p}'(\tilde{r}, \tilde{z}, \tilde{t}) = p'(r, z, t)/(P_a - p_0). \tag{4.40}\]
After changing the variable, we normalize the flow equation (4.4) and the interface condition (4.16) according to the scales in Table 4.1:

\[ \delta \theta_{gi} \hat{P}_a \frac{\partial \hat{p}_i'}{\partial t} - \frac{\delta}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left[ \hat{k}_i (\hat{P}_a - \hat{p}_i') \frac{\partial \hat{p}_i'}{\partial \hat{r}} \right] - \frac{\partial}{\partial \hat{z}} \left[ \hat{k}_i (\hat{P}_a - \hat{p}_i') \frac{\partial \hat{p}_i'}{\partial \hat{z}} \right] = 0 \quad \text{in } \Omega_i \ (i = 1, 2, 3), \]  
(4.41)

\[ \delta \theta_{gf} \hat{P}_a \frac{\partial \hat{p}_f'}{\partial t} - \hat{k}_f (\hat{P}_a - \hat{p}_f') \frac{\partial \hat{p}_f'}{\partial \hat{r}} + \hat{k}_f (\hat{P}_a - \hat{p}_f') \frac{\partial \hat{p}_f'}{\partial \hat{z}} = 0 \quad \text{in } \Omega_f, \]  
(4.42)

\[ - \hat{k}_i \frac{\partial \hat{p}_i'}{\partial \hat{r}} \frac{\partial \hat{\tilde{F}}_i}{\partial \hat{r}} + \hat{k}_i \frac{\partial \hat{p}_i'}{\partial \hat{z}} = - \delta \hat{k}_i \frac{\partial \hat{p}_i'}{\partial \hat{r}} \frac{\partial \hat{\tilde{F}}_i}{\partial \hat{r}} + \delta \hat{k}_i \frac{\partial \hat{p}_i'}{\partial \hat{z}} \quad \text{on } \Gamma_i \ (i = 1, 2). \]  
(4.43)

Recall that \( \delta_k = O(\delta) \). We obtain perturbation equations by expanding the pressure deviations \( \hat{p}_i' \) and \( \hat{p}_f' \) according to (4.38).

In the coarse zone \( \Omega_i \ (i = 1, 2, 3) \), the first two orders of flow equation follow from (4.41):

\[ - \frac{\partial}{\partial \hat{z}} \left[ \hat{k}_i (\hat{P}_a - \hat{p}_i^{(0)}) \frac{\partial \hat{p}_i^{(0)}}{\partial \hat{z}} \right] = 0, \]  
(4.44)

and

\[ \theta_{gi} \hat{P}_a \frac{\partial \hat{p}_i^{(0)}}{\partial t} - \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left[ \hat{k}_i (\hat{P}_a - \hat{p}_i^{(0)}) \frac{\partial \hat{p}_i^{(0)}}{\partial \hat{r}} \right] \]

\[ - \frac{\partial}{\partial \hat{z}} \left[ \hat{k}_i (\hat{P}_a - \hat{p}_i^{(0)}) \frac{\partial \hat{p}_i^{(1)}}{\partial \hat{z}} \right] + \frac{\partial}{\partial \hat{z}} \left[ \hat{k}_i \hat{p}_i^{(1)} \frac{\partial \hat{p}_i^{(0)}}{\partial \hat{z}} \right] = 0. \]  
(4.45)

As for the boundary conditions along the lens surfaces \( \Gamma_i \ (i = 1, 2) \), pressure continuity from (4.15) gives:

\[ \hat{p}_i^{(0)} = \hat{p}_f^{(0)} \quad \text{on } \Gamma_i \ (i = 1, 2), \]  
(4.46)

while flux continuity from (4.43) gives at the first two orders:

\[ \hat{k}_i \frac{\partial \hat{p}_i^{(0)}}{\partial \hat{z}} = 0 \quad \text{on } \Gamma_i \ (i = 1, 2), \]  
(4.47)

\[ - \hat{k}_i \frac{\partial \hat{p}_i^{(0)}}{\partial \hat{r}} \frac{\partial \hat{\tilde{F}}_i}{\partial \hat{r}} + \hat{k}_i \frac{\partial \hat{p}_i^{(1)}}{\partial \hat{z}} \frac{\delta_k}{\delta} \frac{\partial \hat{p}_f^{(0)}}{\partial \hat{z}} \quad \text{on } \Gamma_i \ (i = 1, 2). \]  
(4.48)

Also, the zero flux conditions on the bottom and the top boundaries of the coarse
zone give:
\[ \frac{\partial \hat{p}_i^{(0)}}{\partial \hat{z}} = \frac{\partial \hat{p}_i^{(1)}}{\partial \hat{z}} = 0 \quad (i = 1, 2, 3) \quad \text{on} \quad \hat{z} = 0 \quad \text{and} \quad \hat{z} = \hat{d}_3. \]  
(4.49)

From (4.44) and the boundary conditions (4.47) and (4.49), it is clear that the leading order pressure in the coarse zone is uniform in \( \hat{z} \) within a layer. Hence,

\[ \hat{p}_i^{(0)} = \hat{p}_i^{(0)}(\hat{r}, \hat{t}) \quad (i = 1, 2, 3). \]  
(4.50)

By this result the last term on the left-hand side of (4.45) vanishes. We next integrate (4.45) with respect to \( \hat{z} \) across a particular layer and use Leibniz's rule, the boundary condition (4.49) and the interface conditions (4.46) and (4.48). Specifically, in the bottom coarse layer \( \Omega_1 \), the integration is from 0 to \( \hat{F}_1(\hat{r}) \):

\[ \hat{d}_1(\theta_{g1}) \hat{P}_a \frac{\partial \hat{p}_1^{(0)}}{\partial \hat{t}} - \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left[ \hat{r} \hat{d}_1(\hat{k}_1)(\hat{P}_a - \hat{p}_1^{(0)}) \frac{\partial \hat{p}_1^{(0)}}{\partial \hat{r}} \right] \]
\[ = \left( \frac{\delta_k}{\delta} \right) \left[ \hat{k}_f(\hat{P}_a - \hat{p}_f^{(0)}) \frac{\partial \hat{p}_f^{(0)}}{\partial \hat{z}} \right]_{\hat{z} = \hat{F}_1}. \]  
(4.51)

In the upper coarse layer \( \Omega_2 \), the integration is from \( \hat{F}_2(\hat{r}) \) to \( \hat{d}_3 \),

\[ \hat{d}_2(\theta_{g2}) \hat{P}_a \frac{\partial \hat{p}_2^{(0)}}{\partial \hat{t}} - \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left[ \hat{r} \hat{d}_2(\hat{k}_2)(\hat{P}_a - \hat{p}_2^{(0)}) \frac{\partial \hat{p}_2^{(0)}}{\partial \hat{r}} \right] \]
\[ = - \left( \frac{\delta_k}{\delta} \right) \left[ \hat{k}_f(\hat{P}_a - \hat{p}_f^{(0)}) \frac{\partial \hat{p}_f^{(0)}}{\partial \hat{z}} \right]_{\hat{z} = \hat{F}_2}. \]  
(4.52)

In the outer coarse layer \( \Omega_3 \), the integration is from 0 to \( \hat{d}_3 \) :

\[ (\theta_{g3}) \hat{P}_a \frac{\partial \hat{p}_3^{(0)}}{\partial \hat{t}} - \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left[ \hat{r}(\hat{k}_3)(\hat{P}_a - \hat{p}_3^{(0)}) \frac{\partial \hat{p}_3^{(0)}}{\partial \hat{r}} \right] = 0. \]  
(4.53)

In the above equations, the angle brackets denote depth-averages; for example,

\[ \langle \hat{k}_1 \rangle(\hat{r}) = \frac{1}{\hat{d}_1} \int_0^{\hat{F}_1} \hat{k}_1(\hat{r}, \hat{z}) d\hat{z}. \]  
(4.54)
The boundary terms in (4.51) and (4.52) represent leakage into or from the fine-grained lens $\Omega_f$, for which the leading order flow equation is finally found from (4.42):

\[
\theta_{gf} \hat{p}_a \frac{\partial \hat{p}_f^{(0)}}{\partial \hat{t}} - \left( \frac{\delta_k}{\delta} \right) \frac{\partial}{\partial \hat{z}} \left[ \hat{k}_f (\hat{p}_a - \hat{p}_f^{(0)}) \frac{\partial \hat{p}_f^{(0)}}{\partial \hat{z}} \right] = 0. \tag{4.55}
\]

In summary (4.51)–(4.53) govern the unsteady, essentially horizontal flow in the coarse layers, with leakage from the lens. Equation (4.55) accounts for the essentially vertical flow through the semipervious lens. Thus in all layers the flow equations are just one-dimensional; this simplification is of the same genre as the classical hydrological (quasi-three-dimensional) approximation introduced heuristically by Hantush and Jacob (1955) in the theory of wells in a layered stratum with sharply contrasting permeabilities. Clearly, even without axial symmetry, the present analysis can be modified straightforwardly. The approximate flow would be two-dimensional (horizontal) in the coarse layers, and vertical in the lens. The mathematical saving of the approximation is still considerable.

To solve the above equations, we need the pressure continuity condition (4.46) on the interface, and the following radial boundary conditions as described in §4.2.2:

\[
\frac{\partial \hat{p}_1^{(0)}}{\partial \hat{r}} = 0 \quad \text{at } \hat{r} = 0, \tag{4.56}
\]

\[
\frac{\partial \hat{p}_2^{(0)}}{\partial \hat{r}} = 0 \quad \text{for } 0 < \hat{t} < \hat{T}, \quad \text{and} \quad \hat{p}_2^{(0)} = 1 \quad \text{for } \hat{t} > \hat{T}, \quad \text{at } \hat{r} = \hat{r}_0, \tag{4.57}
\]

\[
\hat{p}_1^{(0)} = \hat{p}_2^{(0)} = \hat{p}_3^{(0)} \quad \text{at } \hat{r} = \hat{r}_b, \tag{4.58}
\]

\[
\hat{d}_1 (\hat{k}_1) \frac{\partial \hat{p}_1^{(0)}}{\partial \hat{r}} + \hat{d}_2 (\hat{k}_2) \frac{\partial \hat{p}_2^{(0)}}{\partial \hat{r}} = \hat{d}_3 (\hat{k}_3) \frac{\partial \hat{p}_3^{(0)}}{\partial \hat{r}} \quad \text{at } \hat{r} = \hat{r}_b, \tag{4.59}
\]

\[
\hat{p}_3^{(0)} = 0 \quad \text{at } \hat{r} \to \infty. \tag{4.60}
\]

Once the pressure is solved in various layers, the leading order specific discharge components can be found from Darcy’s law:

\[
\langle \hat{u}_i^{(0)} \rangle = \langle \hat{k}_i \rangle \frac{\partial \hat{p}_i^{(0)}}{\partial \hat{r}} \quad (i = 1, 2, 3), \tag{4.61}
\]
\[
\hat{\psi}_f^{(0)} = \frac{\delta k}{\hat{k}_f} \hat{p}_f^{(0)} \frac{\partial p_f^{(0)}}{\partial \hat{z}}. 
\]

(4.62)

If the entire ground surface is unsealed, significant vertical flow will result; the region within a radius of the order of the layer depth \(\bar{r}\) from the extraction well will require a fully two-dimensional \((\hat{r}, \hat{z})\) analysis. If, on the other hand, the ground surface is only sealed within a radius comparable to the lens radius from the well, the flow in the upper layer below the pavement would still be essentially horizontal and governed by (4.52), while the pressure deviation \(p_z^{(0)}\) vanishes outside the paved zone. Near the edge of the pavement a locally two-dimensional \((\hat{r}, \hat{z})\) refinement is needed.

### 4.4.2 Chemical Vapor Transport

**Coarse Layers**

Normalizing the variables according to the scales in table 1, the transport equation (4.5) and the interface condition (4.17) become:

\[
\begin{align*}
\delta \theta_{gi} \hat{P}_a \frac{\partial \hat{C}_{gi}}{\partial t} + \frac{\delta}{\hat{r}} \frac{\partial}{\partial \hat{r}} (\hat{r} \hat{u}_i \hat{C}_{gi}) + \frac{\delta}{\hat{z}} \frac{\partial}{\partial \hat{z}} (\hat{w}_i \hat{C}_{gi}) \\
- \frac{\delta}{P_e \hat{r}} \frac{\partial}{\partial \hat{r}} \left( \hat{r} \hat{D}_i \frac{\partial \hat{C}_{gi}}{\partial \hat{r}} \right) - \frac{1}{P_e \hat{z}} \frac{\partial}{\partial \hat{z}} \left( \hat{D}_i \frac{\partial \hat{C}_{gi}}{\partial \hat{z}} \right) \\
= -\frac{\delta^2 \phi_{ai}}{H} \frac{D_{wi}}{\alpha_i^2 \hat{u}_c} \sum_{n=1}^{\infty} \int_0^i e^{-\lambda_{ni}(t-\tau)} \frac{\partial \hat{C}_{gi}}{\partial \hat{r}} d\hat{r} \quad \text{in } \Omega_i (i = 1, 2, 3),
\end{align*}
\]

(4.63)

\[
\begin{align*}
- \delta \left( \hat{u}_i \hat{C}_{gi} - \frac{\hat{D}_i}{P_e} \frac{\partial \hat{C}_{gi}}{\partial \hat{r}} \right) \frac{\partial \hat{F}_i}{\partial \hat{r}} + \left( \delta \hat{w}_i \hat{C}_{gi} - \frac{\hat{D}_i}{P_e} \frac{\partial \hat{C}_{gi}}{\partial \hat{z}} \right) \\
= -\delta^2 \left( \hat{u}_f \hat{C}_{gf} - \frac{\delta P_e}{\delta \hat{r}} \frac{\partial \hat{C}_{gf}}{\partial \hat{r}} \right) \frac{\partial \hat{F}_i}{\partial \hat{r}} \\
+ \delta \left( \hat{w}_f \hat{C}_{gf} - \frac{\delta P_e}{\delta \hat{z}} \frac{\partial \hat{C}_{gf}}{\partial \hat{z}} \right) \quad \text{on } \Gamma_i (i = 1, 2),
\end{align*}
\]

(4.64)

where

\[
\hat{\lambda}_{ni} = \frac{\lambda_{ni} \hat{r}}{(\hat{u}_c \hat{P}_a)} = \frac{n^2 \pi D_{ei} \hat{r}}{(\alpha_i^2 \hat{u}_c \hat{P}_a)} \quad (n = 1, 2, 3, \cdots, \quad i = 1, 2, 3).
\]

(4.65)
Recall from (4.31) and (4.25) that \( Pe \geq O(1) \) and \( \delta_D = O(\delta) \). Since it has been assumed in (4.35) that the diffusion time in a coarse aggregate is comparable to the advection time, the source term on the right-hand side of (4.63) must be of order \( \delta \).

Let us now substitute the expansions of \( \hat{C}_g \), \( \hat{u} \) and \( \hat{w} \) according to (4.38) into (4.63), (4.64) and (4.14). The first two orders of perturbation equations are as follows.

**O(1):**

\[
- \frac{1}{Pe} \frac{\partial}{\partial \hat{z}} \left( \hat{D}_i \frac{\partial \hat{C}_{gi}^{(0)}}{\partial \hat{z}} \right) = 0 \quad \text{in } \Omega_i(i = 1, 2, 3), \tag{4.66}
\]

\[
- \frac{\hat{D}_i}{Pe} \frac{\partial \hat{C}_{gi}^{(0)}}{\partial \hat{z}} = 0 \quad \text{on } \Gamma_i(i = 1, 2), \tag{4.67}
\]

\[
\frac{\partial \hat{C}_{gi}^{(0)}}{\partial \hat{z}} = 0 \quad (i = 1, 2, 3) \quad \text{on } \hat{z} = 0 \text{ and } \hat{z} = \hat{d}_3. \tag{4.68}
\]

Clearly the above conditions imply that the leading order concentrations in the coarse layers are independent of \( \hat{z} \). That is,

\[
\hat{C}_{gi}^{(0)} = \hat{C}_{gi}^{(0)}(\hat{r}, \hat{t}) \quad (i = 1, 2, 3). \tag{4.69}
\]

**O(\( \delta \)):**

\[
\theta_{gi} \hat{P}_a \frac{\partial \hat{C}_{gi}^{(0)}}{\partial \hat{t}} + \frac{1}{\hat{r} \frac{\partial}{\partial \hat{r}}} (\hat{r} \hat{u}_i^{(0)} \hat{C}_{gi}^{(0)}) + \frac{\partial}{\partial \hat{z}} (\hat{w}_i^{(0)} \hat{C}_{gi}^{(0)}) - \frac{1}{Pe} \frac{\partial}{\partial \hat{r}} \left( \hat{r} \hat{D}_i \frac{\partial \hat{C}_{gi}^{(1)}}{\partial \hat{r}} \right) - \frac{1}{Pe} \frac{\partial}{\partial \hat{z}} \left( \hat{D}_i \frac{\partial \hat{C}_{gi}^{(0)}}{\partial \hat{z}} \right) = A_i \quad \text{in } \Omega_i(i = 1, 2, 3), \tag{4.70}
\]

\[
- \hat{u}_i^{(0)} \hat{C}_{gi}^{(0)} - \frac{\hat{D}_i}{Pe} \frac{\partial \hat{C}_{gi}^{(0)}}{\partial \hat{r}} \frac{\partial \hat{r}_i}{\partial \hat{r}} + \hat{w}_i^{(0)} \hat{C}_{gi}^{(0)} - \frac{\hat{D}_i}{Pe} \frac{\partial \hat{C}_{gi}^{(1)}}{\partial \hat{z}} = \left( \hat{w}_i^{(0)} \hat{C}_{gi}^{(0)} - \frac{\delta_D \hat{D}_i}{\delta Pe} \frac{\partial \hat{C}_{gf}^{(0)}}{\partial \hat{z}} \right) \quad \text{on } \Gamma_i(i = 1, 2), \tag{4.71}
\]

\[
\hat{w}_i^{(0)} = 0, \quad \frac{\partial \hat{C}_{gi}^{(1)}}{\partial \hat{z}} = 0 \quad (i = 1, 2, 3) \quad \text{on } \hat{z} = 0 \text{ and } \hat{z} = \hat{d}_3. \tag{4.72}
\]
The phase exchange term on the right-hand side of (4.70) is

$$A_i = -6\xi_i\sigma_i\hat{P}_a \sum_{n=1}^{\infty} \int_0^i e^{-\lambda_n(t-\tau)} \frac{\partial C_{g1}^{(0)}}{\partial \hat{r}} d\hat{r} \quad (i = 1, 2, 3),$$

(4.73)

where for $i = 1, 2, 3$,

$$\xi_i = \frac{\phi_i D_{wi}\theta_{ai}}{HD_{ci}} = \frac{[K_{di}(1 - \phi_i)\rho_s + \phi_i]\theta_{ai}}{H},$$

(4.74)

and

$$\sigma_i = \frac{D_{ei}\hat{r}}{a_i^2 \bar{u}_c\hat{P}_a},$$

(4.75)

and

$$\hat{\lambda}_n = n^2\pi^2\sigma_i \quad (n = 1, 2, 3, \cdots).$$

(4.76)

As in the air flow problem, we integrate (4.70) across the three coarse layers, and use Leibniz's rule and the boundary conditions (4.72) or the interface condition (4.71) to get depth-integrated equations. Thus, in the bottom coarse layer $\Omega_1$, the integration is from 0 to $\hat{F}_1(\hat{r})$:

$$\hat{d}_1(\theta_{g1})\hat{P}_a \frac{\partial \hat{C}_{g1}^{(0)}}{\partial \hat{t}} + \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}}(\hat{r}\hat{d}_1(\hat{u}_{1}^{(0)})\hat{C}_{g1}^{(0)}) - \frac{1}{P_e\hat{r}} \frac{\partial}{\partial \hat{r}} \left( \hat{r}\hat{d}_1(\hat{D}_1) \frac{\partial \hat{C}_{g1}^{(0)}}{\partial \hat{r}} \right)$$

$$= \hat{d}_1(A_1) + \left[ \hat{w}_f^{(0)} \hat{C}_{g1}^{(0)} - \left( \frac{\delta D_f}{\delta P_e} \right) \frac{\partial \hat{C}_{g1}^{(0)}}{\partial \hat{z}} \right]_{\hat{z}=\hat{F}_1}. \quad (4.77)$$

In the upper coarse layer $\Omega_2$, we integrate from $\hat{F}_2(\hat{r})$ to $\hat{d}_2$:

$$\hat{d}_2(\theta_{g1})\hat{P}_a \frac{\partial \hat{C}_{g2}^{(0)}}{\partial \hat{t}} + \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}}(\hat{r}\hat{d}_2(\hat{u}_{2}^{(0)})\hat{C}_{g2}^{(0)}) - \frac{1}{P_e\hat{r}} \frac{\partial}{\partial \hat{r}} \left( \hat{r}\hat{d}_2(\hat{D}_2) \frac{\partial \hat{C}_{g2}^{(0)}}{\partial \hat{r}} \right)$$

$$= \hat{d}_2(A_2) + \left[ \hat{w}_f^{(0)} \hat{C}_{g2}^{(0)} - \left( \frac{\delta D_f}{\delta P_e} \right) \frac{\partial \hat{C}_{g2}^{(0)}}{\partial \hat{z}} \right]_{\hat{z}=\hat{F}_2}. \quad (4.78)$$

In the outer coarse layer $\Omega_3$, the integration is from 0 to $\hat{d}_3$:

$$\langle \theta_{g3} \rangle \hat{P}_a \frac{\partial \hat{C}_{g3}^{(0)}}{\partial \hat{t}} + \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}}(\hat{r}\langle \hat{u}_{3}^{(0)} \rangle\hat{C}_{g3}^{(0)}) - \frac{1}{P_e\hat{r}} \frac{\partial}{\partial \hat{r}} \left( \hat{r}\langle \hat{D}_3 \rangle \frac{\partial \hat{C}_{g3}^{(0)}}{\partial \hat{r}} \right) = \langle A_3 \rangle. \quad (4.79)$$
Similar to the flow equations, the transport equations in the three coarse layers (4.77)–(4.79) are radially one-dimensional. The leakage terms in (4.77) and (4.78) couple the transport in $\Omega_1$ and $\Omega_2$ with that in the fine lens $\Omega_f$, which will be discussed in §4.4.2. The radial boundary conditions required to complete the above problem are

$$\frac{\partial \hat{C}^{(0)}_{g_1}}{\partial \hat{r}} = 0 \quad \text{at} \quad \hat{r} = 0,$$

$$\hat{C}^{(0)}_{g_2} = 1 \quad \text{for} \quad 0 < \hat{t} < \hat{T}, \quad \text{and} \quad \frac{\partial \hat{C}^{(0)}_{g_2}}{\partial \hat{r}} = 0 \quad \text{for} \quad \hat{t} > \hat{T}, \quad \text{at} \quad \hat{r} = \hat{r}_0,$$

$$\hat{C}^{(0)}_{g_1} = \hat{C}^{(0)}_{g_2} = \hat{C}^{(0)}_{g_3} \quad \text{at} \quad \hat{r} = \hat{r}_b,$$

$$\hat{d}_1 \left( \langle \hat{u}_1^{(0)} \rangle \hat{C}^{(0)}_{g_1} - \frac{\langle \hat{D}_1 \rangle}{Pe} \frac{\partial \hat{C}^{(0)}_{g_1}}{\partial \hat{r}} \right) + \hat{d}_2 \left( \langle \hat{u}_2^{(0)} \rangle \hat{C}^{(0)}_{g_2} - \frac{\langle \hat{D}_2 \rangle}{Pe} \frac{\partial \hat{C}^{(0)}_{g_2}}{\partial \hat{r}} \right) = \hat{d}_3 \left( \langle \hat{u}_3^{(0)} \rangle \hat{C}^{(0)}_{g_3} - \frac{\langle \hat{D}_3 \rangle}{Pe} \frac{\partial \hat{C}^{(0)}_{g_3}}{\partial \hat{r}} \right) \quad \text{at} \quad \hat{r} = \hat{r}_b,$$

$$\hat{C}^{(0)}_{g_3} = 0 \quad \text{at} \quad \hat{r} \to \infty.$$  

Also, similar to the flow, if the ground surface is only paved within a radius comparable to the lens radius from the well, the transport in the upper layer underneath the pavement would still be governed by (4.78), while the concentration $\hat{C}^{(0)}_{g_2}$ vanishes outside the paved zone. Near the edge of the pavement a locally two-dimensional ($\hat{r}, \hat{z}$) refinement is needed.

**Fine-grained Lens**

Because of the fine-grained structure of the lens, (4.5) can be greatly simplified. We assume that in the lens the aggregate diffusion time scale is much shorter than the global advection time scale, or

$$D_{ef} \hat{t} / a_f^2 = O(\delta^{-1}) \quad \text{so that} \quad \lambda_{nf} \hat{t} = n^2 \pi^2 D_{ef} \hat{t} / a_f^2 \gg 1 \quad (n = 1, 2, \cdots),$$

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where $a_f$ is the radius of an aggregate and $D_{ef}$ is the sorption-retarded aggregate diffusivity given by (4.7), both for the lens. As shown in Appendix F, the right-hand side of (4.5) can be approximated by the asymptotic expansion (F.2):

$$RHS(4.5) \sim -\frac{\phi_f D_{wf} \theta_{af}}{H D_{ef}} \left( \frac{\partial C_{gf}}{\partial t} - \frac{a_f^2}{15 D_{ef}} \frac{\partial^2 C_{gf}}{\partial t^2} + \ldots \right),$$

(4.86)

where $D_{wf}$ is the aqueous diffusivity in an aggregate in the lens. While the leading term above can be combined with the unsteady term on the left-hand side of (4.5), the second term is of the order $\frac{a_f^2}{D_{ef} t} (= O(\delta) \ll 1)$ smaller. Using the scales listed in Table 1, we may show that to the leading order $O(\delta^0)$,

$$\beta_f \hat{P}_a \frac{\partial \hat{C}_{gf}^{(0)}}{\partial \hat{t}} + \frac{\partial}{\partial \hat{z}} (\hat{w}_f^{(0)} \hat{C}_{gf}^{(0)}) - \frac{\delta_D}{\delta Pe} \frac{\partial}{\partial \hat{z}} \left( \hat{D}_f \frac{\partial \hat{C}_{gf}^{(0)}}{\partial \hat{z}} \right) = 0$$

(4.87)

where $\beta_f$ is the retardation factor given by

$$\beta_f = \theta_{af} + \frac{\phi_f D_{wf} \theta_{af}}{H D_{ef}} = \theta_{af} + \frac{[K_{df}(1 - \phi_f) \rho_s + \phi_f] \theta_{af}}{H} = \theta_{af} + \xi_f.$$

(4.88)

Note that $\xi_f$ is the lens counterpart of $\xi_i$ defined in (4.74). Now, owing to local equilibrium chemical partitioning in aggregates, this term gives rise to retardation to vapor transport in the lens.

Again similar to the flow, the leading order transport in the fine lens is vertically one-dimensional and the concentration $\hat{C}_{gf}^{(0)}$ depends on $\hat{t}$ only parametrically. The boundary conditions are

$$\hat{C}_{gf}^{(0)} = \hat{C}_{gi}^{(0)} \quad \text{on} \quad \Gamma_i (i = 1, 2).$$

(4.89)

So far the approximate equations are valid for soil layers which can be slightly inhomogeneous, in that the soil properties within a layer can depend continuously on space over the scale $\tilde{r}$ horizontally and the scale $\tilde{d}$ vertically.
4.4.3 Dimensionless Parameters

The intensity of well-pressure is characterized by the ratio \( \hat{P}_a \) given by (4.37). It is larger for a smaller pumping rate, and vice-versa. As the pressure deviation in the well \( (P_a - p_0) \) can be a finite fraction of the atmospheric pressure \( (P_a) \), the dimensionless parameter \( \hat{P}_a \) is in general of order unity. The Péclet number \( Pe \) measures the relative importance of advection over diffusion in the radial transport in the coarse layers where flow is significant. According to its definition in (4.30), \( Pe \) is inversely proportional to \( \hat{P}_a \). Several other dimensionless parameters important to the physical and chemical process are discussed below.

1. Aggregate parameters \( \sigma_i, \xi_i \) (\( i = 1, 2, 3 \)) and \( \beta_f \)

   The physical significance of these parameters has been discussed in Chapters 2 and 3. Briefly \( \sigma_i \), defined in (4.75), is the ratio of advection time to microscopic aggregate diffusion time in a coarse layer, which reflects the depletion rate of a chemical in aggregates relative to the advective transport. It is the key parameter to indicate the departure from local equilibrium of phase partitioning. In the limit of \( \sigma_i \gg 1 \), local equilibrium exists between aggregate aqueous concentration and vapor concentration in the air pores. On the other hand, if \( \sigma_i \ll 1 \), a kinetic situation prevails, i.e., aggregate concentration responds slowly to changes in vapor concentration. The parameter \( \xi_i \), defined in (4.74), is a ratio of chemical mass partitioned in aggregates to that in vapor phase per bulk volume in a coarse layer under equilibrium partitioning. A larger \( \xi_i \) corresponds to a greater fraction of the chemical to reside in the coarse aggregates, and therefore implies a higher retardation to the transport. The corresponding parameter \( \xi_f \) for the lens is a part of the retardation factor \( \beta_f = \theta_{rf} + \xi_f \) given by (4.88), as a result of local equilibrium exchange between vapor and aggregate phases in the fine-grained lens. Similarly, a larger \( \beta_f \) means higher partitioning into the aqueous and the sorbed phases, and causes a slower transport in the lens.
2. Soil-layer properties $\delta_k/\delta$ and $\delta_D/\delta$

The two ratios $\delta_k/\delta$ and $\delta_D/\delta$ measure the contrasts in advective and diffusive transport rates respectively, between the fine-grained lens and the coarse layers. If these ratios are small, both advection and diffusion across the lens will take place more slowly than the horizontal transport in the coarse zone. In such a case, the chemical concentration can change relatively fast in the coarse zone, but only modestly in the lens. As a consequence a rapid initial clean-up of the vapor phase in the coarse zone does not guarantee final remediation of the entire soil system, since rebound due to slow diffusion from the lens may continue long after soil venting is stopped.

4.5 Numerical Examples and Discussions

We now apply the first-order approximate equations to study the effects of a low-permeability lens on soil vapor extraction. In the following numerical examples, we further assume that the soil within each layer is homogeneous. Therefore the material properties in each layer are constants and equal to their own scales. As a result, all normalized conductivities and diffusivities become one, i.e., $\hat{k}_i = \hat{k}_f = \hat{D}_i = \hat{D}_f = 1$ where $i = 1, 2, 3$. It is now more convenient to replace the coarse layer subscript $i = 1, 2, 3$ by $c$, i.e., $\theta_{gi} = \theta_{gc}$, $\sigma_i = \sigma_c$ and $\xi_i = \xi_c$. We also choose the following length scales: $\bar{r} = r_b$ and $\bar{d} = d_3$ so that $\hat{r}_b = \hat{d}_3 = 1$. As for the lens geometry, an ellipsoid is chosen whose boundaries are given by

$$
\begin{pmatrix}
\hat{F}_2(\hat{r}) \\
\hat{F}_1(\hat{r})
\end{pmatrix}
= 0.5 \pm 0.1(1 - \hat{r}^2)^{1/2}.
$$

(4.90)

The lens is centered at the mid-level of the stratum $\bar{z} = 0.5$ and has a maximum thickness of 0.2 at $\hat{r} = 0$. By symmetry about the center-plane of the lens, the thicknesses of $\Omega_1$ and $\Omega_2$ are given by the same function:

$$
\hat{d}_1 = \hat{d}_2 = 0.5 - 0.1(1 - \hat{r}^2)^{1/2}.
$$

(4.91)
The initial boundary value problem is solved numerically by the method outlined in Appendix G. For computational convenience, the inner boundary conditions at \( \hat{r} = 0 \) are applied at \( \hat{r} = \hat{r}_0 \) instead. Since a very small \( \hat{r}_0 \) is chosen, the error is expected to be insignificant.

Due to the high cost of power the applied well pressure cannot in practice drop below 50% of the atmospheric pressure (Baehr et al., 1989). Hence we consider only the range \( \hat{P}_a = 20–2 \) which is equivalent to \( p_0/P_a = 0.95–0.5 \). Let us take a typical sand layer for which \( \tilde{k}_c P_a/\tilde{D}_c = 100 \), which corresponds to a permeability scale \( \tilde{k}_c = O(10^{-8}) \) m² (Pa s)⁻¹, the Péclet number is then related to \( \hat{P}_a \) by

\[
P_e = \frac{\tilde{k}_c (P_a - p_0) / \tilde{D}_c}{\left(\frac{\tilde{k}_c P_a}{\tilde{D}_c}\right) / \hat{P}_a} = 100 / \hat{P}_a.
\]

Hence the above range of pumping pressure also corresponds to the range \( Pe = 5–50 \).

The initial period of contamination is chosen to be \( 0 < \hat{t} < \hat{T} = 100 \). Pumping begins at \( \hat{t} = 100 \) and is maintained at a constant rate. To have some ideas of the time in reality let us take a site with a lens radius \( \tilde{r} = 30 \) m, the advection velocity scale is in the range of \( \tilde{u}_c = 10^{-6}–10^{-5} \) m s⁻¹, according to (4.29). The time scale is \( \hat{t} = O(10) \) days from (4.36). The total time of contamination is roughly three years.

The following input values are chosen for all numerical examples:

\[
\hat{r}_0 = 0.05, \quad \theta_{gc} = 0.5, \quad \xi_c = 1, \quad \theta_{gf} = 0.1.
\]

As sandy materials tend to have a lower sorption coefficient, a relatively small \( \xi_c = 1 \) is assumed for the coarse layers. On the other hand, clayey materials are usually richer in organic matters and therefore have a larger sorption coefficient. Two values of \( \beta_f = 5 \) and 50 are considered in the computations. Thus, four sets of values of \( \delta_k/\delta, \delta_D/\delta, \sigma_c \) and \( \beta_f \) are chosen for comparison (Table 4.2). From now on we shall for simplicity omit the overhead hats and superscripts in all normalized quantities.
Table 4.2: Four cases of computation.

<table>
<thead>
<tr>
<th>Case</th>
<th>$\delta_k/\delta$</th>
<th>$\delta_D/\delta$</th>
<th>$\sigma_c$</th>
<th>$\beta_f$</th>
<th>Effects to Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>base case; pumping rate</td>
</tr>
<tr>
<td>II</td>
<td>0.1</td>
<td>0.1</td>
<td>1</td>
<td>5</td>
<td>lens permeability and diffusivity</td>
</tr>
<tr>
<td>III</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>5</td>
<td>aggregate diffusivity</td>
</tr>
<tr>
<td>IV</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>50</td>
<td>retardation in lens</td>
</tr>
</tbody>
</table>

Figure 4-2: Contours of vapor concentration $C_g$ (flood) as a function of time before pumping for Case I: $\delta_k/\delta = 1$, $\delta_D/\delta = 1$, $\sigma_c = 1$, $\beta_f = 5$. 
Figure 4-3: Contours of vapor concentration $C_g$ (flood) and air pressure $p/P_a$ (dashes) as a function of time during pumping, with $Pe = 5$, for Case I.
Figure 4-4: Contours of vapor concentration $C_g$ (flood) and air pressure $p/P_a$ (dashes) as a function of time during pumping, with $P\epsilon = 50$, for Case I.
4.5.1 Effects of Pumping Rate

In Case I which is also the base case for comparison, we take $\delta_k/\delta = 1$, $\delta_D/\delta = 1$, $\sigma_c = 1$ and $\beta_f = 5$. Figure 4-2 shows how the chemical vapor spreads in various layers as a function of time before pumping. Clearly the semipervious lens obstructs much of the vapor from diffusing into the bottom layer. Except very far from the center, there always exists an appreciable concentration gradient across the lens, implying a persistent flux from the top coarse layer to the bottom coarse layer. For example, the maximum vapor concentration in the bottom layer at large times is only 0.3, while that in the top layer is 1.0. While the high concentration levels are confined largely within the upper layer and the lens, the vapor front spreads to a distance more than 2.5 times the lens radius at $t = 100$.

The spatial and temporal variations of the vapor concentration during pumping with two pumping rates $Pe = 5$ and $Pe = 50$ are shown respectively in Figures 4-3 and 4-4. Also plotted in dashes are the contours of the pressure ratio $p/P_a$, from which the flow development can be inferred. In either case the flow becomes almost steady when the pumping time is larger than 10 ($t = 110$). Also beyond this pumping time the concentration gradient across the lens is substantially reduced, resulting in a practically uniform concentration profile across the entire stratum. This is expected since the diffusion time across the lens is of order unity as shown in (4.33). Therefore when pumping is long enough, vertical diffusion is completed, horizontal advection becomes the major mode of transport in the lens. Clearly, vapor is depleted more rapidly with a higher pumping rate or a stronger advection in all the layers. Note that for the lower pumping rate $Pe = 5$ (Figure 4-3), the vapor concentration at far distances continues to rise with time, despite pumping. This is because far from the well advection is too weak to counter the outward diffusive transport. The situation is reversed only at a very large time when the radial concentration gradient becomes small enough.

Since advection is controlled by the air flow, we show in Figure 4-5 the three specific discharge components $u_1$, $u_2$ and $\bar{w}_f$ as functions of $r$ at $t = 110$ for the
two pumping rates, where \( \bar{w}_f \) is the depth-averaged vertical specific discharge in the lens. Note that the horizontal and the vertical components are normalized differently according to table 1. Also note that the scale used in the case \( Pe = 50 \) is 10 times that in the case \( Pe = 5 \). Taking this into account, it is clear that when the pressure vacuum in the well increases by 10 times, the velocity components increase in most locations more than 10 times. If the velocity scale \( \bar{u}_c \) has an order of \( 10^{-5} \) m s\(^{-1} \) as estimated above, the horizontal velocity at the well is then roughly 0.003 mm s\(^{-1} \) and 0.05 mm s\(^{-1} \) for \( Pe = 5 \) and \( Pe = 50 \) respectively. Pumping causes a much higher velocity near the center in the top layer than in the bottom layer, but the difference diminishes rapidly with radial distance. At a normalized radial distance of 0.5 (i.e., half of the lens radius), both \( u_2 \) and \( \bar{w}_f \) already decrease to less than 10% of their maximum values at the well. This explains the long time required to carry vapor farther than this distance, especially in the outer layer, to the pumping well.

It is also of interest to compare (Figure 4-6) the effluent vapor concentration at the well \( (C_{gw}) \), with the maximum vapor concentration in the lens \( (C_{gm}) \) and the maximum aqueous concentration in the coarse layers \( (C_{wm}) \). In the field only the effluent vapor concentration is measured in the well to assess the progress of the clean-up. Clearly a stronger pumping causes the concentration in each layer to reduce very fast at first, and then very slowly in the long run. This tailing effect reflects the slow process of advecting the remote vapor (i.e., that already spread to large radial distances) back to the pumping well. With a stronger pumping the decay curves of the two maximum concentrations are further apart from that of the effluent vapor concentration.

4.5.2 Effects of Lens Conductivity and Diffusivity

We now consider Case II for a much less pervious lens with \( \delta_k/\delta = \delta_d/\delta = 0.1 \); the aggregate properties \( \sigma_e = 1 \), and \( \beta_f = 5 \) are kept the same. As expected, the lens offers even more resistance to the diffusion of vapor into the bottom layer during the contamination stage (Figure 4-7). The concentration gradient across the lens is more prominent, and the vapor diffuses to the bottom layer through the lens center.
Figure 4-5: Components of specific discharge: $u_1$ in the bottom layer (short dashes), $\bar{w}_f$ in the lens (long dashes) and $u_2$ in the upper layer (solid) as a function of radial distance at $t = 110$ for Case I: (a) $Pe = 5$; (b) $Pe = 50$, where the specific discharge scale is 10 times of (a).
Figure 4-6: Effluent vapor concentration $C_{gw}$ (solid), maximum vapor concentration in the lens $C_{gm}$ (short dashes) and maximum aqueous concentration in the coarse layers $C_{wm}$ (long dashes) as a function of time during pumping for Case I: (a) $Pe = 5$; (b) $Pe = 50$. 
Figure 4-7: Contours of vapor concentration $C_g$ (flood) as a function of time before pumping for Case II: $\delta_k/\delta = 0.1$, $\delta_D/\delta = 0.1$, $\sigma_c = 1$, $\beta_f = 5$.

and around the lens tip as well (Figure 4-7c). At $t = 100$ the maximum vapor concentration in the lens is only 0.08. The concentration distributions in the outer layer far from the lens are however close to those at the same instant in Case I. This suggests that the effect of the lens diffusivity on the spread of vapor to the outer layer decreases with distance.

The cases of small pumping rate ($Pe = 5$) and large pumping rate ($Pe = 50$) are shown respectively in Figures 4-8 and 4-9. Clearly for the same pumping rate the concentration in the lens is removed more slowly than Case I. A lower lens permeability therefore results in a slower response in lens concentration to pumping. For example, when $Pe = 50$ and $t = 101$, the maximum concentration in the lens remains as high as 0.8 while that in the top layer has already dropped below 0.2 (Figure 4-9b).
Figure 4-8: Contours of vapor concentration $C_q$ (flood) and air pressure $p/P_a$ (dashes) as a function of time during pumping, with $Pe = 5$, for Case II.
Figure 4-9: Contours of vapor concentration $C_g$ (flood) and air pressure $p/P_a$ (dashes) as a function of time during pumping, with $Pe = 50$, for Case II.
Figure 4-10: Components of specific discharge: \( u_1 \) in the bottom layer (short dashes), \( \bar{\bar{u}}_f \) in the lens (long dashes) and \( u_2 \) in the upper layer (solid) as a function of radial distance at \( t = 110 \) for Case II: (a) \( Pe = 5 \); (b) \( Pe = 50 \), where the specific discharge scale is 10 times of (a).

However, similar to Case I, the concentration profile across the layers becomes more uniform at larger pumping times.

The effects of a lower lens permeability on the velocity components are further shown in Figure 4-10. As compared to Figure 4-5, it can be seen that while the horizontal velocity in the pumping top layer is not much affected, the vertical velocity in the lens and the horizontal velocity in the bottom layer are dramatically reduced. This explains the much weaker advection and therefore slower decay of the vapor concentration in the lens than Case I.

The time variations of the effluent vapor concentration \( C_{gw} \) at the well, the maximum aqueous concentration in coarse layers \( C_{wm} \) and the maximum concentration in the lens \( C_{gm} \) for Case II are shown in Figure 4-11. While the decay rates for \( C_{gw} \) and \( C_{wm} \) are close to those in Case I, the slower change of \( C_{gm} \) to respond to pumping is
Figure 4-11: Effluent vapor concentration $C_{gw}$ (solid), maximum vapor concentration in the lens $C_{gm}$ (short dashes) and maximum aqueous concentration in the coarse layers $C_{um}$ (long dashes) as a function of time during pumping for Case II: (a) $Pe = 5$; (b) $Pe = 50$.

obvious. There is a larger difference between the effluent vapor concentration and the maximum concentrations in the soil, especially during the early stage of pumping.

4.5.3 Effects of Aggregate Diffusivity

Keeping $\delta_k/\delta = \delta_D/\delta = 0.1$ and $\beta_f = 5$ as in Case II, we examine in Case III the effects of a smaller aggregate diffusion rate $\sigma_c = 0.1$ in the coarse layers. Physically a smaller $\sigma_c$ implies further departure from local equilibrium between concentrations of vapor phase and aqueous phase. However the spread of vapor, during both contamination and pumping stages, is not appreciably different from Case II. This can be illustrated by Figure 4-12 which shows the time changes of $C_{gw}$, $C_{gm}$ and $C_{um}$ in Case III. As compared to Figure 4-11, the difference is evident only at the start of pumping.
Figure 4-12: Effluent vapor concentration $C_{gw}$ (solid), maximum vapor concentration in the lens $C_{gm}$ (short dashes) and maximum aqueous concentration in the coarse layers $C_{wm}$ (long dashes) as a function of time during pumping for Case III: $\delta_k/\delta = 0.1$, $\delta_D/\delta = 0.1$, $\sigma_c = 0.1$, $\beta_f = 5$, (a) $Pe = 5$; (b) $Pe = 50$.

when the maximum aqueous concentration now drops more slowly and the effluent vapor concentration drops more abruptly. The difference however diminishes with time when all the concentrations eventually come to the state of tailing. The result is reasonable since the diffusive flux in an aggregate is significant only in a time scale of order unity. Thus the effects of the aggregate diffusion rate is only important in the early stage of pumping. In the long run local phase equilibrium prevails in both coarse and fine soils.

4.5.4 Effects of Lens Retardation Factor

We now consider in Case IV the effects of the chemical property in the lens, with the same $\delta_k/\delta = \delta_D/\delta = 0.1$ and $\sigma_c = 0.1$, but a larger $\beta_f = 50$, which is increased by a
Figure 4-13: Contours of vapor concentration $C_g$ (flood) as a function of time before pumping for Case IV: $\delta_k/\delta = 0.1$, $\delta_D/\delta = 0.1$, $\sigma_c = 0.1$, $\beta_f = 50$.

factor of 10 from Case III. Recall from (4.88) that the retardation factor $\beta_f$ increases with the sorption partition coefficient which in turn depends on properties of the soil and the chemical. For a higher retardation factor both the advection and the diffusion in the lens are expected to be further slowed down. Figure 4-13 shows the vapor diffusion before pumping. Now the transport across the lens is so slow that the chemical vapor has to spread outward across the entire radius above the lens before diffusing inward into the bottom layer (Figure 4-13c). The maximum concentration in the bottom layer is now located near the tip of the lens and is less than 0.02 at $t = 100$.

Figures 4-14 and 4-15 show how the vapor concentration changes in response to the small pumping rate ($Pe = 5$) and large pumping rate ($Pe = 50$) respectively.
Figure 4-14: Contours of vapor concentration $C_g$ (flood) and air pressure $p/P_a$ (dashes) as a function of time during pumping, with $Pe = 5$, for Case IV.
Figure 4-15: Contours of vapor concentration $C_g$ (flood) and air pressure $p/P_a$ (dashes) as a function of time during pumping, with $Pe = 50$, for Case IV.
Figure 4-16: Effluent vapor concentration $C_{gw}$ (solid), maximum vapor concentration in the lens $C_{wm}$ (short dashes) and maximum aqueous concentration in the coarse layers $C_{wm}$ (long dashes) as a function of time during pumping for Case IV: (a) $Pe = 5$; (b) $Pe = 50$.

Since the travel time is inversely proportional to the retardation factor, the effective transport rate in the lens will be 10 times slower in this case than Case II. The further sluggishness in the attenuation of concentration in the lens is evident in either pumping case as compared to Figures 4-8 and 4-9. During the early period of pumping the maximum vapor concentration in the lens is almost constant in time (Figure 4-16). This case exhibits the largest discrepancy between the decays of the effluent vapor concentration and the maximum concentration in the lens.

4.5.5 Purge Time

To find out how the speed of clean-up depends on the above effects and the pumping pressure, we define the purge time as the time required to reduce the maximum vapor
Figure 4-17: Purge time as a function of $Pe$ for Cases I, II, III and IV.

concentration in the lens to 0.01. The results are plotted in Figure 4-17.

For the same Péclet number or pumping intensity, the purge time is obviously longer for a lens of lower permeability (Case II), and longer still for a lens of higher retardation factor (Case IV). A smaller aggregate diffusion rate in the coarse layer (Case III) however has little effect on the purge time. Thus the clean-up rate is basically controlled by the permeability, diffusivity and retardation factor of the lens.

Of course the purge time also decreases with increasing vacuum pressure in the well. The reduction is more than 50% as Péclet number increases from 5 to 20. The shortening in purge time however becomes progressively insignificant when Péclet number increases further above 30. Since the cost of pumping depends on both the time and the strength of pumping, it is desirable to clean up the soil in the shortest possible time without unnecessarily too high a pumping rate. This is a matter of optimization involving economical factors.
4.6 Concluding Remarks

In this chapter we have derived the leading order asymptotic flow and transport equations for soil vapor extraction in an unsaturated zone containing a thin lens of low permeability. The key assumptions are (i) the layer thickness is much smaller than the characteristic horizontal length scale; and (ii) there is a sharp contrast between conductivities and diffusivities of the semipervious lens and the coarse layers. The small parameters enable us to perform a perturbation analysis which reduces the dimensions of the governing equations for the air flow and the vapor transport in various layers. Specifically the flow and transport are basically horizontal along the coarse layers and vertical across the lens. While the flow depends on the pressure drop in the well and the permeability ratio, the transport of chemical depends on the Péclet number, the aggregate parameters and the diffusivity ratio. For very permeable soil and strong pumping, advection dominates the transport mechanism.

Results of some numerical computations clarify the significance of the pumping strength and the soil properties. In particular the lens properties (air conductivity and chemical retardation factor) are critical in regulating the rate of vapor removal. Transport across the lens is the slowest in the case of a large retardation factor, low permeability and weak pumping. The aggregate diffusivity in the coarse layer also affects the phase change kinetics in the early stage of pumping, and becomes less influential in the long run. In all cases the effluent vapor concentration drops more abruptly than the peak concentration in the lens immediately after the start of pumping, but they all exhibit tailing in the long run as the more remote vapor is being extracted.

While a single axi-symmetrical lens is treated here, it is straightforward to extend our approximation to more realistic situations where there are several wells and multiple semipervious lenses of general plan form. The problem in the coarse layers will be horizontally two-dimensional. Numerical computation will be more demanding but still far less cumbersome than the task of solving a fully three-dimensional problem in all layers. Future development should include the effects of an underlying saturated
zone where phase exchange between vapor and dissolved phase in the groundwater has to be taken into account. Still more challenging is the problem of thermal air-sparging where hot air is injected into the saturated zone to enhance volatilization of the dissolved phase.

So far, we have assumed that residual NAPL is not present in the soil being treated, and the transport of one chemical component is independent of that of another. In the next chapter, we shall extend the aggregate diffusion model so that it also governs the case of multicomponent vapor transport in the presence of free and trapped phases of residual NAPL.
Chapter 5

Transport of Multicomponent Vapor Due to Air Venting in Unsaturated Soil with Residual NAPL

5.1 Introduction

In this final chapter, we shall study the case of soil vapor extraction from an unsaturated zone contaminated by residual NAPL as well as other phases of a multicomponent volatile organic compound mixture.

As we have examined in the preceding chapters, the effectiveness of soil vapor extraction (SVE), as a method to remediate an unsaturated zone contaminated with volatile organic compounds (VOC), relies on two factors: how fast the soil vapor can be removed, and how fast mass transfer into the venting stream from the other phases (i.e., aqueous phase in soil moisture, non-aqueous phase liquid (NAPL) and sorbed phase on solid grains) can occur on the microscopic scale. While the vapor transport rate is usually controlled by the pumping rate and the soil permeability, the interphase mass transfer rate depends on the distributions of the phases in the soil.
microstructure. It is crucial for a mathematical model of SVE to contain the essential features of the physico-chemical process on the microscale, in order to bring forth the relevant parameters controlling the effects of phase exchange on the macroscopic vapor transport.

Local equilibrium is the common assumption used by many existing models for multiphase transport in unsaturated soils (e.g., Marley and Hoag, 1984; Abriola and Pinder, 1985; Corapcioglu and Baehr, 1987; Baehr et al., 1989; Johnson et al., 1990; Kaluarachchi and Parker, 1990; Rathfelder et al., 1991; Ho and Udell, 1992). Although this assumption can lead to simplification by relating concentrations of all phases with the equilibrium partition laws, the local equilibrium models often fail to account for kinetic behavior such as "tailing" and "rebound during shutdown" exhibited by effluent vapor concentrations (see Figure 2-3; Crow et al., 1987; DiGiulio, 1992). In some other models (e.g., Sleep and Sykes, 1989; Brusseau, 1991; Lingineni and Dhir, 1992; Armstrong et al., 1994), the interphase mass transfer rates are described by ad hoc first-order relations which nevertheless contain empirical transfer coefficients that cannot be readily estimated and may change in value over the course of venting (Fischer et al., 1996).

The selective transport of constituents during the evaporation of multicomponent NAPL in unsaturated media has also received some attention. Baehr (1987) showed by numerical simulations that the aromatic gasoline constituents, due to higher water/air partition coefficients, dominate in the total hydrocarbon partitioned in an unsaturated zone. Rathfelder et al. (1991), Lingineni and Dhir (1992), and Ho et al. (1994) conducted through-flow venting experiments in laboratory-packed columns emplaced with residual multicomponent NAPL, but no residual water. In particular, Rathfelder et al. (1991) and Ho et al. (1994), both using a local equilibrium model, have been able to predict the successive rise in the effluent vapor concentration of the heavier components upon depletion of the lighter ones. The temporal and spatial variations of the liquid compositions along the column were also investigated by Ho et al. (1994). They found that the individual components propagate with separate evaporation fronts which move at a speed proportional to their vapor pressure or
volatility. In addition, condensation of less volatile components was also observed to occur downstream of their evaporation fronts. These experiments suggest that in the absence of water content, the NAPL can readily equilibrate with vapor in the local pores. However, Hayden et al. (1994) and Wilkins et al. (1995) found that in columns emplaced with residual NAPL and residual water the deviation of effluent concentrations from the local equilibrium values is remarkable over extended periods of venting. The NAPL-vapor phase mass transfer appears to be rate-limited in the presence of soil moisture. Lingineni and Dhir (1997) also studied the kinetics in NAPL evaporation rate-limited by diffusion in the liquid phase.

More recently, Ostendorf et al. (1997) carried out a venting experiment on an intact core taken from a site contaminated with weathered fuel. Their data clearly manifest the multicomponent effects. In particular, the vapor concentration of a heavy component may increase for some time and exhibits a maximum in the course of venting, which is in sharp contrast to the behavior of a lighter component whose concentration decreases monotonically with time, and has a smoother spatial distribution. They also obtained elution curves with appreciable tailing, a sign of departure from local equilibrium. Their findings have motivated us to develop a model which is capable of describing the vapor transport in an unsaturated medium with microscopic phase change from multicomponent residual NAPL which is not necessarily in local equilibrium with the vapor phase.

In natural unsaturated soils, the NAPL is often distributed into two phases: free and trapped (Parker and Lenhard, 1987). Free NAPL is a thin oil film or lens in direct contact with mobile air, while trapped NAPL are discontinuous islands of oil occluded within the water phase; both phases are immobilized by capillary forces when the NAPL saturation is reduced to the residual level. The NAPL entrapment in a two-phase system has been extensively examined. Typically NAPL is the non-wetting phase while water is the wetting phase. The immiscible displacement of NAPL by water always results in a fraction of the NAPL being snapped off and left behind as blobs or ganglia in the otherwise water-filled pore space (e.g., Chatzis et al., 1983; Wilson and Conrad, 1984). In a three-phase system the fluid distribution
Figure 5-1: Schematic diagram of the distribution of water, NAPL and air in a three-fluid porous medium system (adapted from Hofstee et al., 1997 and after Leverett, 1941).

is much more complex and depends on the spreading coefficient of the NAPL, which is related to its interfacial tensions with the water and the gas phases (Wilkins et al. 1995). A spreading NAPL which has low interfacial tensions spreads out as a thin film between the water and the gas phases, while a non-spreading NAPL exists as discontinuous lenses between them. In any case, following the order of wettability, water always occupies the smaller pores and wets the solid surface, while air fills the larger pores and NAPL forms a film between the two phases (Figure 5-1, and see, e.g., Blunt and Scher, 1995; Blunt et al., 1995; Zhou and Blunt, 1997). Microscopic evidence of NAPL films in a three-phase system has been provided by Hayden and Voice (1993).

Suggested by the above observations, a reasonable microscopic three-phase fluid distribution may be constructed as follows (see Figure 5-2). If both water and NAPL are at their residual saturations, air is the only mobile phase and continuously occupies the larger pores (macropores). The smaller pores (micropores) are filled with immobile water, “trapped” NAPL and trapped air, where water is adjacent to solid surfaces, trapped air is in the center of the void and “trapped” NAPL is a thin film sandwiched between water and air. An entity composed of a cluster of solid particles and the immobile and trapped phases can be regarded as an aggregate with
Figure 5-2: Conceptual model of microscopic distributions of air (free and trapped) with vapor, immobile water with dissolved phase, and NAPL (free and trapped) in an aggregate of soil grains with sorbed phase.

microporosity. Being either a thin film surrounding an aggregate, or a pendular ring or lens between aggregates, the “free” NAPL resides outside the micropores and is directly exposed to the mobile air. In this study we assume that the “free” NAPL is so small in saturation that it remains practically stagnant (but evaporates) even in the presence of air flow. With this conceptual model, we can now study the various interphase mass transfer processes more systematically. While the free NAPL can readily be vaporized into the macropores, mass transfer from the trapped NAPL is rate-limited by the slow diffusion in the surrounding water, as the aqueous diffusivity is smaller than the air diffusivity by at least four orders of magnitude. Equilibrium partitioning between trapped NAPL and mobile air is clearly not true in general. This kinetic effect on the macroscale vapor transport has however not been well-studied in the literature.

The objective of this study is to develop a kinetic model for multicomponent vapor transport due to air venting in an unsaturated zone in which both free and trapped phases of residual NAPL exist. An idealized microstructure incorporating the above features of phase distributions will be proposed in §5.2. It is basically an extension of the spherical aggregate model developed in Chapter 2 for soil vapor extraction in the
absence of NAPL. In this case trapped NAPL is distributed inside, while free NAPL is spread as a thin film outside each spherical aggregate. The microscale transport, solely by aqueous diffusion, is detailed in §5.3. The mass exchange between aggregates and mobile phases appears as a source term in the macroscale vapor transport equation which is deduced in §5.4. In the complete problem there is coupling not only between the microscale and the macroscale transports, but also between the individual components. Normalization of the equations is then presented in §5.5 in order to bring forth the dimensionless parameters pertinent in this problem. The normalization also facilitates the use of a simplified model mixture composed of a few selected components to approximate the real mixture which may contain a large number of components. In §5.6, the model is tested by comparing with the data of Ostendorf et al. (1997). Using a five-alkane mixture for the modeling, the agreement between prediction and data is clearly demonstrated. The simulations in §5.7 are to further examine the dynamic multicomponent effects. For simplicity, vapor transport in a radial flow in an axi-symmetrical soil layer contaminated by a three-aromatic NAPL composed of benzene, toluene and o-xylene is considered. Discussions will be focused on the effects of free and trapped NAPL on the spatial and temporal variations of the component vapor and total concentrations. Mass transfer at the microscale is also examined.

5.2 Soil Microstructure and Phase Distributions

Based on the preceding discussions, an idealized three-fluid distribution in a soil microstructure consisting of regular packing of spherical porous aggregates is proposed. Referring to Figure 5-3a, inside a unit cell $\Omega'$ is a soil aggregate $\Omega'_a$ surrounded by macropore space occupied by the free NAPL $\Omega'_o$ and the mobile air $\Omega'_g$. We assume that the volume fraction of the free NAPL is so low that it spreads as a thin film on the surface of an aggregate and remains virtually stagnant even in the presence of air flow in the macropores.

The microstructure inside an aggregate is shown in a blow-up in Figure 5-3b. All
fluids in the micropores are retained by capillary forces. The solid grains $\Omega_s$ are wetted by immobile water $\Omega_w$ which in turn encloses the trapped NAPL $\Omega_o$ and the residual air $\Omega_g$. The saturation level of the trapped NAPL is also so low that it exists as a thin layer separating the water and the trapped air. Sorption of solute onto organic matters on the solid surface is also assumed to take place.

The aggregate model is essentially a conceptualization for taking into consideration various transport mechanisms on the microscale, and their interaction with the macroscale. The macroscale advective diffusion of vapor in the mobile region (interaggregate pores) is effectively coupled to the microscale diffusion of solute in the immobile region (intra-aggregate pores). The assumption that the aggregates are spheres is merely to simplify the computations for the rates of phase exchange between the two regions. Ultimately, we may view that the radius of an aggregate "a" which is just the characteristic dimension of an immobile region is one of the few calibration parameters in the model.

For the chemical partitioning, a species which exists in the NAPL is also vaporized in air (both free and trapped), dissolved in the immobile water, and sorbed onto the solid grains. We ignore any concentration gradient in a NAPL film, because of its small thickness, in the course of phase change of its components so that it can be regarded as a locally uniform mixture at all times.

As two length scales will be used in this study, we shall denote the microscale (aggregate) radial coordinate by $r$ and the macroscale coordinates by $x'$. All quantities depending solely on $x'$ will be distinguished by primes, including the domains $\Omega'$, $\Omega'_a$, $\Omega'_o$ and $\Omega'_g$ in Figure 5-3.

### 5.3 Aqueous Diffusion in a Spherical Aggregate

Let there be $N$ components in the NAPL mixture initially. For component $i$ ($i = 1, \cdots, N$), we denote the mass concentration (mass per phase volume) of its vapor in trapped air by $C_{gi}(r, x', t)$, aqueous phase in immobile water by $C_{wi}(r, x', t)$ and separate phase in trapped NAPL by $C_{ai}(r, x', t)$. The sorbed solid phase concentration,
Figure 5-3: Schematic diagram of idealized microscopic fluid distributions: (a) a unit cell $\Omega'$ containing a spherical aggregate $\Omega'_a$, free NAPL $\Omega'_o$ and mobile air $\Omega'_g$; (b) a unit cell $\Omega$ inside an aggregate where $\Omega_s$ is solid grain, $\Omega_w$ is immobile water, $\Omega_o$ is trapped NAPL, $\Omega_g$ is trapped air, $\Gamma_{go}$ is the interface between $\Omega_g$ and $\Omega_o$, $\Gamma_{wo}$ is the interface between $\Omega_w$ and $\Omega_o$, and $\Gamma_{ws}$ is the interface between $\Omega_w$ and $\Omega_s$. 
denoted by $C_{si}(r, x', t)$, is the mass of chemical per mass of soil grains. The aggregate concentration (i.e., sum of mass in all phases per bulk volume of aggregate) for a component can then be expressed as:

$$C_{ai}(r, x', t) = \phi(S_o C_{oi} + S_w C_{wi} + S_g C_{gi}) + (1 - \phi) \rho_s C_{si} \quad (i = 1, \ldots, N), \quad (5.1)$$

where $\phi$ is the volume fraction of void in an aggregate, i.e., the microporosity, $\rho_s$ is the solid density, and $S_o$, $S_w$ and $S_g$ are the respective saturations (phase volume per volume of void) of trapped NAPL, water and air in an aggregate. By definition,

$$S_o + S_w + S_g = 1. \quad (5.2)$$

Since water is the only connected phase, the mass transport inside an aggregate will solely rely on aqueous diffusion. If further a spherical aggregate of radius $a$ with radial symmetry is assumed, the aqueous diffusion can be described by

$$\frac{\partial C_{ai}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \phi S_w D_{wi}^* \frac{\partial C_{wi}}{\partial r} \right) \quad 0 < r < a \quad (i = 1, \ldots, N), \quad (5.3)$$

where $t$ is the time, $r$ is the radial coordinate from the center of the sphere, and $D_{wi}^*$ is the effective aqueous diffusivity accounting for the presence of the solid grains and other phases in an aggregate. By virtue of the small length-scale of the micropores, local chemical equilibrium among the various partitions is expected. Invoking the equilibrium partition laws and assuming linear sorption isotherm, we may relate the concentrations as follows:

$$C_{wi} = \gamma_i \chi_i C_{wi}^{sat}, \quad (5.4)$$

$$C_{gi} = \gamma_i \chi_i C_{gi}^{sat} = \gamma_i \chi_i H_i C_{wi}^{sat} = H_i C_{wi}, \quad (5.5)$$

$$C_{si} = K_{di} C_{wi}, \quad (5.6)$$

where $\gamma_i$ is the activity coefficient of component $i$ in the NAPL mixture, $C_{wi}^{sat}$ and $C_{gi}^{sat}$ are respectively the saturation aqueous and vapor concentrations, $H_i$ is the Henry’s law constant, and $K_{di}$ is the sorption partition coefficient. In addition $\chi_i$ is the mole
fraction of component $i$ in the NAPL mixture defined by

$$\chi_i = \frac{C_{oi}/M_i}{\sum_{j=1}^{N} C_{oj}/M_j}$$

(5.7)

in which $M_j$ are the molecular weights of corresponding components. Note that $C_{oi}/M_i$ is the molar concentration of component $i$ in NAPL (in units of moles per unit volume of NAPL) and that the sum of all mole fractions equals unity, i.e.,

$$\sum_{i=1}^{N} \chi_i = 1.$$  

(5.8)

Note that the activity coefficients $\gamma_i$ become close to unity when the components have similar molecular structures (Schwarzenbach et al., 1993, p. 48). We also remark that the above equilibrium assumptions are applied on the microscale, and therefore differ from the usual assumption of local equilibrium on the macroscale. For an ideal chemical mixture, the total volume is equal to the sum of partial volumes of individual components:

$$\sum_{j=1}^{N} \frac{C_{oj}}{\rho_{oj}} = 1,$$

(5.9)

where $\rho_{oj}$ are the liquid densities of the pure components. By this relation, we may express $C_{oi}$ explicitly in terms of $\chi_i$:

$$C_{oi} = \frac{\chi_i M_i}{\sum_{j=1}^{N} \chi_j M_j / \rho_{oj}}.$$  

(5.10)

We remark that in general the aqueous and the vapor concentrations of a component are much smaller than its concentration in the NAPL. For example, from (5.5) and (5.7), we may show that on assuming unity activity coefficients,

$$C_{gi} = C_{oi} \frac{C_{gi}^{sat}/M_i}{\sum_{j=1}^{N} C_{oj}/M_j} \ll C_{oi},$$

(5.11)

by the fact that the saturation vapor molar concentration of a component ($C_{gi}^{sat}/M_i$) is always much smaller than the molar concentration of a NAPL mixture ($\sum_{j=1}^{N} C_{oj}/M_j$).
To illustrate, let us consider a mixture of equal mole fractions \( \chi_i = 1/3 \) for \( i = 1, 2, 3 \) of benzene, toluene and o-xylene. Using their properties at \( 25^\circ\text{C} \) given in Table 5.4, and the relation (5.10), we may estimate that the concentration of the mixture \( \sum_{j=1}^{3} C_{oj}/M_j = 9.5 \text{ mol L}^{-1} \), which is much greater than the saturated vapor concentrations \( C_{gi}^{sat}/M_i = 4.1 \times 10^{-3} \) (benzene), \( 1.2 \times 10^{-3} \) (toluene) and \( 2.7 \times 10^{-4} \) mol L\(^{-1} \) (o-xylene). For this study, we assume that the NAPL is at a so low saturation level \( S_o/S_w \ll 1 \) that it forms a thin film between trapped air and immobile water.

Substituting (5.4)–(5.6) and (5.10) into (5.1), and using (5.11), we may write

\[
C_{ai} = \phi(S_o\alpha_i + 1)\beta_i C_{wi} \quad (i = 1, \cdots, N),
\]

where

\[
\alpha_i = \frac{M_i/(\gamma_i C_{wi}^{sat} \beta_i)}{\sum_{j=1}^{N} C_{wj} M_j/(\gamma_j C_{wj}^{sat} \rho_{oj})},
\]

and

\[
\beta_i = S_w + (1 - S_w)H_i + (1 - \phi)K_{di}\rho_s/\phi.
\]

Note that \( \alpha_i(r, x', t) \) is a function of all species concentrations \( C_{wj} \), \( (j = 1, \cdots, N) \), while \( \beta_i \) depends only on the properties of aggregate and chemical \( i \).

If the properties within an aggregate are constant, the aqueous diffusion equation (5.3) may now be written as:

\[
\frac{\partial}{\partial t}[(S_o\alpha_i + 1)C_{wi}] = \frac{S_wD_{wi}^*}{\beta_i r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_{wi}}{\partial r} \right) \quad 0 < r < a \quad (i = 1, \cdots, N).
\]

We have so far obtained the aggregate diffusion equation by heuristic arguments. In fact, the above equation can also be deduced more formally by the homogenization theory as detailed in Appendix H. It is shown that the effective diffusivity \( D_{wi}^* \) is a function of the aggregate microstructure and the water content only.

Recall that in the presence of NAPL the aqueous concentration is governed by
(5.4). Therefore, with (5.8),

$$
\sum_{i=1}^{N} \frac{C_{wi}}{\gamma_i C_{wi}^{sat}} = 1, \quad \text{for } S_o > 0. \tag{5.16}
$$

The boundary conditions for the above diffusion equation are given by the zero-flux at the center and the equilibrium partitioning on the outer surface:

$$
r^2 \left. \frac{\partial C_{wi}}{\partial r} \right|_{r \to 0} = 0, \tag{5.17}
$$

$$
C_{wi}(r = a, x', t) = C'_{gi}(x', t)/H_i, \tag{5.18}
$$

where $C'_{gi}$ is the vapor concentration in macropores for which the governing equations are to be deduced in the next section.

Equations (5.15)–(5.18) constitute the problem for the $N+1$ unknowns: $C_{wi}(r, x', t)$ where $i = 1, \ldots, N$, and $S_o(r, x', t)$ which vary on both the aggregate and the macroscopic scales. With additional initial conditions, they must be solved together with the vapor concentrations $C'_{gi}(x', t)$ which depends on the macroscale coordinate $x'$.

Owing to the term $S_o \alpha_i$ on the left-hand side of (5.15), the transports of individual components are nonlinearly coupled with one another. The coupling disappears only when $S_o$ becomes zero throughout the aggregate, or when the NAPL is completely dissolved. When this becomes true, the aqueous concentrations are decoupled and can be found separately (Chapter 2):

$$
C_{wi} = \frac{C'_{gi}}{H_i} - \frac{2a}{H_i r} \sum_{n=1}^{\infty} \left\{ \frac{(-1)^n e^{-\lambda_n r}}{n \pi} \sin \frac{n \pi r}{a} \int_0^t e^{-\lambda_n (t-\tau)} \frac{\partial C'_{gi}}{\partial \tau} \, d\tau \right\}, \tag{5.19}
$$

where

$$
\lambda_n = \frac{n^2 \pi^2 S_w D_{wi}^*}{\beta_i \alpha^2}. \tag{5.20}
$$
5.4 Vapor Transport on the Macroscale

Recall that all quantities which depend on the macroscale only are distinguished by a prime. By virtue of the large air diffusivity, the vapor concentration in the free air \( C'_{gi}(x', t) \) is essentially uniform over a unit cell \( \Omega' \); this fact can be justified by the mathematical theory of homogenization in Chapter 2. With vapor advection and diffusion being the major transport mechanisms, the effective transport equation for component \( i \) on the macroscale can be written as:

\[
\frac{\partial C'_{ti}}{\partial t} + \nabla' \cdot (\theta_g \bar{u} C'_{gi}) - \nabla' \cdot (\theta_g D_{gi} \nabla' C'_{gi}) = 0 \quad (i = 1, \ldots, N),
\]

(5.21)

where \( \theta_g = |\Omega_g' + \Omega_o'|/|\Omega'| \sim |\Omega_g'|/|\Omega'| \) is the macroporosity, \( \bar{u} \) is the air seepage velocity, \( D_{gi} \) is the diffusivity in the interaggregate air. The total bulk concentration \( C'_t(x', t) \), which equals the total concentration of component \( i \) over a unit cell \( \Omega' \), is given by

\[
C'_t(x', t) = \theta_g [S'_o C'_{oi} + (1 - S'_o) C'_{gi}] + \theta_a \langle C_{ai} \rangle \quad (i = 1, \ldots, N),
\]

(5.22)

where \( S'_o(x', t) = |\Omega_o'|/|\Omega_g' + \Omega_o'| \) is the free NAPL saturation in macropores, \( \theta_a = |\Omega_a'|/|\Omega'| = 1 - \theta_g \) is the bulk volume fraction of aggregates, \( C'_t(x', t) \) is the concentration in the free NAPL and \( \langle C_{ai} \rangle(x', t) \) is the mean value of \( C_{ai} \), defined in (5.12), over an aggregate \( \Omega_a' \). Since the free NAPL is in the form of a thin film, chemicals within must be uniformly distributed and the equilibrium partition laws apply. Hence

\[
C'_{gi} = \gamma_i \chi'_i C'^{sat}_{gi},
\]

(5.23)

where

\[
\chi'_i = \frac{C'_{oi}/M_i}{\sum_{j=1}^N C'_{oj}/M_j}.
\]

(5.24)

Again, we use the volume totality relation \( \sum_{j=1}^N C'_{oj}/\rho_{oj} = 1 \) to express \( C'_{oi} \) explic-
itly in terms of $\chi'_i$:

$$C'_{oi} = \frac{\chi'_i M_i}{\sum_{j=1}^{N} \chi'_j M_j / \rho_{oj}},$$

(5.25)

which is similar to (5.10). On replacing $\chi'_i$ by using (5.23), we may further write

$$C'_{oi} = \alpha'_i C''_{gi},$$

(5.26)

where

$$\alpha'_i (\mathbf{x}', t) = \frac{M_i / (\gamma_i C_{gi}^{sat})}{\sum_{j=1}^{N} C'_{gj} M_j / (\gamma_j C_{gj}^{sat} \rho_{oj})},$$

(5.27)

which is parallel to $\alpha_i$ in the aggregate problem. The free NAPL saturation is also assumed to be much smaller than unity:

$$S'_o \ll 1.$$  

(5.28)

On substituting the above relations into (5.21), we obtain a macroscale vapor transport equation in terms of $C'_{gi}$:

$$\theta_g \frac{\partial}{\partial t} \left[ (S'_o \alpha'_i + 1) C'_{gi} \right] + \nabla' \cdot (\theta_g \bar{u} C'_{gi}) - \nabla' \cdot (\theta_g D_{gi} \nabla' C''_{gi}) = -\theta_a \frac{\partial (C_{ai})}{\partial t}$$

$$(i = 1, \cdots, N).$$

(5.29)

Similar to the aggregate diffusion problem, the component concentrations are constrained by the totality condition in the presence of NAPL:

$$\sum_{i=1}^{N} \chi'_i = \sum_{i=1}^{N} \frac{C'_{gi}}{\gamma_i C_{gi}^{sat}} = 1, \quad \text{for } S'_o > 0,$$

(5.30)

in view of (5.23).

In addition, initial and boundary conditions on the macroscale must be imposed (e.g., zero concentration at a large distance, and zero concentration gradient at the screen of a pumping well). Then, (5.29) aided by (5.30) define the macroscale transport problem for $N + 1$ unknowns: $C'_{gi}(\mathbf{x}', t)$ where $i = 1, \cdots, N$, and $S'_o(\mathbf{x}', t)$. In the absence of soil aggregation, the aggregate source term may be omitted; (5.29) reduces
Figure 5-4: The transport processes on the macroscale and the microscale.

to the local equilibrium theory considered by Ho et al. (1994).

Note that in addition to the intercomponent coupling, there is also coupling between the aggregate diffusion and the macroscale transport problems. While by (5.18) the boundary value of $C_{wi}(r = a)$ is affected by the local value of $C_{gi'}$, the change in the total mass in aggregates is a source term for the vapor transport on the right-hand side of (5.29). Figure 5-4 summarizes the transport processes at the two different scales. As noted earlier, the coupling between components disappears when all NAPL phases are removed or when both $S'_{o}$ and $S_{o}$ are identically zero. If this is true, the effective vapor transport equation becomes

$$
\theta_g \frac{\partial C_{gi'}}{\partial t} + \nabla' \cdot (\theta_g \tilde{u} C_{gi'}) - \nabla' \cdot (\theta_g D_{gi'} \nabla' C_{gi'}) = - \frac{6 S_w \phi D^*_{wi} \theta_a}{a^2 H_i} \sum_{n=1}^{\infty} \int_0^t e^{-\lambda_n (t-\tau)} \frac{\partial C_{gi'}}{\partial \tau} d\tau,
$$

as has been obtained previously by Chapter 2.
5.5 Normalization

In the present study, we shall further assume for simplicity that the soil and the initial NAPL (free and trapped) composition are homogeneous such that the soil properties $a$, $\phi$, $\theta_g$ and $D_g$, and the initial mole fractions $\chi_{i0} (i = 1, \cdots, N)$ are all constant in space. We shall also focus on the case of ideal NAPL mixing so that the activity coefficients are all equal to unity, i.e., $\gamma_i = 1 (i = 1, \cdots, N)$. Initial phase equilibrium on the macroscale is also assumed so that the initial concentrations are given by

$$C'_{gi}(x', t = 0) = H_i C_{wi}(0 < r < a, x', t = 0) = \chi_{i0} C^\text{sat}_{gi}. \quad (5.32)$$

We now introduce the following normalized variables (distinguished by a hat):

$$(C'_{gi}, C_{wi}, C_{ai}, C'_{ti}, C'_{oi}, C_{oi}) = \chi_{i0} C^\text{sat}_{gi} (\hat{C}'_{gi}, \hat{C}_{wi}/H_i, \phi \beta_i \hat{C}_{ai}/H_i, \theta_g \hat{C}'_{ti}, \hat{C}'_{oi}, \beta_i \hat{C}_{oi}/H_i),$$

$$\hat{\nabla}' = L'^{-1} \hat{\nabla}', \quad t = (L'/U')\hat{t}, \quad \hat{u} = U' \hat{u}, \quad r = a \hat{r} \quad (5.33)$$

where $L'$ is a characteristic macroscopic length scale, and $U'$ is the characteristic air seepage velocity. Note that by the above normalization the normalized initial vapor and aqueous concentrations are always equal to unity:

$$\hat{C}'_{gi}(\hat{x}', \hat{t} = 0) = \hat{C}_{wi}(0 < \hat{r} < 1, \hat{x}', \hat{t} = 0) = 1. \quad (5.34)$$

In terms of the normalized variables, the total bulk concentration (5.22) becomes

$$\hat{C}'_{ti}(\hat{x}', \hat{t}) = (S'_o \alpha_i' + 1) \hat{C}'_{gi} + \xi_i \langle \hat{C}_{ai} \rangle \quad (i = 1, \cdots, N), \quad (5.35)$$

while the macroscale vapor transport equation (5.29) can be written as:

$$\frac{\partial}{\partial \hat{t}} \left[ (S'_o \alpha_i' + 1) \hat{C}'_{gi} \right] + \hat{\nabla}' \cdot (\hat{u} \hat{C}'_{gi}) - P e_i^{-1} \nabla'^2 \hat{C}'_{gi} = -\xi_i \frac{\partial \langle \hat{C}_{ai} \rangle}{\partial \hat{t}} \quad (i = 1, \cdots, N), \quad (5.36)$$

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where
\[ \alpha_i' \left( \hat{x}', \hat{t} \right) = \frac{M_i / C_{gi}^{sat}}{\sum_{j=1}^{N} \chi_{j0} C_{gj}^{sat} M_j / \rho_{oj}}, \]  
(5.37)
and
\[ Pe_i = \frac{L' U'}{D_{gi}}, \]  
(5.38)
\[ \xi_i = \frac{\phi \beta_i \theta_a}{H_i \theta_g}. \]  
(5.39)
Equation (5.30) now reads
\[ \sum_{i=1}^{N} \chi_{i0} C_{gi}^{'} = 1, \quad \text{for} \ S_o' > 0. \]  
(5.40)
Also the normalized free NAPL concentration is
\[ C_{x0}^{'}(\hat{x}', \hat{t}) = \alpha_i' \hat{C}_{gi}^{'}(\hat{x}', \hat{t}), \]  
(5.41)
so that \( S_o' \hat{C}_{x0} = S_o' \alpha_i' \hat{C}_{gi} \), a local storage term on the left-hand side of (5.36), is the mass of component \( i \) in free NAPL per bulk volume.

On the microscale, the normalized form of the aggregate diffusion equation is
\[ \frac{\partial}{\partial \hat{t}} \left( (S_o \alpha_i + 1) \hat{C}_{wi} \right) = \frac{\sigma_i}{\hat{r}^2} \frac{\partial}{\partial \hat{r}} \left( \hat{r}^2 \frac{\partial \hat{C}_{wi}}{\partial \hat{r}} \right) \quad (i = 1, \cdots, N), \]  
(5.42)
where
\[ \alpha_i(\hat{r}, \hat{x}', \hat{t}) = \frac{M_i / (C_{wi}^{sat} \beta_i)}{\sum_{j=1}^{N} \chi_{j0} \hat{C}_{wj} M_j / \rho_{oj}}, \]  
(5.43)
and
\[ \sigma_i = \frac{S_w D_{wi}^{sat} L'}{a^2 \beta_i U'}. \]  
(5.44)
The retardation factor \( \beta_i \) is defined in (5.14). Equation (5.16) becomes
\[ \sum_{i=1}^{N} \chi_{i0} \hat{C}_{wi} = 1, \quad \text{for} \ S_o > 0, \]  
(5.45)
while the boundary conditions (5.17) and (5.18) are

\[ \hat{r}^2 \frac{\partial \hat{C}_{wi}}{\partial \hat{r}} \bigg|_{\hat{r} \to 0} = 0, \]  

(5.46)

\[ \hat{C}_{wi}(\hat{r} = 1, \hat{x}', \hat{t}) = \hat{C}_{gi}'(\hat{x}', \hat{t}). \]  

(5.47)

Equations (5.42)–(5.47) govern \( \hat{C}_{wi}(\hat{r}, \hat{x}', \hat{t}) \) and \( S_o(\hat{r}, \hat{x}', \hat{t}) \) in terms of \( \hat{C}_{gi}'(\hat{x}', \hat{t}) \). Once solved, the normalized aggregate concentration is obtained from (5.12):

\[ \hat{C}_{ai}(\hat{r}, \hat{x}', \hat{t}) = (S_o\alpha_i + 1)\hat{C}_{wi} \quad (i = 1, \cdots, N) \]  

(5.48)

whose aggregate mean value, required to compute the source term on the right-hand side of (5.36), is calculated from

\[ \langle \hat{C}_{ai} \rangle = 3 \int_0^1 \hat{r}^2 \hat{C}_{ai} d\hat{r}. \]  

(5.49)

The normalized trapped NAPL concentration is

\[ \hat{C}_{oi}(\hat{r}, \hat{x}', \hat{t}) = \alpha_i\hat{C}_{wi}(\hat{r}, \hat{x}', \hat{t}), \]  

(5.50)

so that \( S_o\hat{C}_{oi} = S_o\alpha_i\hat{C}_{wi} \), a local storage term on the left-hand side of (5.42), is the mass of component \( i \) in trapped NAPL per aggregate volume.

The input parameters required for a solution of the present problem include the chemical properties \( C_{gi}^{sat}, C_{wi}^{sat}, M_i, \rho_{oi} \) and \( \chi_{i0} \), and four dimensionless parameters \( Pe_i, \xi_i, \sigma_i \) and \( \beta_i \). The physical significance of these dimensionless parameters is as follows. Depending on the pumping rate, \( Pe_i \) is the Péclet number for the significance of advection over diffusion in the macroscale vapor transport of component \( i \). The parameter \( \xi_i \) is a ratio of the total mass of component \( i \) in an aggregate (in the absence of trapped NAPL) to the mass of the component in macropore vapor phase under equilibrium partitioning between the two regions. Generally, a larger \( \xi_i \) corresponds to a greater fraction of the species to reside in aggregates, and gives rise to a higher retardation to the macroscale vapor transport. The parameter \( \sigma_i \) is a ratio of time
scales between the macroscopic vapor advection and the microscopic aqueous diffusion in an aggregate. It reflects the rate of mass change of a component in the immobile and the trapped phases relative to the advective transport. A higher value of $\sigma_i$ amounts to a faster response of the aggregate concentration to the vapor concentration, and vice-versa. Finally, the parameter $\beta_i$, which appears in $\alpha_i$, $\xi_i$ and $\sigma_i$, is a retardation factor to the aqueous diffusion in an aggregate due to additional partitioning in trapped vapor and sorbed phases. A higher value of $\beta_i$, because of higher $K_{di}$ for example, will result in a smaller $\sigma_i$ or slower aggregate diffusion, as well as a larger $\xi_i$ or slower macroscale vapor transport. The three parameters: $Pe_i$, $\xi_i$ and $\sigma_i$ have also appeared in the original aggregate diffusion model presented in Chapter 2. In that case, $\beta_i$ is part of $\sigma_i$ and $\xi_i$ and does not appear by itself.

Note that the influence of the initial NAPL mole fractions $\chi_{i0}$ comes into the normalized problems through the summations in (5.37), (5.40), (5.43) and (5.45), merely as weighting factors in these summations. The normalized initial conditions (5.34) no longer depend on the mole fractions of individual components. In other words, the normalized solutions depend only on the collective, but not individual, effects of the initial mole fractions. By virtue of this, it is possible for modeling purposes to use a simplified NAPL mixture consisting of a few representative components to approximate a real mixture such as gasoline which may have a large number of components. The approximation captures the essence of the problem without excessive computation, and is necessary if comprehensive measurements for all components are not available. One must, of course, choose the representative components such that each characterizes the properties (e.g., vapor pressure, Henry’s law constant) of a certain group of similar constituents in the real mixture, and has an initial mole fraction equal to the sum of those in the group. Then, individual components in the schematized mixture would represent and reflect the gross behavior of the corresponding groups of constituents in the real mixture. This kind of approximation has been adopted by, for examples, DePaoli et al. (1996) and Lingineni and Dhir (1997).
5.6 Comparison with Experiment

5.6.1 The Through-Flow Experiment and Modeling

We first compare our model with the experimental data obtained by Ostendorf et al. (1997), who measured the evaporation of gasoline and diesel fuel vapors sparged out of the field soil sample in an intact core sleeve. Steam cleaned, stainless steel sleeves were driven through, with minimum disturbance, the unsaturated zone and the contaminated capillary fringe of a weathered light petroleum spill site (Ostendorf et al., 1995a). The sleeves were mounted in series in a laboratory incubator at 12.5°C and were subjected to a flow of humidified air, which sparged hydrocarbon vapors out of the contaminated source core for subsequent degradation in the biologically active mid-depth core. Along the axis of the sleeves are a number of sampling ports, so that spatial gradients of vapor concentrations can be measured, in addition to elution concentrations at the column outlet. The set-up of their experimental apparatus is sketched in Figure 5-5.

The contaminant is a mixture of gasoline and diesel range hydrocarbons, subjected to at least 10 years of weathering in the ground. A head space analysis of the liquid phase has identified the fractions of some 27 volatile components (Ostendorf et al., 1995b). Over 80% of the 27 compounds are alkanes, ranging from 2-methylbutane to n-decane, with less than 20% aromatics, including appreciable ethylbenzene and xylene fractions (see Table 5.1). About 60% by mole fraction of NAPL compounds were not individually identified.

The experimental conditions and parameters for the source core reported by Ostendorf et al. (1997) are summarized as follows:

\[
\begin{align*}
\text{column length:} & \quad L' \quad 0.81 \text{ m,} \\
\text{air seepage velocity:} & \quad U' \quad 7.4 \times 10^{-5} \text{ m/s,} \\
\text{total porosity:} & \quad \theta \quad 0.34, \\
\text{macroporosity:} & \quad \theta_g \quad 0.11,
\end{align*}
\]
Figure 5-5: Schematic diagram of experimental apparatus used by Ostendorf et al. (1997).

initial NAPL bulk concentration: \( M_o \) 3.1 kg/m\(^3\),
organic carbon fraction: \( f_{oc} \) 0.001 kg oc/kg soil,
length of column with NAPL: \( L'_o \) 0.38 m from the bottom,
solid grain density: \( \rho_s \) 2,650 kg/m\(^3\),
average NAPL density: \( \bar{\rho}_o \) 810 kg/m\(^3\).

Note that all of the above are measured values. The column length was measured after extrusion, and the porosities were obtained gravimetrically. The initial NAPL bulk concentration, which includes both free and trapped phases, is based upon methylene chloride extracts of core samples from a borehole approximately 2 m apart from the one in which the source core was obtained. The results yield an integrated total mass of 1.19 kg/m\(^2\) over the contaminated sleeve interval \( L'_o = 0.38 \) m. The organic carbon fraction was also measured from soil samples taken from nearby boreholes. We assume that the subsoil conditions do not vary significantly over the intervals.
of these neighboring boreholes. Although Ostendorf et al. (1996) have estimated the free NAPL content to be 16.7% of the total upon calibrating a model of NAPL transport at the site, we shall find the free and trapped NAPL partitions based on the present calibrations, to be explained later. We stress that NAPL is present only along the interval \( L' \) of the column.

For the present soil aggregation model, we may further calculate the following parameters:

\[
\begin{align*}
\text{aggregate volume fraction:} & \quad \theta_a = 1 - \theta_g = 0.886, \\
\text{microporosity:} & \quad \phi = (\theta - \theta_g)/\theta_a = 0.25.
\end{align*}
\]

Also, since the core was taken near the capillary fringe, we may assume that the trapped air saturation is negligible and the water saturation in aggregates \( S_w \sim 1 \).

In the experiments, the vapor concentrations of the following seven components were measured: 2-methylpentane, 2-methylhexane, 2,2,4-trimethylpentane, 3-methylheptane, ethylbenzene, m-xylene and nonane. These compounds cover a range of vapor pressures and molecular weights and can represent the collective response of the volatile components, listed in Table 5.1, during the venting process. For modeling, we have further shortlisted the components and chosen

\[
\begin{align*}
2\text{-methylpentane } & \ C_6\text{H}_{14} , \quad 2\text{-methylhexane } C_7\text{H}_{16} , \\
3\text{-methylheptane } & \ C_8\text{H}_{18} , \quad m\text{-xylene } C_8\text{H}_{10} \quad \text{and nonane } C_9\text{H}_{20}
\end{align*}
\]

to represent groups of compounds with different ranges of vapor pressures, as given in Table 5.2. M-xylene is selected as the only aromatic in the modeling mixture. Note that 2,2,4-trimethylpentane is in the same group as 2-methylhexane. The above four selected alkane components roughly represent compounds with 6, 7, 8 and 9 carbons respectively. Their initial mole fractions are equal to the sum of the mole fractions of components being represented (given in the last column in Table 5.1). These four components have a total mole fraction of about 40%. To make up a unity
Table 5.1: Composition of the weathered fuel contaminant (Ostendorf et al., 1995b).

<table>
<thead>
<tr>
<th>component</th>
<th>molecular weight (g/mol)</th>
<th>vapor pressure (atm, 20°C)</th>
<th>mole fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylbutane</td>
<td>72.2</td>
<td>0.755</td>
<td>0.0668</td>
</tr>
<tr>
<td>pentane</td>
<td>72.2</td>
<td>0.556</td>
<td>0.0244</td>
</tr>
<tr>
<td>2-methylpentane††</td>
<td>86.2</td>
<td>0.225</td>
<td>0.995</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>86.2</td>
<td>0.201</td>
<td>0.631</td>
</tr>
<tr>
<td>hexane</td>
<td>86.2</td>
<td>0.159</td>
<td>1.25</td>
</tr>
<tr>
<td>methylcyclopentane</td>
<td>84.2</td>
<td>0.144</td>
<td>0.437</td>
</tr>
<tr>
<td>2-methylhexane††</td>
<td>100</td>
<td>0.0676</td>
<td>1.58</td>
</tr>
<tr>
<td>2,3-dimethylpentane</td>
<td>100</td>
<td>0.0711</td>
<td>1.51</td>
</tr>
<tr>
<td>3-methylhexane</td>
<td>100</td>
<td>0.0632</td>
<td>1.02</td>
</tr>
<tr>
<td>2,2,4-trimethylpentane†</td>
<td>114</td>
<td>0.0507</td>
<td>2.12</td>
</tr>
<tr>
<td>heptane</td>
<td>100</td>
<td>0.0462</td>
<td>0.57</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>98.2</td>
<td>0.0474</td>
<td>0.961</td>
</tr>
<tr>
<td>2,3,4-trimethylpentane</td>
<td>114</td>
<td>0.0273</td>
<td>1.17</td>
</tr>
<tr>
<td>2,3,3-trimethylpentane</td>
<td>114</td>
<td>0.0274</td>
<td>0.716</td>
</tr>
<tr>
<td>2,3-dimethylhexane</td>
<td>114</td>
<td>0.0234</td>
<td>2.09</td>
</tr>
<tr>
<td>2-methylheptane</td>
<td>114</td>
<td>0.0203</td>
<td>1.74</td>
</tr>
<tr>
<td>3-methylheptane††</td>
<td>114</td>
<td>0.0193</td>
<td>2.53</td>
</tr>
<tr>
<td>2,2,4-trimethylhexane</td>
<td>128</td>
<td>0.0142</td>
<td>0.613</td>
</tr>
<tr>
<td>octane</td>
<td>114</td>
<td>0.0137</td>
<td>1.79</td>
</tr>
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<td>nonane††</td>
<td>128</td>
<td>0.00405</td>
<td>1.34</td>
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<tr>
<td>decane</td>
<td>142</td>
<td>0.00129</td>
<td>1.53</td>
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<tr>
<td>ethylbenzene†</td>
<td>106</td>
<td>0.00935</td>
<td>1.11</td>
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<td>p-xylene</td>
<td>106</td>
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<tr>
<td>m-xylene††</td>
<td>106</td>
<td>0.00811</td>
<td>2.58</td>
</tr>
<tr>
<td>o-xylene</td>
<td>106</td>
<td>0.00643</td>
<td>1.62</td>
</tr>
<tr>
<td>propylbenzene</td>
<td>120</td>
<td>0.00331</td>
<td>1.05</td>
</tr>
<tr>
<td>trimethylbenzene</td>
<td>120</td>
<td>0.00208</td>
<td>8.35</td>
</tr>
</tbody>
</table>

† component whose vapor concentration was measured in the experiment;  
‡ component selected to form the hypothetical mixture for the modeling.
Table 5.2: Hypothetical mixture for modeling of the through-flow problem.

<table>
<thead>
<tr>
<th>component</th>
<th>vapor pressure of compounds being represented (atm, 20°C)</th>
<th>initial mole fraction $X_{i0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylpentane C$<em>6$H$</em>{14}$</td>
<td>$&gt; 0.1$</td>
<td>0.034</td>
</tr>
<tr>
<td>2-methylhexane C$<em>7$H$</em>{16}$</td>
<td>0.1 – 0.05</td>
<td>0.062</td>
</tr>
<tr>
<td>3-methylheptane C$<em>8$H$</em>{18}$</td>
<td>0.05 – 0.01</td>
<td>0.122</td>
</tr>
<tr>
<td>nonane C$<em>9$H$</em>{20}$</td>
<td>0.01 – 0.001 (alkanes)</td>
<td>0.029</td>
</tr>
<tr>
<td>m-xylene C$<em>8$H$</em>{10}$</td>
<td>0.01 – 0.001 (aromatics)</td>
<td>0.171</td>
</tr>
<tr>
<td>undecane C$<em>{11}$H$</em>{24}$</td>
<td>&lt; 0.001</td>
<td>0.582</td>
</tr>
</tbody>
</table>

total mole fraction, we lump all the remaining less volatile components into one heavy component, undecane C$_{11}$H$_{24}$.

Our task is to compare the spatial and temporal variations of the component vapor concentrations generated by our model based on the five-alkane, one-aromatic mixture with the measured data. For venting in such a short column, the air compressibility can be ignored and the flow can reach a steady-state readily. Equations (5.36) and (5.40) are solved for the macroscale vapor concentration and the free NAPL saturation along the column, subject to the following boundary and initial conditions:

\[
\dot{C}_g' - P e_{i}^{-1} \frac{\partial \dot{C}_g'}{\partial \hat{z}'} = 0 \quad \hat{z}' = 0, \quad t > 0, \tag{5.51}
\]

\[
\frac{\partial \dot{C}_g'}{\partial \hat{z}'} = 0 \quad \hat{z}' = 1, \quad t > 0, \tag{5.52}
\]

\[
\dot{C}_g' = 1 \quad 0 < \hat{z}' < 1, \quad t = 0, \tag{5.53}
\]

\[
S_0' = \begin{cases} 
S_{o0}' & 0 < \hat{z}' < 0.47, \\
0 & 0.47 < \hat{z}' < 1,
\end{cases} \quad t = 0, \tag{5.54}
\]

where $\hat{z}'$ is the distance from the bottom of the column, $\hat{z}' = z'/L'$ and $\hat{z}' = 0.38/0.81 = 0.47$ is the initial length of the column contaminated with NAPL. The microscale diffusion problem (5.42)–(5.47) is solved with similar initial conditions:

\[
\dot{C}_{wi} = 1 \quad 0 < \hat{r} < 1, \quad 0 < \hat{z}' < 1, \quad t = 0, \tag{5.55}
\]
\[ S_0 = \begin{cases} S_{00} & 0 < \hat{z}' < 0.47, \\ 0 & 0.47 < \hat{z}' < 1, \quad 0 < \hat{r} < 1, \quad t = 0. \end{cases} \quad (5.56) \]

Numerical solutions to the above problem are obtained using an ADI (alternate-direction-iterative) finite-difference method, which is outlined in Appendix I. To test our numerical code, we have generated results for the through-flow case presented by Ho et al. (1994). In their experiments, only NAPL which is in local equilibrium with pore air is present. Our results for the spatial and temporal changes of the component concentrations are generally in good agreement with theirs.

### 5.6.2 Estimation of Input Parameters for Modeling

Based on the above information, we now evaluate the input parameters for the modeling. We first estimate the chemical properties according to the following methods:

1. Since the mixture is composed predominantly of alkanes, the activity coefficients for all components are assumed to be unity. While this may not be true for the aromatic component, m-xylene, we shall demonstrate that this component was nevertheless subject to biodegradation in the experiment.

2. By ideal gas law, the saturated vapor concentration is

\[ C_{i}^{\text{sat}} = \frac{P_i^0 M_i}{R \Theta} \quad (5.57) \]

where \( P_i^0 \) is the vapor pressure of pure component \( i \), \( R \) is the universal gas constant, and \( \Theta \) is the absolute temperature, which is set to be 285.7 K (12.5°C) for the present case. The vapor pressure may be estimated using the boiling point \( \Theta_b \) of the chemical (Schwarzenbach et al., 1993, p. 73):

\[ \ln P_i^0 \text{ (atm)} = -(4.4 + \ln \Theta_b) \left[ 1.8(\Theta_b / \Theta - 1) - 0.8 \ln(\Theta_b / \Theta) \right]. \quad (5.58) \]

3. The solubilities \( C_{wi}^{\text{sat}} \) at 25°C for the selected components are available from Mackay and Shiu (1981), while the boiling points and liquid densities of the
components can be found from the CRC Handbook of Chemistry and Physics (CRC, 1996). We estimate the temperature effect on the solubility according to (Schwarzenbach et al., 1993, p. 91):

\[
\log C_{w}^{\text{sat}} = - \frac{\Delta H_f^c}{2.303RT} + \text{constant}, \tag{5.59}
\]

where \( \Delta H_f^c \) is the aqueous enthalpy of solution which for alkanes is in the order of -5 kJ/mol (Gill et al., 1976). Hence it can be readily calculated that the solubility changes by a negligible amount of less than 5% when the temperature drops from 25°C to 12.5°C. The Henry’s law constants are then found from the saturated vapor concentration and the solubility \( H_i = C_{sat}^{\text{sat}} / C_{wi}^{\text{sat}} \).

4. Using Millington’s formula (Millington, 1959), we estimate the effective vapor diffusivity in the pore air

\[
D_{gi} = D_{gi}^o \times \frac{\theta_s^{7/3}}{\theta^2} \tag{5.60}
\]

where \( D_{gi}^o \) is the vapor diffusivity in pure air. Using a typical value of \( 10^{-5} \text{ m}^2/\text{s} \) for \( D_{gi}^o \), we get from the above relation \( D_{gi} = 3.3 \times 10^{-7} \text{ m}^2/\text{s} \), from which the Péclet number \( Pe_i = L'U'/D_{gi} = 190 \). This value of \( Pe \), which is large enough for the dominance of advection over diffusion in the transport, is used for all components.

5. The sorption partition coefficient can be expressed as the product

\[
K_{di} = K_{omi}f_{om} \tag{5.61}
\]

where \( K_{omi} \) is the organic matter-water partition coefficient of component \( i \) and \( f_{om} \) is the mass fraction of organic matter in the soil. While \( f_{om} \) is approximately equal to two times \( f_{oc} = 0.001 \text{ kg oc/kg soil} \) (Schwarzenbach et al., 1993, p. 268), \( K_{omi} \) can be estimated from an empirical correlation with the water solubility.
(Schwarzenbach et al., 1993, p. 275):

\[
\log K_{omi} \left( \frac{\text{mol/kg om}}{\text{mol/L water}} \right) = -0.75 \log \left( \frac{C_{wi}^{\text{sat}}}{M_i} \right) \text{ (mol/L water)} + 0.44. \quad (5.62)
\]

So far, we have been able to estimate \textit{a priori} all parameters, except the initial free and trapped NAPL saturations and \( D_{wi}^* / a^2 \), which are to be found by calibration. Our strategy is to assume that for small times, only the evaporation from the most volatile component, 2-methylpentane, is significant so that the component coupling effects may be ignored in this stage. We apply the vapor transport modeling for 2-methylpentane as if it were the only evaporating component; the NAPL saturations and the fractions of other components are kept to their initial values. Also, the NAPL saturations to be found are constrained by the measured value \( M_o = 3.1 \text{ kg/m}^3 \) for the initial total NAPL bulk concentration, or

\[
S'_{o0} \bar{\rho}_o \theta_g + S_{o0} \bar{\rho}_o \phi \theta_a = 3.1 \text{ kg/m}^3. \quad (5.63)
\]

By curve fitting the measured spatial profiles of vapor concentration at two snapshots \( \hat{t} = 10 \) and 24, we have found the following calibrated values:

\[
S'_{o0} \text{ (calibrated)} = 0.01 \quad (\text{or } S_{o0} = 0.0123), \quad \sigma_1 \text{ (calibrated)} = 0.14. \quad (5.54)
\]

Because of (5.63) calibration of \( S'_{o0} \) implies \( S_{o0} \) and vice-versa, so there are only two calibrated quantities. From \( \sigma_1 \), we may calculate for 2-methylpentane, using (5.44) and (5.14) where \( \beta_1 = 31, \)

\[
D_{wi}^* / a^2 = 4 \times 10^{-4} \text{ s}^{-1}. \quad (5.65)
\]

To estimate the values of \( \sigma_i \) for other components, we adjust the value \( D_{wi}^* \) by assuming that it is inversely proportional to the square root of the molecular weight (Schwarzenbach et al. 1993, p. 200).
From $S_{o0}'$ and $S_{o0}$, we calculate that the initial free and trapped NAPL concentrations are respectively

$$S_{o0}' \bar{p}_o \theta_g = 0.9 \text{ kg/m}^3, \quad S_{o0} \bar{p}_o \phi \theta_a = 2.2 \text{ kg/m}^3. \quad (5.66)$$

Hence approximately 30% of the NAPL is in the free phase, which is roughly twice the calibrated value obtained by Ostendorf et al. (1996).

We may also use the value in (5.65) to estimate the order of the aggregate size. If Millington's formula is assumed to be also applicable to microporous media, and with a typical value of $D_w \sim 10^{-9} \text{ m}^2/\text{s}$ for solute diffusion in pure water, we may find that $D_w^* \sim D_w \phi^{1/3} \sim 6.5 \times 10^{-10} \text{ m}^2/\text{s}$. Hence, from (5.65),

$$a \sim 1.3 \text{ mm}, \quad (5.67)$$

which is close to the estimation of 1.4 mm by Ostendorf et al. (1997).

For easy reference, we summarize in Table 5.3 the values of chemical properties and input parameters used for the modeling of the through-flow problem.

### 5.6.3 Results of Comparison

Using the parameters given in Table 5.3, we perform a simulation of the five-alkane, one-aromatic vapor transport under the experimental conditions. It should be emphasized that the theoretical prediction is based upon rather limited calibration; just two parameters are calibrated based on concentration profiles of one component at two instants. Most of the parameters are either measured or estimated independently. Figures 5-6, 5-7, 5-8, 5-9 and 5-10 show the comparisons of the spatial profiles at six snap-shots of the normalized vapor concentration for 2-methylpentane, 2-methylhexane, 3-methylheptane, nonane and m-xylene respectively. The data points have been normalized with respect to the corresponding initial average concentrations. Only the profiles of 2-methylpentane at the first two snap-shots ($\hat{t} = 10, 24$) have been obtained by calibration; the others are entirely prediction based on the estimated pa-
Table 5.3: Chemical properties and parameters at 12.5°C for modeling of the through-flow problem.

<table>
<thead>
<tr>
<th>component</th>
<th>2-methylpentane</th>
<th>2-methylhexane</th>
<th>3-methylheptane</th>
<th>nonane</th>
<th>m-xylene</th>
<th>undecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>$M_i$, g/mol</td>
<td>86.18</td>
<td>100.23</td>
<td>114.23</td>
<td>128.3</td>
<td>106.2</td>
<td>156.31</td>
</tr>
<tr>
<td>$P_i^0$, atm</td>
<td>0.1634</td>
<td>0.0473</td>
<td>0.0132</td>
<td>0.0030</td>
<td>0.0052</td>
<td>0.0003</td>
</tr>
<tr>
<td>$C_{sat}$, kg/m³</td>
<td>1.4 x 10⁻²</td>
<td>2.5 x 10⁻³</td>
<td>7.9 x 10⁻⁴</td>
<td>1.5 x 10⁻⁴</td>
<td>0.16</td>
<td>4.4 x 10⁻⁵</td>
</tr>
<tr>
<td>$C_{gi}$, kg/m³</td>
<td>0.601</td>
<td>0.202</td>
<td>0.064</td>
<td>0.016</td>
<td>0.024</td>
<td>0.002</td>
</tr>
<tr>
<td>$\rho_{oi}$, kg/m³</td>
<td>653</td>
<td>679</td>
<td>706</td>
<td>718</td>
<td>864</td>
<td>740</td>
</tr>
<tr>
<td>$H_i$</td>
<td>43</td>
<td>80</td>
<td>81</td>
<td>110</td>
<td>0.15</td>
<td>50</td>
</tr>
<tr>
<td>$K_{omi}$, L/kg</td>
<td>1.9 x 10³</td>
<td>7.8 x 10³</td>
<td>2.0 x 10⁴</td>
<td>7.8 x 10⁴</td>
<td>360</td>
<td>2.2 x 10⁵</td>
</tr>
<tr>
<td>$K_{di}$, L/kg</td>
<td>4</td>
<td>16</td>
<td>41</td>
<td>155</td>
<td>0.7</td>
<td>448</td>
</tr>
<tr>
<td>$D_{wi}/d_{i}^2$, s⁻¹</td>
<td>4 x 10⁻⁴</td>
<td>3.7 x 10⁻⁴</td>
<td>3.5 x 10⁻⁴</td>
<td>3.3 x 10⁻⁴</td>
<td>3.6 x 10⁻⁴</td>
<td>3 x 10⁻⁴</td>
</tr>
<tr>
<td>$P_{ci}$</td>
<td>190</td>
<td>190</td>
<td>190</td>
<td>190</td>
<td>190</td>
<td>190</td>
</tr>
<tr>
<td>$\beta_i$</td>
<td>31</td>
<td>124</td>
<td>325</td>
<td>1235</td>
<td>7</td>
<td>3560</td>
</tr>
<tr>
<td>$\xi_i$</td>
<td>1.4</td>
<td>3.0</td>
<td>7.8</td>
<td>21.9</td>
<td>88</td>
<td>139</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>0.14</td>
<td>3.3 x 10⁻²</td>
<td>1.2 x 10⁻²</td>
<td>2.9 x 10⁻³</td>
<td>0.58</td>
<td>9 x 10⁻⁴</td>
</tr>
<tr>
<td>$x_{i0}$</td>
<td>0.034</td>
<td>0.062</td>
<td>0.122</td>
<td>0.029</td>
<td>0.171</td>
<td>0.582</td>
</tr>
</tbody>
</table>

Parameters. Note that the flow is moving upward and $\xi' = 1$ is the downgradient exit.

From these plots, we may make the following observations:

1. In each case shown in Figures 5-6-5-9, there is a good agreement between the prediction and the data. Obviously the agreement is better for the two lighter components: 2-methylpentane and 2-methylhexane. Some minor discrepancies which occur at larger times for the heavier components, 3-methylheptane and nonane (Figures 5-8e-f, 5-9e-f), can be ascribed to the fact that our schematized mixture may not have enough low volatility components to properly reflect their responses which become dominant in the long term. In this case, all low volatility compounds (vapor pressure less than 0.001 atm) are lumped into a single component, undecane.

2. Since 2,2,4-trimethylpentane has close properties with 2-methylhexane, we include in Figure 5-7 the data points (crosses) for this component as well. Clearly when normalized the two sets of data are indeed very close to each other. This
supports the use of a component to represent similar compounds in the modeling.

3. Recall that initially the NAPL saturation drops abruptly to zero at $z' = 0.47$. At this NAPL front, a discontinuity of the vapor concentration gradient happens to all components, sooner for a lighter component. Such a gradient change appears to be confirmed by the data.

4. While the vapor concentration of the most volatile component, 2-methylpentane, decreases monotonically with time (Figure 5-6), that of nonane, except near the upstream end, rises with time so that it is greater than the initial value even at a very large time (Figure 5-9). Moreover, the predicted profiles of nonane at $\hat{t} = 10 - 55$, supported by the data, feature a local maximum which moves slowly downgradient (Figure 5-9). Such a rise of vapor concentration with time and a local maximum in the vapor concentration distribution of a heavy component are the distinctive features of a multicomponent transport. We shall further discuss and explain these features in the next problem.

5. Figure 5-10 indicates a discrepancy between predicted and measured profiles for the aromatic component, m-xylene. While the predicted profiles remain essentially uniform above the NAPL source, the measured profiles decrease. We attribute the decrease to aerobic biodegradation, suppressed by toxicity of NAPL in the lower region of the sleeve, but active in the region above. The conclusion is further supported by aerobic microcosms taken from the site (Ostendorf et al., 1997). These microcosms were dosed with a blend of hydrocarbon vapors, including m-xylene and ethylbenzene. Figure 5-11 shows typical chromatograms on Day 1 and Day 14 after dosing. Note the appearance of ethylbenzene and m-xylene peaks on day 1 chromatogram in the headspace of the microcosm vial containing site soil and microorganisms, as dosed with a blend of alkanes and aromatics. Two weeks later, the aromatics are gone, while the alkanes (2-methylhexane, etc) remain. We attribute the loss to biodegradation, since all compounds have roughly similar volatilities, and abiotic control soil (bugs killed
in microcosm) exhibited no loss of aromatics over the same period.

Figure 5-12 shows the comparison of the predicted elution curves with the data for the four alkane components. For comparison, the data for 2,2,4-trimethylpentane (crosses) are also shown in the case for 2-methylhexane. Again, the close agreement in each case is demonstrated. The traits of these curves clearly reflect the volatility of the chemicals. For the most volatile component, 2-methylpentane, the evaporation takes place the fastest and the effluent concentration drops monotonically with time. For each of the medium volatile components, 2-methylhexane and 3-methylheptane, the elution is slower and the effluent concentration drops only after a brief rise with time. The gradual diminishing of the effluent concentration, or tailing, in each of these curves is strong evidence of non-equilibrium phase exchange in the course of vapor transport. It is also seen that the two sets of data for 2-methylhexane and 2,2,4-trimethylpentane fall very close to each other. For the less volatile component, nonane, the effluent concentration rises gradually and drops only when it reaches 26% higher than the initial value. The nonane effluent concentration remains above the initial value until after a long time of venting.

Thus far, we have shown the agreement between modeling prediction based on just two calibrated parameters and experimental data, and pointed out some of the features of a multicomponent transport. We shall further examine and explain these features in details, including changes to the NAPL saturations and microscopic mass transfer, when we study the next problem of simulating a hypothetical case of venting in a radial flow.

5.7 Simulation of a Hypothetical Venting Problem

5.7.1 Axi-symmetrical Problem

For further illustration, we apply the present model to simulate a hypothetical problem of air venting in a horizontal soil layer with radial symmetry (Figure 5-13). The
Figure 5-6: Comparison between computed (line) and measured (dots) vapor concentrations $\hat{C}_g'$ as a function of $\hat{z}'$ and $\hat{t}$ for 2-methylpentane.
Figure 5-7: Comparison between computed (line) and measured (dots) vapor concentrations $\hat{C}_g$ as a function of $\hat{z}'$ and $\hat{t}$ for 2-methylhexane. The data, denoted by crosses, for 2,2,4-trimethylpentane are included for the comparison.
Figure 5-8: Comparison between computed (line) and measured (dots) vapor concentrations $\hat{C}_g'$ as a function of $\hat{z}'$ and $\hat{t}$ for 3-methylheptane.
Figure 5-9: Comparison between computed (line) and measured (dots) vapor concentrations $C'_{g}$ as a function of $z'$ and $\hat{t}$ for nonane.
Figure 5-10: Comparison between computed (line) and measured (dots) vapor concentrations $\hat{C}_g'$ as a function of $\hat{z}'$ and $\hat{t}$ for m-xylene.
Figure 5-11: Typical chromatograms on Days 1 and 14 from GC/FID analysis of the headspace of a microcosm vial containing site soil and microorganisms, as dosed with a blend of alkanes and aromatics.
Figure 5-12: Comparison between computed (line) and measured (squares) effluent vapor concentrations \( \hat{C}_g \) at \( \hat{z} = 1 \) as a function of \( \hat{t} \) for (a) 2-methylpentane, (b) 2-methylhexane, (c) 3-methylheptane and (d) nonane. The data, denoted by crosses, for 2,2,4-trimethylpentane are included in (b) for the comparison.
Figure 5-13: Schematic diagram of an axi-symmetrical vadose zone with impermeable top and bottom boundaries. Residual NAPL is initially released to the cylindrical region \( r' < r'_o \), and the fully-penetrating well has a screen radius \( r' = r'_w \).

unsaturated layer, confined by impermeable top and bottom boundaries, is composed of abiotic, homogeneous and isotropic soil. Throughout the layer, the water saturation is at the residual level so that the macropore air is the only mobile phase. To simplify the computations, an idealized initial contaminant distribution is assumed. At the instant \( t = 0 \), a residual amount of NAPL composed of benzene, toluene and o-xylene is uniformly released into a cylindrical column of soil \( (r' \leq r'_s) \) where a fraction of the NAPL is trapped evenly in the aggregates while the rest remains in the macropores as free phase. As NAPL continues to evaporate and dissolve locally, the macropore vapor diffuses outward to further contaminate the rest of the layer. At \( t = T > 0 \) a vacuum well of radius \( r'_w \) is installed at the center of the column to withdraw air together with vapor from the soil. The pumping goes on until the maximum total concentrations of the components drop to a certain level. The problem is to study the effects of the NAPL, trapped and free, on the multicomponent vapor transport before and during pumping, as a function of \( r' \) and \( t \).

Among the three components benzene is the lightest compound, has the largest vapor pressure and is the most volatile, while o-xylene is the heaviest and the least volatile. Aromatic constituents, because of their relatively high aqueous partitions,
<table>
<thead>
<tr>
<th>NAPL components</th>
<th>relative volatility</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>high</td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
</tr>
<tr>
<td>toluene</td>
<td>medium</td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
</tr>
<tr>
<td>o-xylene</td>
<td>low</td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5-14: Molecular structures of benzene, toluene, and o-xylene.

can completely define the groundwater contaminating potential of a hydrocarbon (Baehr, 1987). Total concentrations of benzene, toluene and xylene, collectively referred to as BTX, are often required by regulations to be measured to determine the contamination level of a site. All these three chemicals are spreading organics (Demond and Lindner, 1993; Wilkins et al., 1995).

For this problem we use the diameter of the initial region of contamination as the characteristic macro length scale and define the normalized variables according to:

$$\hat{r}' = \frac{r'}{L'}, \quad \hat{u}' = \frac{u'}{U'}, \quad \hat{p}' = \frac{p'}{P_a}, \quad \hat{t} = \frac{tU'}{L'}$$

(5.68)

where \(L' = 2r_0\), \(U' = kP_a/(\theta_gL')\), \(k\) is the soil permeability divided by the air dynamic viscosity, \(p'\) is the soil air pressure, and \(P_a\) is the atmospheric pressure. Assuming air as an ideal gas, the unsteady air flow equations for \(\hat{r}' > \hat{r}'_w, \hat{t} > \hat{T}\) are

$$\frac{\partial \hat{p}'}{\partial \hat{t}} - \frac{1}{\hat{r}'^2} \frac{\partial}{\partial \hat{r}'} \left( \hat{r}' \hat{p}' \frac{\partial \hat{p}'}{\partial \hat{r}'} \right) = 0,$$

(5.69)
\[ \dot{u}' = -\frac{\partial \hat{p}'}{\partial \hat{r}'}, \]  

(5.70)

with the boundary conditions

\[ \hat{p}' = \hat{p}'_w, \quad \hat{r}' = \hat{r}'_w, \]  

(5.71)

\[ \hat{p}' = 1, \quad \hat{r}' \to \infty, \]  

(5.72)

and the initial static condition

\[ \hat{p}' = 1 \quad \hat{r}'_w < \hat{r}' < \infty, \quad \hat{t} = \hat{T}, \]  

(5.73)

where \( \hat{p}'_w = p'_w/P_a \) is the normalized well pressure, and \( \hat{T} = T U'/L' \) is the normalized period of contamination before air venting.

The macroscale vapor transport is governed by (5.36), in cylindrical radial coordinate, and (5.40), together with the following boundary and initial conditions:

\[ \frac{\partial \hat{C}'_{gi}}{\partial \hat{r}'} = 0 \quad \hat{r}' = \hat{r}'_w, \quad \hat{t} > 0, \]  

(5.74)

\[ \hat{C}'_{gi} = 0 \quad \hat{r}' \to \infty, \quad \hat{t} > 0, \]  

(5.75)

\[ (\hat{C}'_{gi}, S'_o) = \begin{cases} (1, S'_o) & 0 < \hat{r}' < 0.5, \quad \hat{t} = 0, \\ (0, 0) & \hat{r}' > 0.5, \end{cases} \]  

(5.76)

where \( S'_o \) is the initial saturation of free NAPL in macropores. The microscale aqueous diffusion is solved from (5.42)-(5.47), and the following initial conditions:

\[ (\hat{C}'_{wi}, S_o) = \begin{cases} (1, S_o) & 0 < \hat{r}' < 0.5, \quad 0 < \hat{r} < 1, \quad \hat{t} = 0, \\ (0, 0) & \hat{r}' > 0.5, \end{cases} \]  

(5.77)

where \( S_o \) is the initial saturation of trapped NAPL in micropores. The above problems are solved using a similar numerical method as that for the through-flow problem in §5.6. The steps of the method are outlined in Appendix I.

To separate the effects of trapped and free NAPL, we shall consider two different
### Table 5.4: Chemical properties and parameters at 20°C for modeling of the radial flow problem.

<table>
<thead>
<tr>
<th>component</th>
<th>benzene</th>
<th>toluene</th>
<th>o-xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_i ) (g/mol)</td>
<td>78.11</td>
<td>92.14</td>
<td>106.17</td>
</tr>
<tr>
<td>( C_{sat}^{ui} ) (kg/m³)</td>
<td>1.34</td>
<td>0.40</td>
<td>0.13</td>
</tr>
<tr>
<td>( C_{sat}^{gi} ) (kg/m³)</td>
<td>0.32</td>
<td>0.11</td>
<td>0.029</td>
</tr>
<tr>
<td>( \rho_{oi} ) (kg/m³)</td>
<td>876</td>
<td>865</td>
<td>876</td>
</tr>
<tr>
<td>( H_i )</td>
<td>0.24</td>
<td>0.28</td>
<td>0.22</td>
</tr>
<tr>
<td>( K_{omi} ) (L_{water}/kg_{om})</td>
<td>47</td>
<td>134</td>
<td>336</td>
</tr>
<tr>
<td>( K_{di} ) (L_{water}/kg_{solid})</td>
<td>0.235</td>
<td>0.67</td>
<td>1.68</td>
</tr>
<tr>
<td>( D_{gi}^c ) (m²/s)</td>
<td>8.8 \times 10^{-6}</td>
<td>7.9 \times 10^{-6}</td>
<td>7.2 \times 10^{-6}</td>
</tr>
<tr>
<td>( D_{gi} ) (m²/s)</td>
<td>2 \times 10^{-6}</td>
<td>1.8 \times 10^{-6}</td>
<td>1.7 \times 10^{-6}</td>
</tr>
<tr>
<td>( D_{wi}^* / a^2 ) (s⁻¹)</td>
<td>1 \times 10^{-7}</td>
<td>9.2 \times 10^{-8}</td>
<td>8.6 \times 10^{-8}</td>
</tr>
<tr>
<td>( P_{ei} )</td>
<td>100</td>
<td>110</td>
<td>121</td>
</tr>
<tr>
<td>( \beta_i )</td>
<td>2.22</td>
<td>4.94</td>
<td>11.17</td>
</tr>
<tr>
<td>( \xi_i ) (Case I)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( \xi_i ) (Case II)</td>
<td>6.48</td>
<td>12.35</td>
<td>35.53</td>
</tr>
<tr>
<td>( \sigma_i )</td>
<td>0.0157</td>
<td>0.0065</td>
<td>0.0027</td>
</tr>
<tr>
<td>( \chi_{ii0} )</td>
<td>0.3333</td>
<td>0.3333</td>
<td>0.3333</td>
</tr>
</tbody>
</table>

There are two types of soil to facilitate comparison:

- **Case I:** non-aggregated soil with \( \phi = 0.0 \),
- **Case II:** aggregated soil with \( \phi = 0.3 \) and \( S_{\alpha\phi} = 0.01 \).

Case I is a special limit where the aggregates reduce to solid grains. There is no immobile water or trapped NAPL and each grain is covered by a free NAPL film which is in turn surrounded by vapor in macropore. The source term on the right-hand side of (5.36) vanishes, and the aggregate diffusion problem can be ignored. A similar local equilibrium problem, but with a unidirectional through-flow in a short column, has been studied by Ho *et al.* (1994). In Case II there are trapped and immobile phases in the aggregates. For easy reference we summarize in Table 5.4 the chemical properties and other input parameters to be used in the computations. Their values are obtained as follows. The three aromatic components in the NAPL mixture
are, in the order of increasing molecular weight or decreasing vapor pressure, benzene, toluene and o-xylene, of which the properties are readily found in the literature (e.g., Perry and Green, 1984). As these compounds have similar molecular structures, their activity coefficients can be taken to be unity. The following parameters are chosen for all computations:

\[
\hat{p}_w' = 0.5, \quad \hat{r}_w' = 0.05, \quad r_o' = 5 \text{ m}, \quad \theta_g = 0.3, \quad S_w = 0.7, \quad S_{o0}' = 0.01,
\]

\[
\hat{T} = 100, \quad \rho_s = 2.65 \text{ kg/L}, \quad f_{om} = 0.005, \quad k = 6 \times 10^{-10} \text{ m}^2/\text{Pa.s}.
\]

The fraction of organic matter, \(f_{om}\), is required to calculate the sorption partition coefficient \(K_{di} = K_{omi} f_{om}\) where \(K_{omi}\) is the organic matter-water partition coefficient which can be estimated with the chemical’s water solubility (Schwarzenbach et al., 1993, p. 274). Adopting Millington formula (Millington, 1959), the effective gas diffusivity can be estimated from

\[
D_{g_i} = D_{g_i}^\circ \frac{\theta_g^{7/3}}{(\theta_g + \phi \theta_a)^2} = 0.23 D_{g_i}^\circ
\]

where \(D_{g_i}^\circ\) is the diffusivity of the component vapor in pure air. For the present three components, the values of \(D_{g_i}^\circ\) are obtainable from Fuller et al. (1965). For the aqueous diffusivities, we first assume that \(D_{w1}^*/a^2\) is equal to \(10^{-7} \text{ s}^{-1}\). Then \(D_{w2}^*/a^2\) and \(D_{w3}^*/a^2\) are estimated by assuming that the diffusion coefficient is inversely proportional the square of the molecular weight. Having established the values of these site and material properties, the dimensionless parameters \(Pe_i, \beta_i, \xi_i\) and \(\sigma_i\) can then be computed accordingly. Finally an initial NAPL composition of equal mole fractions \((\chi_{10} = \chi_{20} = \chi_{30} = 1/3)\) of the three components is assumed.

From the above parameters, we can also estimate from (5.68) that \(L' = 10 \text{ m}, U' = 2 \times 10^{-5} \text{ m/s}\), and therefore the time scale for the macroscale vapor transport is \(L'/U' = 5 \times 10^5 \text{ sec} \sim 6 \text{ days}\). The contamination period prior to pumping is \(\hat{T} = 100\) which roughly corresponds to a period of 1.5 years.
Figure 5-15: Macro-spatial and temporal variations of the three component vapor concentrations $\chi_{i0} \hat{C}_{gi}$ for Case I. The dashes denote the initial distributions.

5.7.2 Case I: Non-aggregated Soil with Free NAPL Only

We first consider the case of non-aggregated soil (i.e., no micropores or trapped phases), with a view to studying the effects of free NAPL alone on the vapor transport in a radial flow field. The vapor concentrations $\chi_{i0} \hat{C}_{gi}''$ and the total bulk concentrations $\chi_{i0} \hat{C}_{ti}$ for the three components are plotted respectively in Figures 5-15 and 5-16 as functions of $\tilde{r}'$ and $\hat{t}$. The initial distributions are shown by the dashed lines which are discontinuous at the outer edge $\tilde{r}' = 0.5$. Subsequent profiles of $\hat{C}_{ti}'$ are also discontinuous at this location because free NAPL saturation drops abruptly there. In the period $0 < \hat{t} < 100$, there is no air flow and the vapors diffuse radially outward. From $\hat{t} = 100$ onward, air flow is induced by a suction well at the center with a screen radius $\tilde{r}'_w = 0.05$. From these plots, the following observations can be made:
Figure 5-16: Macro-spatial and temporal variations of the three component total concentrations $x_{10} \hat{C}_{t1}$ for Case I. The dashes denote the initial distributions.
1. As expected, the clean-up time is longer for a less volatile component. While benzene is mostly removed at $\hat{t} = 150$, toluene is not purged until after $\hat{t} = 175$ and o-xylene is still abundant at $\hat{t} = 225$.

2. The three components exhibit different spatial and temporal variations of vapor concentration (Figure 5-15). The benzene and the toluene vapor concentrations have smooth spatial distributions at all times. The benzene vapor concentration decreases monotonically with time, while over much of the spill site the toluene vapor concentration rises briefly before decaying. Meanwhile, the o-xylene vapor concentration profiles exhibit two local sharp peaks which rise while moving towards each other. Concentrations between the two peaks increase with time until they approach unity which corresponds to the vapor concentration in equilibrium with pure o-xylene liquid. The above behavior can be more readily understood if we also examine the spatial and temporal variations of the free NAPL saturation $S'_0$ as shown in Figure 5-17. Clearly the region between the two peaks correspond to where the NAPL saturation is non-zero. The NAPL has two evaporation fronts: one near the well (the near front) where the flow velocity is higher, and the other at the upstream (the far front) which is blown with clean air drawn from afar. As long as the local NAPL saturation is non-zero, the normalized vapor concentrations are given by the mole fractions of the components in the NAPL, the sum of which is fixed to be unity. Each component is however evaporated at a different rate determined by its volatility. When the lightest component is being removed from the NAPL, its mole fraction drops while those of the others increase. This explains the momentary increase of the toluene vapor concentration before benzene is largely volatilized. Eventually when toluene is also volatilized, the o-xylene vapor concentration becomes unity and the NAPL becomes virtually a pure liquid phase of o-xylene. This so-called "selective evaporation" always happens to a greater extent at the two fronts. In particular, the NAPL at the far front is always the most concentrated in o-xylene in the course of venting. All the NAPL has become
Figure 5-17: Macro-spatial and temporal variations of the free NAPL saturation $S'_o$ for Case I. The dashes denote the initial distribution.

virtually pure o-xylene at $\hat{t} = 200$ when its maximum saturation is reduced to 40% of the initial value. The maximum o-xylene vapor concentration is then close to unity until the whole distribution drops rapidly to zero soon after the NAPL is completely wiped out at about $\hat{t} = 250$. These component interaction effects are qualitatively consistent with our earlier observations when studying the through-flow problem. Evaporation fronts of individual components were also found in the column tests by Ho et al. (1994).

3. The sharp change in gradient across the two fronts in the o-xylene vapor concentration distributions is related to the abrupt vanishing of NAPL saturation at these two locations and does not suggest numerical inaccuracy. To check this point, a simple local analysis can be carried out as follows. Suppose near the far front the NAPL saturation profile can be approximated by a jump

$$S'_o(\hat{r'}, \hat{t}) \sim S'_{o^-} H[\hat{r}'_c(\hat{t}) - \hat{r}']$$  (5.79)

where $S'_{o^-}$ is the jump value, $H$ is the Heaviside step function and $\hat{r}'_c(\hat{t})$ is the current position of the front. On substituting (5.79) into (5.36) which is then
integrated with respect to \( \hat{r}' \) across the discontinuity at \( \hat{r}' = \hat{r}_c' \), we can obtain

\[
\frac{d\hat{r}_c'}{dt} = \left. \frac{\partial \hat{C}_{gi}'}{\partial \hat{r}'} \right|_{\hat{r}'=\hat{r}_c'} \left( Pe_i S_o' - \alpha_i' \hat{C}_{gi}' \right)^{-1} \quad \text{at} \quad \hat{r}' = \hat{r}_c'.
\] (5.80)

Clearly the receding speed of the evaporation front is directly proportional to the change in vapor concentration gradient across the front. To verify the above relationship, we have compared the speed of the front obtained by numerically keeping track of the position of the front as a function of time, and that computed from the theoretical relation (5.80) directly. The two results are in good agreement as shown in Figure 5-18. Some minor discrepancy can be ascribed to the fact that the NAPL front is not perfectly described by a jump, especially in the final stage of volatilization. This plot also indicates that the front is moving at an almost steady speed until it suddenly speeds up tremendously just before the NAPL is completely evaporated.

4. The total concentration \( \hat{C}_{ti} \) (i.e., mass of component \( i \) in all phases per bulk volume) is dominated by the mass of free NAPL per bulk volume; it becomes relatively small when the free NAPL is volatilized (Figure 5-16). For benzene and toluene, the smooth distributions of the total concentrations decrease monotonically as pumping continues. However for o-xylene the total concentration, or free NAPL bulk concentration, immediately downstream of the far front (the peak) rises to be higher than the initial value for most of the time (see \( \hat{t} = 100-200 \) curves for o-xylene in Figure 5-16). Since NAPL is an immobile phase, any local increase in mass of NAPL can only be brought about by “condensation” of vapor phase. The rationale for the condensation of o-xylene vapor into NAPL can be explained as follows. At the far front, the o-xylene vapor concentration is always the maximum and therefore has a positive downstream gradient (see the o-xylene curves in Figure 5-15). Advection of vapor towards the well causes a net increase of vapor concentration in downstream pores already filled with o-xylene vapor in equilibrium with the liquid phase.
Figure 5-18: The moving speed of the far evaporation front as a function of time. Solid line denotes the speed calculated by keeping track of the movement of the front; squares denote the speed calculated from the jump relation (5.80).
The phase equilibrium between vapor and NAPL can be restored only after the extra amount of vapor is condensed into liquid to give a higher mole fraction of o-xylene in the NAPL mixture. The condensation process stops only when the positive vapor concentration gradient diminishes. Such condensation of heavier components downstream cf an evaporation front was also observed in the column experiments by Ho et al. (1994).

5.7.3 Case II: Aggregated Soil with Trapped NAPL

In this case we focus on the additional effects of immobile water and trapped NAPL in an aggregated soil. Let us first examine the macroscopic transport behavior.

Macroscale Variations

The vapor concentrations \( \chi_{10} \hat{C}_{gi} \) and the total bulk concentrations \( \chi_{10} \hat{C}_{ti} \) for the three components, and the NAPL saturations for free and trapped phases are plotted respectively in Figures 5-19, 5-20 and 5-23 as functions of \( \hat{r}' \) and \( \hat{t} \). Again, the initial distributions are shown by the dashed lines which are discontinuous at the outer edge \( \hat{r}' = 0.5 \). Subsequent profiles of \( \hat{C}_{ti} \) and \( \langle \hat{C}_{ai} \rangle \) are also discontinuous at this location because the NAPL saturations drop abruptly there. Features from these plots can be summarized as below:

1. The pumping time required to clean up each component is prolonged by the presence of the immobile and trapped phases. As compared to Case I, the clean-up time lengthens more for heavier components, ranging from two times for benzene to over three times for o-xylene (see Figure 5-19).

2. As in Case I, the o-xylene vapor concentration exhibits an increase with time, approaching unity, in the free NAPL region (where the free NAPL saturation is non-zero). However the vapor concentration drops more slowly than Case I after the free NAPL at that position is volatilized. This is because even in the absence of free NAPL the aggregates are still producing vapor into the macropores. As a result, the o-xylene vapor concentration decays only gradually.
Figure 5-19: Macro-spatial and temporal variations of the three component vapor concentrations $\chi_{i0} \hat{C}_{gi}$ for Case II. The dashes denote the initial distributions.
Figure 5-20: Macro-spatial and temporal variations of the three component total concentrations $\chi_{i0} \hat{C}_t^i$ for Case II. The dashes denote the initial distributions. The profiles for $\hat{\tau} > 0.5$ diminish monotonically from $\hat{t} = 100$ onward.
with a smooth profile after the free NAPL is completely volatilized (see Figure 5-19 for \( t > 300 \)).

3. The total concentration is dominated by the mass of free NAPL and the mass in aggregates per bulk volume. As in Case I but at a slower rate, the total concentrations of benzene and toluene decrease monotonically with time while that of o-xylene features an increase as the peak vapor concentration is being advected downstream (see Figure 5-20). Such increase in total concentration is again caused by a net influx of vapor associated with a positive concentration gradient. In this case, the additional mass is partly condensed to free NAPL (as the peaks on the o-xylene curves \( t = 100-250 \) in Figure 5-21 are higher than the initial value), and partly transferred into storage in aggregates (as the top parts of the o-xylene curves \( t = 100-300 \) in Figure 5-22 are higher than the initial value). See also the next paragraph for a microscopic reasoning. The free NAPL region is distinguishable, being the more concave part in an o-xylene total concentration profile (compare the o-xylene concentration profiles in Figures 5-20 and 5-21 and the free NAPL saturation distributions in Figure 5-23a). Again, the total concentration decays slowly and its distribution becomes smooth after the free NAPL is completely volatilized (see Figure 5-20).

4. In the presence of aggregates, the volatilization of the free NAPL is retarded, by a factor over 30% in this example. The free NAPL \( S'_o \) has two abrupt evaporation fronts, and is completely volatilized much sooner than the trapped NAPL (see Figure 5-23a). In the presence of free NAPL, the mean trapped NAPL saturation \( \langle S_o \rangle \) has an approximately uniform distribution which drops slower than where the free NAPL is gone (see Figure 5-23b). However the trapped NAPL saturation is not completely purged even long after the free NAPL has vanished (see the next paragraph).
Figure 5-21: Macro-spatial and temporal variations of the three component free NAPL bulk concentrations $\chi_{i0}S'_o\hat{C}'_{oi}$ for Case II. The dashes denote the initial distributions.
Figure 5-22: Macro-spatial and temporal variations of the three component mean aggregate concentrations (total mass in trapped NAPL, aqueous and sorbed phases over an aggregate volume) $\chi_{i0}(\tilde{C}_{ai})$ for Case II. The dashes denote the initial distributions. The profiles for $\tau' > 0.5$ diminish monotonically from $t = 100$ onward.
Figure 5-23: Macro-spatial and temporal variations of (a) the free NAPL saturation $S'_o$ and (b) the mean trapped NAPL saturation $\langle S_o \rangle$ for Case II. The dashes denote the initial distributions.
Microscale Variations

To gain further insight, it is also of interest to examine how mass transfer of each component takes place within an aggregate. Figures 5-24 and 5-25 show respectively the microscopic distributions of the aqueous concentrations and the trapped NAPL saturation in an aggregate at the macroscale position \( \hat{r}' = 0.25 \) (i.e., in the middle of the spill zone). For benzene, the aqueous concentration decreases monotonically with time, implying a constant depletion of this most volatile component from the aggregate. Toluene is first fed into and then removed from the aggregate, in response to the increase and then decrease in macropore vapor concentration here. The feeding of o-xylene into the aggregate lasts even longer and results in a more pronounced increase in the o-xylene aqueous concentration. Therefore while the lighter components are being removed from the aggregate, more of the heaviest component is being stored in the aggregate (the macro-spatial increase in the aggregate storage of o-xylene where free NAPL is present is clearly shown in Figure 5-22). This trend stops only when the macropore o-xylene vapor concentration begins to drop, or when the free NAPL saturation at this macroscale position vanishes. This happens around \( \hat{t} = 300 \) for \( \hat{r}' = 0.25 \) (see Figures 5-21 and 5-23a). After this moment, the trapped NAPL saturation profile exhibits a front which retreats as NAPL dissolution goes on (Figure 5-25). The o-xylene aqueous concentration has a discontinuous gradient across this front. In the outer region o-xylene diffuses outward, while in the inner region the o-xylene aqueous concentration continues to rise to approach unity, as the trapped NAPL becomes purer in o-xylene (Figure 5-24). Note that the trapped NAPL is not completely removed even at a large time; its rate of disappearance decreases as it is more confined to the center of the aggregate (Figure 5-25). The NAPL trapped at the core of an aggregate requires a very long time to be removed.

For comparison, we also show the microscopic distributions of aqueous concentration and trapped NAPL saturation in Figures (5-26)–(5-27) for the macroscale position \( \hat{r}' = 0.5 \) (outer boundary of the spill site), and in Figures (5-28)–(5-29) for the macroscale position \( \hat{r}' = 0.5 \) (adjacent to the well). For concentrations of the two
Figure 5-24: Micro-spatial and temporal variations of the component aqueous concentrations $\chi_{i0}\hat{C}_{wi}$, at the macro-position $\hat{r}' = 0.25$ (middle of spill site), for Case II. The dashes denote the initial distributions.

For more volatile components, benzene and toluene, the variations are qualitatively the same as in the macroscale position $\hat{r}' = 0.25$. However for the aqueous concentration of o-xylene, there is always a peak value located at the trapped NAPL dissolution front, which forms after the free NAPL in these macroscale positions vanishes (cf. Figure 5-23a). The peak value continues to rise as the NAPL front recedes inward until it approaches unity. From the peak concentration position, o-xylene is transported both inward and outward. This type of behavior associated with selective dissolution of components in an aggregate is similar to that associated with selective evaporation of components in macropore space.

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Figure 5-25: Micro-spatial and temporal variations of the trapped NAPL saturation $S_o$, at the macro-position $\hat{r}' = 0.25$ (middle of spill site), for Case II. The dashes denote the initial distribution.
Figure 5-26: Micro-spatial and temporal variations of the component aqueous concentrations $\chi_{10} \hat{C}_{w1}$, at the macro-position $\hat{r}' = 0.5$ (outer boundary of spill site), for Case II. The dashes denote the initial distributions.
Figure 5-27: Micro-spatial and temporal variations of the trapped NAPL saturation $S_o$, at the macro-position $\hat{r}' = 0.5$ (outer boundary of spill site), for Case II. The dashes denote the initial distribution.
Figure 5-28: Micro-spatial and temporal variations of the component aqueous concentrations $\chi_{i0}\hat{C}_{wi}$, at the macro-position $\hat{r}' = 0.05$ (adjacent to well), for Case II. The dashes denote the initial distributions.
Figure 5-29: Micro-spatial and temporal variations of the trapped NAPL saturation $S_o$, at the macro-position $\hat{r}' = 0.05$ (adjacent to well), for Case II. The dashes denote the initial distribution.
**Effluent Vapor Concentration**

Finally let us compare the effluent vapor concentrations for the three components that can be measured at the pumping well, for Cases I and II (Figure 5-30). In either case, the benzene concentration decreases monotonically with time, while the toluene concentration first drops and then rises briefly before it drops back. The change for the o-xylene concentration is more dramatic. After the initial rise, it drops momentarily as the free NAPL near the well is volatilized. This is followed by a pronounced increase to more than twice the initial value until the free NAPL is completely volatilized. In Case I where the aggregate effects are absent, the o-xylene concentration finally drops abruptly all the way down to zero. However, with trapped NAPL, the final drop in Case II is much milder; it ends up in a tail where the effluent concentration decays at a persistently slow rate. In fact, the effluent tailing is characteristic for all transports with non-equilibrium phase exchange on the macroscale. Obviously the trapped phases in aggregates retard the removal of all components, more for the heavier than the lighter ones. The results in Case II are qualitatively similar to the elution curves (Figure 5-12) obtained for the unidirectional through-flow problem.

The elution curves can be useful in calibrating the free NAPL saturation. Very often only the total NAPL saturation can be measured readily in practice. As discussed above, the time at which the effluent concentration of the heaviest component drops abruptly is the time when the free NAPL is completely volatilized, and therefore can be used to calibrate the amount of free NAPL present in the soil. If the total NAPL saturation is known, the trapped NAPL saturation can then be found from their difference. If not, the decaying speed of the tailing, which depends on the amount of trapped NAPL in aggregates, can be used to calibrate the trapped NAPL saturation.
Figure 5-30: Effluent vapor concentrations for the three components in Case I (dashes), and Case II (solid lines).
5.8 Concluding Remarks

Based on the spherical aggregate diffusion model, we have presented a multicomponent vapor transport theory for soil vapor extraction in unsaturated soils with mass exchange kinetics due to free and trapped phases of residual NAPL. The assumptions are that the free NAPL is in direct contact with the mobile air, and the trapped NAPL together with aqueous, sorbed and trapped vapor phases are distributed inside the aggregates. While local equilibrium between the “free” NAPL and the macropore vapor is readily attained, the mass transfer between the “trapped” phases and the macropore vapor is rate-limited by aqueous diffusion. Equations (5.15)–(5.18) govern the aqueous diffusion and the trapped NAPL saturation in a microscale aggregate, while equations (5.30)–(5.29) are for the vapor transport and the free NAPL saturation on the macroscale. Through mass exchange between phases, the two problems are coupled to each other. Individual components also interact with one-another in the transport as long as they are tied by the totality condition of mole fractions in the presence of NAPL. The normalized problems are expressible in terms of four dimensionless parameters which are functions of flow, soil and chemical properties. The normalization also facilitates, for modeling purposes, the use of a hypothetical mixture composed of a few representative components to approximate a real mixture of more complex composition.

We have compared the present theory with experimental data obtained from a venting of multicomponent vapor in an intact core taken from a contaminated site. The predicted vapor concentrations, for both spatial distributions and effluent, have been in good agreement with the measured data for four alkanes, which are selected to represent the most volatile components in the real contaminant. The distinctive features of a multicomponent transport, namely, for a heavy component the vapor concentration may increase and has a local maximum value at the evaporation front in the course of venting, are clearly seen in both the simulation and the measured data.

The multicomponent dynamics is further studied for a horizontal soil layer with
a radial venting into a vertical well. For a three-component NAPL composed of benzene, toluene and o-xylene, we have found, whether or not the soil is of the aggregate type, the following distinctive behavior associated with the volatility of the components: (1) the less volatile or heavier the component is, the longer time it takes to purge this component from the soil; (2) the vapor concentration of the less volatile components can rise for some time as a result of selective evaporation of the NAPL; the rise shows up in the effluent concentrations; (3) the o-xylene vapor concentration gradient is discontinuous at the two evaporation fronts of the free NAPL, the moving speed of which can be found by a local analysis; (4) towards the final stage, the NAPL becomes virtually a pure liquid phase of o-xylene; (5) condensation of o-xylene happens immediately downstream of the far evaporation front. The presence of trapped NAPL and soil aggregation bring about the following additional effects: (1) the clean-up time is prolonged, more for a heavier component; (2) the free NAPL is volatilized at a lower rate; (3) the rise and the subsequent fall of the o-xylene vapor concentration are much retarded; the concentration does not drop abruptly upon complete volatilization of the free NAPL; (4) the tailing is appreciable in the effluent concentrations, a strong sign of deviation from local equilibrium. A microscale examination at the middle of the contaminated site reveals that during an intermediate stage the heavier components are fed into aggregates in response to the increase of vapor concentration in the macropores. This accumulation in trapped storage causes a longer time for these components to be removed eventually. The trapped NAPL also exhibits an inward receding front after the free NAPL at the same macroscale position is volatilized. The trapped NAPL at the core of an aggregate is however not removed until after a very long time of pumping.

In contrast to a first-order kinetic model which does not account for physical and chemical processes on the microscale, the present model reduces the number of fitting parameters to the minimum. While the assumption of uniform spherical aggregates may appear extreme, this idealization enables us to construct a purely deductive theory, relatively free of empiricism, and allows us to explain and predict many intricate phenomena from basic principles. For some manufactured materials the present
theory can of course be further checked in details for both the approximations and the implications rigorously. For natural materials with irregular grains, the radius of spherical aggregates in our model can be regarded as one of the two calibrated parameters, the other being the ratio of the saturations of free and trapped NAPL. The usefulness of the present model has been clearly demonstrated by comparison with column tests with soil samples from the field.

To further enhance the usefulness of our theory it would be desirable to have more well-controlled experiments for a thorough comparison. In particular, we suggest a laboratory venting experiment on an unsaturated column emplaced with residual NAPL of known initial composition and total saturation. All the chemical and soil properties should be measured or estimated independently. The free and trapped NAPL saturations however may need to be calibrated using the elution curve method mentioned earlier. During venting, not only the vapor concentrations of all the components but also the NAPL saturation and composition should be measured, so that the local phase change rates predicted by the theory can be checked.

The present theory can be used for modeling more realistic configurations of air venting, where the finite length of the well screen, soil heterogeneity, ground surface conditions and so on must be accounted for. Fully three dimensional schemes for numerical computations are of course necessary and should be worthwhile.
General Summary and Conclusions

In this thesis, we have applied asymptotic methods to develop theories for two problems of geoenvironmental interests: (I) ground subsidence of finite amplitude due to water pumping and surface loading; (II) soil vapor extraction in an unsaturated zone composed of aggregated soils.

In Chapter 1, we have studied the combined and simultaneous effects of water withdrawal and surface loads on the ground subsidence of an aquifer system with a hard and porous layer confined by two soft and semipervious layers. An asymptotic analysis has been performed for the case where there is a large contrast of hydraulic conductivities between the aquifer and the semipervious layers. At the leading order, the seepage flow in the system can be proved to be one-dimensional in each layer, being horizontal in the highly porous aquifer and vertical in the semipervious layers. Also, the deformation in the soft semipervious layers is primarily vertical, allowing the use of empirically established, one-dimensional laws for finite soil strain. For the simple case with radial symmetry, we have compared several types of foundations: rigid and sealed; soft and sealed; soft and unsealed. In the “rigid” case the foundation can only settle uniformly and the contact stress varies with time and space, while in the “soft” cases the settlement is non-uniform with the contact stress remains constant in time. In any case, the settlement of the foundation at large time is much larger than its immediate ground surface, and the settlement is also larger than the algebraic sum of the settlement due solely to pumping and that due solely to loading. From the depth variations of void ratio and drawdown beneath and out-
side the foundation, we find that large soil compaction beneath a sealed cover is the consequence of water depletion without recharge. The contact stress underneath a rigid foundation may change as a result of pumping; this could lead to local structural damages. Further extension of the present theory is worthwhile to examine the effects of multiple wells and more complex soil structure and surface loading. Loss of axial symmetry would certainly demand greater numerical effort. Nevertheless the combination of Lagrangian coordinates and asymptotic approximation is a promising tool for the development of practical numerical models which can account for nonlinearity consistently and efficiently.

In Chapter 2, we have reviewed the application and the existing modelings for soil vapor extraction as a remediation for an unsaturated zone contaminated with volatile organic compounds. Having pointed out the inadequacy of the local equilibrium and the first-order kinetic theories, we adopt the so-called aggregate diffusion model to describe the microscale mass transfer processes. In this chapter, the macroscale equations governing the convective diffusion of a volatile organic compound during soil vapor extraction are derived systematically. Although the macroscale effective equations of flow and chemical transport can be developed by intuitive arguments, a formal derivation is presented by the theory of homogenization in order to prescribe precisely the underlying assumptions and the degree of accuracy, and to prepare grounds for further extensions to three-scale media (e.g., multilayered soil). Specifically the basic assumptions are: (i) the soil matrix is composed of a nearly periodic array of spherical aggregates, (ii) within an aggregate water is immobile because of capillary forces, (iii) the aggregates are much smaller than the macroscale, and (iv) diffusion in the aggregates is much slower than that in the pore air. Local equilibrium is confirmed as a limiting case of the present theory when the aggregate diffusion time is much shorter than the global advection time. The significance of the resulting theory is that the kinetics of phase exchange between macropore vapor and aggregates is described by, not a first-order relation with empirical coefficients, but a series of convoluted time integrals containing physical parameters that can be reliably determined experimentally.
In Chapter 3, applications of the aggregate diffusion model deduced in Chapter 2 are presented. The problem of vapor transport in a one-dimensional short column is solved by Laplace transform, and the results are compared favorably with the experiments by Gierke et al. (1992). The problem of SVE by a vacuum well in a radially symmetric contaminated region is computed for the two cases of sealed and permeable ground surfaces. The effects of air velocity, aggregate size and diffusivity, and chemical sorptivity on the SVE operation performance are examined. In general a higher sorptivity and/or a larger aggregate size can result in a longer SVE operation. The optimum air velocity is such that the advection time is comparable to the aggregate diffusion time. If contaminant removal is rate-limited by aqueous diffusion, the vapor concentration can drop rapidly to a low level while the aqueous concentration is still very high. In such case, measuring only the effluent vapor concentration will not be adequate to monitor the operation. A temporary pumping shut-down may however be useful to tell how much rate-limited the process is by checking the rebound of the vapor concentration. In the case where air is drawn across a permeable ground surface surrounding the well, the contaminant which is deep in the layer and far from the well will take a long time to be removed by vapor extraction.

In Chapter 4, we have studied the effects of soil heterogeneity on vapor transport in a vadose zone which consists of highly porous sand layers sandwiching a thin and semipervious lens. Each soil layer is modeled as a periodic array of spherical aggregates formed by solid grains and immobile water trapped by surface tension. Volatile chemicals are vaporized in the mobile air in pores between aggregates, dissolved in the intra-aggregate water, and adsorbed on the surface of soil grains. Using the effective transport equations derived for the aggregated soils, we consider shallow layers with sharp contrast in physical properties. An asymptotic analysis has been developed for an axi-symmetric geometry, yielding quasi-one-dimensional governing equations for individual layers. In particular at the leading order the flow and chemical transport are horizontal in the coarse layers but vertical in the semipervious lens. Numerical results are presented for a simple example to demonstrate the significance of the lens permeability, diffusivity and retardation factor, and the aggregate diffusivity in
the coarse layers, on the vapor transport during the stages of contamination and air-venting.

In Chapter 5, we have extended the aggregate diffusion model to study the case where free and trapped phases of multicomponent NAPL also exist in the soil. On the microscale, the soil particles are assumed to form spherical aggregates with micropores filled with immobile water, trapped phases of NAPL and air. The interaggregate space is occupied with mobile air, and a thin film of free NAPL adheres on the aggregate surface. While the free NAPL can readily be in equilibrium with macropore vapor, the mass transfer from aggregates is rate-limited by aqueous diffusion. With this model, we can predict the vapor concentrations of various chemical species and the free NAPL saturation over the macroscale, based on the detailed understanding of the aqueous concentrations of the species and the trapped NAPL saturation within the aggregates. The model has been compared favorably with some experimental data of sparging multicomponent vapor out of an intact core taken from a contaminated site. The multicomponent distinctive features, clearly exhibited by the data, are further examined in the simulations of a three-aromatic vapor transport under a radial flow field. It is found that while the vapor concentration of the most volatile component drops monotonically with time, those of the less volatile may rise as their mole fractions in the NAPL increase. The vapor concentration of a heavy component may have a local maximum at the evaporation front of the free NAPL. In the case of radial flow, the free NAPL has two receding evaporation fronts. Condensation of the heavy component downstream of the far front causes a temporary increase of its total concentration there. With trapped NAPL and soil aggregation, the macroscale transport is retarded and the effluent concentrations end up in noticeable tailing.

For future developments, the present vapor transport theories can readily be extended to simulate realistic problems of general three dimensions, for various types of boundary conditions including the presence of groundwater table, and for multiwell operations including air pumping and injection. The homogenization method can be applied to deduce effective equations for vapor transport in a multilayered, i.e., threescale, vadose zone. For further validation, it will be desirable if field data, including
spatial measurements of concentrations of various phases and NAPL saturations, are available to compare predictions by the theories.

Still more challenging is to develop an integrated flow and transport model for the coupled air-sparging/venting system by which chemicals are vaporized into the subsurface air stream created by air pumping into the saturated soil (air sparging) and the air withdrawal in the unsaturated soil (air venting). Despite increasing application of the system in practice, basic studies on the associated flow and transport have been rather limited. To have air flow through a water-saturated porous medium under induced pressure gradient, the air sparging alone poses a nontrivial fluid/soil mechanics problem yet to be studied. Some recent flow visualization experiments have indicated that the air flow takes the form of channels, rather than bubbles as supposed by some previous workers. There is also a possibility of soil fracturing, creating undesirable short-circuit channels, as a result of strong air injection. The decrease in hydraulic conductivity caused by air sparging will impede the natural groundwater flow from passing through the cone of influence of the pumping, causing a local elevation of the water table. The effects of such an interaction between air injection and natural groundwater flow are yet to be understood. Also, the flow and transport in the capillary fringe zone, a challenging problem by itself, needs to be carefully sorted out for this sparging/venting system. As a desirable side effect, air venting also enhances biodegradation as oxygen being flushed into the subsurface. The biodegradation of chemical which is rate-limited by oxygen transport should be integrated into the coupled model.
Appendices
Appendix A

Numerical Scheme for the Ground Subsidence Problem in Chapter 1

The initial-boundary-value problem in Chapter 1 is solved by an ADI scheme of finite differences. All the interfaces are initially horizontal. The computational domain, as shown in Figure A-1, consists of a rectangular uniform array of grid points arranged in $NY + 1$ columns of interval $\Delta Y$, and $NZ1 + 1$ and $NZ2 + 1$ rows of interval $\Delta Z$ for the lower and the upper semipervious layers respectively. The bottom and the top faces are $\bar{\Gamma}_0 : Z = 0$ and $\Gamma_3 : Z = (NZ1 + NZ2)\Delta Z$, while the interface between the two aquitards is $\Gamma_I : Z = NZ1 \times \Delta Z$. Note that across $\Gamma_I$ the variable $s^*$ is continuous by virtue of (1.70), but the soil parameters such as void ratio and permeability are discontinuous as they pertain to different aquitards below and above the interface. Therefore, two indices $j = NZ1 + 1$ and $j = NZ1 + NZ2 + 2$ are used to denote $\Gamma_I^-$ and $\Gamma_I^+$ respectively. Note also that the far field condition (1.115) is implemented by prescribing $s^*_{NY+1,j}$, i.e., $s^*$ at the last column, being zero at all time. Therefore the horizontal dimension of the computational domain which corresponds to a physical radius $R_w \exp(NY \Delta Y)$, must be large enough to cover the radius of influence within the time domain of the computations. For simplicity we shall denote $\tau_{zz}|_{f_3}$ and $z'|_{f_3}$ by $\tau_3$ and $z'_3$ respectively, and the expressions $NZ1 + 1$, $NZ1 + NZ2 + 1$ are replaced by $NZ1$ and $NZ3$ respectively.

Since the diffusion equation (1.105) contains spatial derivatives only in the $z$-
Figure A-1: Computational domain and discretizations.
direction, its numerical solutions can be sought by a one-dimensional finite difference scheme along each column of the grid points provided that boundary/interface conditions are known. On the other hand, the interface equation (1.113) and the ground surface equation (1.117) control variables in two horizontal planes and can be solved numerically only when the interior values of \( s^* \) are known. By an alternating-direction scheme, we essentially solve these two sets of equations in a staggered manner. In the first time step, we get solutions of the interior \( s^* \) using the prescribed initial boundary condition, and after obtaining the interior solutions we find the interface and the ground surface variables at the same time level. To further satisfy the boundary condition on a rigid and plane foundation, we iteratively solve the above equations while adjusting the contact stress until the requirement is satisfied. The above procedure is repeated in each time step in advancing the solutions to any desired time level. The logical sequences of the solution algorithm are summarized in a flow-chart as shown in Figure A-2. The major components of the computations involved are explained in further details as follows.

A.1 Solution for Interior Drawdowns by Two-Step Crank-Nicolson Method

Along the \( i \)th \((i = 1, \ldots, NY)\) column, we solve for \( s_{i,j}^{(n+1)} \) of the \((n+1)\)th time level where \( j = 2, \ldots, NZ1 \) and \( j = NZ1 + 2, \ldots, NZ1 + NZ2 \) by a two-step implicit Crank-Nicolson method. First define

\[
\zeta_{i,j}^{(n)} = \frac{\Delta T}{2\beta_{i,j}^{(n)} \Delta Z^2},
\]

(A.1)

\[
\kappa_p_{i,j}^{(n)} = \frac{1}{2} (\kappa_{i,j+1}^{(n)} + \kappa_{i,j}^{(n)}),
\]

(A.2)

\[
\kappa_n_{i,j}^{(n)} = \frac{1}{2} (\kappa_{i,j}^{(n)} + \kappa_{i,j-1}^{(n)}).
\]

(A.3)
Figure A-2: Flowchart of numerical solution algorithm.
The first step, \textit{(the prediction step)}, is to use parameters and solutions of the \(n\)th time level (i.e., \(t = n\Delta t\)) to generate a \textit{predicted} solution \(\hat{s}^{(n+1)}\) for the \((n + 1)\)th time level:

\[
\begin{align*}
-\zeta_{i,j}^{(n)} \kappa n_{i,j}^{(n)} \hat{s}_{i,j-1}^{(n+1)} + (1 + \zeta_{i,j}^{(n)} (\kappa n_{i,j}^{(n)} + \kappa p_{i,j}^{(n)})) \hat{s}_{i,j}^{(n+1)} - \zeta_{i,j}^{(n)} \kappa p_{i,j}^{(n)} \hat{s}_{i,j+1}^{(n+1)} \\
= \zeta_{i,j}^{(n)} \kappa n_{i,j}^{(n)} s_{i,j-1}^{(n)} + (1 - \zeta_{i,j}^{(n)} (\kappa n_{i,j}^{(n)} + \kappa p_{i,j}^{(n)})) s_{i,j}^{(n)} + \\
\zeta_{i,j}^{(n)} \kappa p_{i,j}^{(n)} s_{i,j+1}^{(n)} - (k \tau_{3i}^{(n+1)} - \tau_{3i}^{(n)})
\end{align*}
\tag{A.4}
\]

where \(k \tau_{3i}^{(n+1)}\) stands for the \(k\)th iterate of the new time level contact stress in the \(i\)th column. The above equations constitute a tridiagonal matrix system which, with the proper boundary conditions, can be solved by a standard routine (e.g., see Press \textit{et al.}, 1992).

With the predicted solutions, the soil parameters are updated and averaged between the old and the updated ones:

\[
\zeta_{i,j}^{(n+\frac{1}{2})} = \frac{1}{2} (\zeta_{i,j}^{(n)} + \hat{\zeta}_{i,j}^{(n+1)}),
\tag{A.5}
\]

\[
\kappa p_{i,j}^{(n+\frac{1}{2})} = \frac{1}{2} (\kappa p_{i,j}^{(n)} + \hat{\kappa p}_{i,j}^{(n+1)}),
\tag{A.6}
\]

\[
\kappa n_{i,j}^{(n+\frac{1}{2})} = \frac{1}{2} (\kappa n_{i,j}^{(n)} + \hat{\kappa n}_{i,j}^{(n+1)}).
\tag{A.7}
\]

The second step, or the correction step, is to repeat calculations in the first step but now the averaged parameters are used to obtain \(s^{(n+1)}\):

\[
\begin{align*}
-\zeta_{i,j}^{(n+\frac{1}{2})} \kappa n_{i,j}^{(n+\frac{1}{2})} s_{i,j-1}^{(n+1)} + (1 + \zeta_{i,j}^{(n+\frac{1}{2})} (\kappa n_{i,j}^{(n+\frac{1}{2})} + \kappa p_{i,j}^{(n+\frac{1}{2})})) s_{i,j}^{(n+1)} \\
-\zeta_{i,j}^{(n+\frac{1}{2})} \kappa p_{i,j}^{(n+\frac{1}{2})} s_{i,j+1}^{(n+1)} = \zeta_{i,j}^{(n+\frac{1}{2})} \kappa n_{i,j}^{(n+\frac{1}{2})} s_{i,j-1}^{(n)} \\
+(1 - \zeta_{i,j}^{(n+\frac{1}{2})} (\kappa n_{i,j}^{(n+\frac{1}{2})} + \kappa p_{i,j}^{(n+\frac{1}{2})})) s_{i,j}^{(n)} \\
+\zeta_{i,j}^{(n+\frac{1}{2})} \kappa p_{i,j}^{(n+\frac{1}{2})} s_{i,j+1}^{(n)} - (k \tau_{3i}^{(n+1)} - \tau_{3i}^{(n)}).
\end{align*}
\tag{A.8}
\]

Solutions are again obtained by invoking a routine for tridiagonal systems.
A.2 Iterative Solution for Interface Drawdowns 
and Ground Surface Displacements

The two equations (1.113) and (1.117) are solved simultaneously by iterations. A left 
superscript will be used as an iteration counter. A second order approximation for 
the z-derivative is adopted. For example,

\[
\frac{\partial s^*}{\partial Z} \bigg|_{Z=0^+} = -3s^*_{j=1} + 4s^*_{j=2} - s^*_{j=3} \frac{2\Delta Z}{2} + O(\Delta Z^2). \quad (A.9)
\]

Equation (1.117) is numerically integrated by a forward time difference; the difference 
equation for the \((k + 1)\)th iterate of the top surface displacement at the \((n + 1)\)th 
time level is

\[
k+1 \frac{z^{(n+1)}}{z_i} = z_i^{(n)} + \frac{S_i \Delta T}{2\Delta Z} \left(k_{i,N_{23}}^{(n+1)} (3s_{i,N_{23}}^{(n+1)} - 4s_{i,N_{23}+1}^{(n+1)} + s_{i,N_{23}-1}^{(n+1)})
\right.

\left. - k_{i,N_{23}+1}^{(n+1)} \left(\frac{3}{2} (s_{i,N_{23}}^{(n+1)} + s_{i,N_{23}+1}^{(n)}) + 4s_{i,N_{23}+1}^{(n+1)} - s_{i,N_{23}-1}^{(n+1)} \right) \right)
\left. + k_{i,N_{22}}^{(n+1)} \left(\frac{3}{2} (s_{i,N_{22}}^{(n+1)} + s_{i,N_{22}+1}^{(n)}) - 4s_{i,N_{22}+1}^{(n+1)} + s_{i,N_{22}-1}^{(n+1)} \right) \right) \quad (A.10)
\]

where an average is used between the old time value and the current new time value 
for the interface drawdown \(s_{i,N_{21}}^{(n+1)}\). We then proceed to find the \((k + 1)\)th iterate of 
\(s_{i,N_{21}}^{(n+1)}\) by approximating (1.113) with

\[
k+1 s_{i-1,N_{21}}^{(n+1)} = (2 + 3\eta_i(k_{i,N_{23}}^{(n+1)} + k_{i,N_{21}}^{(n+1)})) k+1 s_{i,N_{21}}^{(n+1)} + k+1 s_{i+1,N_{21}}^{(n+1)} =
\]

\[
-k+1 j_i^{(n+1)} \frac{z_{i-1}^{(n+1)}}{z_i} + 2 k+1 j_i^{(n+1)} - k+1 j_i^{(n+1)} \frac{z_{i+1}^{(n+1)}}{z_i} +
\]

\[
-\eta_i \left(k_{i,N_{23}}^{(n+1)} (4s_{i,N_{23}}^{(n+1)} - s_{i,N_{23}+1}^{(n+1)}) + k_{i,N_{21}}^{(n+1)} (4s_{i,N_{21}}^{(n+1)} - s_{i,N_{21}-1}^{(n+1)}) \right), \quad (A.11)
\]

where

\[
\eta_i = \frac{R_i^2 \Delta Y^2}{2TR_i \Delta Z}. \quad (A.12)
\]

Equation (A.11) is again a tridiagonal system which is solved together with the boundary 
conditions (1.114) and (1.115). We then continue the iteration of solving (A.10) 
and (A.11) in succession until the solutions have satisfactorily converged.
A.3 Updating Soil Parameters

Each time when solutions of the above equations, either for the interior or the interfacial points, are found after one cycle in an iterative process, the soil parameters at the corresponding grid points have to be adjusted immediately. This is accomplished by using the constitutive equations described in §1.6.3. The change in effective stress is first obtained by (1.66), or

$$
\sigma'_{zz} = s^* + \tau_3.
$$

(A.13)

Then the change in void ratio $e - \bar{e}$ and the coefficient of compressibility $a_w$ are obtained from (1.81) and (1.82). With the updated void ratio, the hydraulic conductivity is then adjusted according to (1.83). The new values of the coefficients $\kappa$ and $\beta$ are then computed according to (1.102).

A.4 Boundary Conditions Beneath the Foundation

The case of soft foundation is trivial, only the rigid foundation is discussed here. Beneath the rigid foundation, the settlement is uniform in $R$. The constant value is however unknown and must be subjected to (1.112), which can be approximated as

$$
\sum_{i=I_1}^{I_2} 2\pi R_w^2 e^{2Y_i \tau_3} \Delta Y = -W
$$

(A.14)

where $I_1$ and $I_2$ are the indices for the two columns corresponding to $R_w$ and $R_o$ respectively. Rearranging, we can write (A.14) as

$$
\sum_{i=I_1}^{I_2} e^{2Y_i \tau_3} = \frac{-W}{2\pi R_w^2 \Delta Y} \equiv \mathcal{W}
$$

(A.15)

where $\mathcal{W}$ is a constant. Even in linear elasticity the boundary value problem is usually solved by the method of integral equations.

In the present nonlinear problem, the following iterative method is adopted to
determine both the contact stress and the settlement simultaneously. We first obtain the settlement $z'_{3,i}$ from the $k$th iterate of the contact stress $t_{3,i}$, $i = I_1, \ldots, I_2$, which are then adjusted according to:

$$
k^{+1}t_{3,i} = \left(\frac{z'_{3,i+1}}{z'_{3,i}}\right)^\alpha k_{3,i} \quad i = I_1, \ldots, I_2 - 1,
$$

(A.16)

where $0 < \alpha \ll 1$ is an empirical exponent. The idea behind (A.16) is simply that if the displacement at the inner column $i$ is greater than that at the outer column $i + 1$, then the stress at the $i$th column ought to be reduced, and vice-versa. The power $\alpha$ has to be small so that the adjustment factor will be very close to unity in order to avoid excessive overshootings. From numerical experiments, we find $\alpha$ to be in the range 0.01 to 0.05 for reasonable rate of convergence. The above method will adjust all columns of stress except $i = I_2$ which is however fixed by (A.15):

$$
k^{+1}t_{3,i_2} = \frac{\mathcal{W} - \sum_{i = I_1}^{I_2 - 1} k^{+1}t_{3,i} \exp(2Y_i)}{\exp(2Y_{i_2})}.
$$

(A.17)

The adjusted stress values are then used in a new cycle to determine the drawdowns and the surface displacements. Iterations must go on until all the ground settlement at all points under the foundation are equal within some tolerance.

Near the well the pumping effect can be so strong that the soils tend to consolidate faster than those farther away from the well. Therefore a uniform settlement across a radial distance under the building is possible only if the contact stress decreases towards the well. For large pumping rate or a small building weight it is possible that the contact stress nearest to the well eventually becomes zero, implying that the footing is no longer supported by the underlying soil. We terminate the computations when this situation arises.
Appendix B

The Spatial Averaging Theorem for Two-Scale Porous Media

The theory of homogenization is a systematic method of averaging for deriving effective equation on the macroscale, when the medium is periodic on the microscales (Bensoussan et al., 1978; Sanchez-Palencia, 1980; Keller, 1980; Bakhvalov and Panasenko, 1989). In particular, it has been applied extensively to porous media which can be divided into periodic cells of characteristic dimension \( \ell \), which is much smaller than the macroscale \( \ell' \) characterizing the flow at large. The method of multiple scales is used by introducing microscale and macroscale variables \( \mathbf{x} \) and \( \mathbf{x}' = \varepsilon \mathbf{x} \) where \( \varepsilon = \ell / \ell' \ll 1 \). In deriving the effective equations one often needs to interchange differentiation with respect to the macroscale variable \( \langle \nabla' \cdot \mathbf{f} \rangle \), and volume averaging over a unit cell, \( \nabla' \cdot \langle \mathbf{f} \rangle \), where the averaging operator is defined by

\[
\langle \mathbf{f} \rangle = \frac{1}{\Omega} \int_{\Omega_f} \mathbf{f} dV \tag{B.1}
\]

where \( \Omega_f \) is the fluid-filled pore space in the cell with the volume \( \Omega \). The interchange of differentiation and integration is a trivial matter if \( \Omega_f \) is uniform with respect to the macroscale coordinates. However when \( \Omega_f \) or equivalently the porosity \( n \equiv \Omega_f / \Omega \) varies in \( \mathbf{x}' \), the two operations do not commute. Greater care is needed.

A spatial averaging theorem has long been known in the method of volume av-
eraging, as developed by Anderson and Jackson (1967), Slattery (1967), Whitaker (1967) and others. The theorem states that the interchange of volume averaging and spatial differentiation introduces a surface integral on the fluid-solid interface within an averaging volume. The volume averaging method however does not distinguish between fast and slow spatial scales. Therefore, in order to make use of this theorem in homogenization theory, multiple-scale expansions must be introduced.

In this appendix we shall modify the spatial averaging theorem, by using a derivation different from those of Howes and Whitaker (1985) and Whitaker (1985). As is fundamental to homogenization theory, we divide the porous medium into periodic cells, denoted by $\Omega$. Within each cell let us denote the fluid-solid interface by $\Gamma_{fs} : S(\vec{x}) = 0$, the fluid domain by $\Omega_f : S(\vec{x}) > 0$, and the solid domain by $\Omega_s : S(\vec{x}) < 0$, where $\vec{x}$ are the spatial coordinates before expansion. The volume of $\Omega$ is assumed to be spatially invariant.

An integral of any vector $f(\vec{x})$ over $\Omega_f(\vec{x})$ can be replaced by an integral over $\Omega$ with the help of the Heaviside step function $H(S)$:

$$\int_{\Omega_f} f \, dV = \int_{\Omega} fH(S) \, dV$$  \hspace{1cm} (B.2)

where

$$H(S) = \begin{cases} 0, & \text{if } S < 0 \\ 1, & \text{if } S > 0. \end{cases}$$  \hspace{1cm} (B.3)

After changing the integration domain to $\Omega$, differentiation and integration may be interchanged. Let $\Omega_\epsilon$ be a thin shell enclosing the interface $\Gamma_{fs}$ with a thickness $2\epsilon$ where $\epsilon$ is infinitesimally small, and $\Omega_f^-$ be the rest of the fluid volume inside the cell: $\Omega_f^- = \Omega_f - \Omega_f \cap \Omega_\epsilon$. Then,

$$\vec{\nabla} \cdot \int_{\Omega_f} f \, dV = \vec{\nabla} \cdot \int_{\Omega} fH(S) \, dV = \int_{\Omega} \vec{\nabla} \cdot (fH) \, dV$$

$$= \int_{\Omega_f^-} \vec{\nabla} \cdot f \, dV + \int_{\Omega_\epsilon} \left[(\vec{\nabla} \cdot f)H + f \cdot \vec{\nabla}H\right] \, dV.$$  \hspace{1cm} (B.4)
The first $\Omega_\epsilon$-integral vanishes as $\epsilon \to 0$ and can be disregarded. Therefore,

$$\nabla \cdot \int_{\Omega_\epsilon} f \, dV = \int_{\Omega_\epsilon} \nabla \cdot f \, dV + \int_{\Omega_\epsilon} f \cdot \nabla H \, dV. \quad (B.5)$$

We now introduce multiple-scale coordinates

$$\tilde{x} \rightarrow (x, x'), \quad (B.6)$$

and replace the gradient operator according to

$$\nabla \rightarrow \nabla + \epsilon \nabla'. \quad (B.7)$$

From (B.5) we get

$$(\nabla + \epsilon \nabla') \cdot \int_{\Omega_\epsilon} f \, dV = \int_{\Omega_\epsilon} (\nabla + \epsilon \nabla') \cdot f \, dV + \int_{\Omega_\epsilon} f \cdot (\nabla + \epsilon \nabla') H \, dV. \quad (B.8)$$

At the leading order,

$$\nabla \cdot \int_{\Omega_\epsilon} f \, dV = \int_{\Omega_\epsilon} \nabla \cdot f \, dV + \int_{\Omega_\epsilon} f \cdot \nabla H \, dV. \quad (B.9)$$

The left-hand side vanishes since the $\Omega$-average cannot depend on $x$. On the right-hand side, note first that

$$\nabla H(S) = \frac{dH(S)}{dS} \nabla S = \delta(S) \nabla S \quad (B.10)$$

where $\delta(S)$ is the Dirac delta function of $S$. Hence

$$\int_{\Omega_\epsilon} f \cdot \nabla H \, dV = \int_{\Omega_\epsilon} f \cdot [\delta(S) \nabla S] \, dV$$

$$= \int_{\Gamma_{f_\epsilon}} \int_{-\epsilon}^\epsilon f \cdot [\delta(S) \nabla S] \, d\zeta \, dA \quad (B.11)$$

where $\zeta$ is the normal distance from $\Gamma_{fS}$ (or $S = 0$). Changing the independent
variable from $\zeta$ to $S$ by

$$dS = |\nabla S| d\zeta \tag{B.12}$$

we can write the last integral as

$$\int_{\Gamma_{fs}} \int_{-\infty}^{\infty} f \cdot \left[ \delta(S) \frac{\nabla S}{|\nabla S|} \right] dS dA = \int_{\Gamma_{fs}} f \cdot \left[ \frac{\nabla S}{|\nabla S|} \right] dA. \tag{B.13}$$

Note that

$$\mathbf{n} = -\left[ \frac{\nabla S}{|\nabla S|} \right]_{s=0} \tag{B.14}$$

is the unit normal vector to $\Gamma_{fs}$ pointing into the solid. Therefore (B.9) is just the result of Gauss:

$$\int_{\Omega_f} \nabla \cdot f dV = \int_{\Gamma_{fs}} f \cdot \mathbf{n} dA \tag{B.15}$$

where the surface integral along the cell boundary of the fluid domain has vanished because of $\Omega$-periodicity.

At the order $O(\epsilon)$ we have from (B.8)

$$\nabla' \cdot \int_{\Omega_f} f dV = \int_{\Omega_f} \nabla' \cdot f dV + \int_{\Omega_f} f \cdot \nabla' H dV. \tag{B.16}$$

Following the same steps as in the leading order, the last integral can be converted into a surface integral:

$$\int_{\Omega_f} f \cdot \nabla' H dV = \int_{\Omega_f} f \cdot [\delta(S) \nabla' S] dV$$

$$= \int_{\Gamma_{fs}} \int_{-\epsilon}^{\epsilon} f \cdot [\delta(S) \nabla' S] d\zeta dA$$

$$= \int_{\Gamma_{fs}} \int_{-\infty}^{\infty} f \cdot \left[ \delta(S) \frac{\nabla' S}{|\nabla S|} \right] dS dA$$

$$= \int_{\Gamma_{fs}} f \cdot \left[ \frac{\nabla' S}{|\nabla S|} \right] dA. \tag{B.17}$$

Putting (B.17) back into (B.16), and letting $\epsilon \to 0$, we obtain

$$\nabla' \cdot \langle f \rangle = \langle \nabla' \cdot f \rangle + \frac{1}{|\Omega|} \int_{\Gamma_{fs}} f \cdot \left[ \frac{\nabla' S}{|\nabla S|} \right] dA. \tag{B.18}$$
This is the spatial averaging theorem governing the interchange of averaging over the fluid volume in a micro-cell and the macroscale differentiation. In general the surface integral in (B.18) vanishes only when \( f \) is zero on the fluid-solid interface \( \Gamma_{fs} \), as is true when \( f \) is a fluid velocity in a rigid medium by virtue of the no-slip, no-flux boundary conditions.
Appendix C

Symmetry and Positive Definiteness of \((D_g^*)_{il}\)

Recall the cell problem (2.67)–(2.68) in Chapter 2:

\[
\frac{\partial^2 N_i}{\partial x_j \partial x_j} = 0 \quad \text{in} \quad \Omega_g, \tag{C.1}
\]

\[
\frac{\partial N_i}{\partial x_j} n_j = n_l \quad \text{along} \quad \Gamma_{ga}. \tag{C.2}
\]

Multiplying (C.1) with \(N_i\) and integrating over \(\Omega\), we get after integration by parts

\[
\iiint_\Omega \frac{\partial}{\partial x_j} \left( N_i \frac{\partial N_i}{\partial x_j} \right) d\Omega = \iiint_\Omega \frac{\partial N_i}{\partial x_j} \frac{\partial N_i}{\partial x_j} d\Omega. \tag{C.3}
\]

By Gauss theorem and (C.2), the left-hand side becomes

\[
\iint_{\Gamma_{ga}} N_i \frac{\partial N_i}{\partial x_j} n_j d\Gamma = \iint_{\Gamma_{ga}} N_i n_l d\Gamma. \tag{C.4}
\]

Since the right-hand side of (C.3) is symmetric with respect to the interchange of \(i\) and \(l\), it follows that

\[
\iint_{\Gamma_{ga}} N_i n_l d\Gamma = \iint_{\Gamma_{ga}} N_l n_i d\Gamma \tag{C.5}
\]
or
\[ \int_{\Omega} \int_{\Omega} \frac{\partial N_i}{\partial x_i} d\Omega = \int_{\Omega} \int_{\Omega} \frac{\partial N_i}{\partial x_i} d\Omega. \] (C.6)

Therefore the diffusion tensor
\[ (D^*_g)_{i\mu} = -\frac{D_\theta}{\theta_g} \left( \frac{\partial N_i}{\partial x_i} \right)_g + D_g \delta_{i\mu} \] (C.7)

must be symmetric.

From (C.3)–(C.6), we get
\[ \frac{D_g}{\theta_g} \left( \left( \frac{\partial N_i}{\partial x_j} \frac{\partial N_i}{\partial x_j} \right)_g - \left( \frac{\partial N_i}{\partial x_i} \right)_g \right) = 0. \] (C.8)

Adding the above equation to \((D^*_g)_{i\mu}\) in (C.7):
\[ (D^*_g)_{i\mu} = \frac{D_g}{\theta_g} \left( \left( \frac{\partial N_i}{\partial x_j} \frac{\partial N_i}{\partial x_j} \right)_g - \left( \frac{\partial N_i}{\partial x_i} \right)_g + \theta_g \delta_{i\mu} \right) \]
\[ = \frac{D_g}{\theta_g} \left( \frac{\partial (N_i - x_i)}{\partial x_j} \frac{\partial (N_i - x_i)}{\partial x_j} \right)_g. \] (C.9)

Clearly a bilinear product of the above tensor with any nonzero vector is always positive. Hence \((D^*_g)_{i\mu}\) must be positive definite.
Appendix D

Heuristic Derivation of Effective SVE Transport Equations

On the macroscale, the transport of vapor in macropores is governed by

\[
\theta_g \frac{\partial C_g}{\partial t} + \nabla \cdot (\theta_g u C_g) - \nabla \cdot (\theta_g D_g \nabla C_g) = -\theta_a \frac{\partial \bar{C}_a}{\partial t}. \tag{D.1}
\]

On the left-hand side, \( C_g \) denotes the concentration of VOC in the gaseous phase, \( t \) the time, \( \theta_g \) the inter-aggregate porosity, \( u \) and \( D_g \) the seepage velocity and the molecular diffusivity in the inter-aggregate air. The right-hand side represents the average rate of mass transfer from the aggregates to the surrounding air, with \( \bar{C}_a \) being the volume-averaged total VOC (aqueous and sorbed phases) concentration in an aggregate, and \( \theta_a = 1 - \theta_g \) being the volume fraction of aggregates.

The average transfer rate from the spherical aggregates is computed by considering the microscale diffusion process in each aggregate:

\[
\frac{\partial C_a}{\partial t} = \frac{\phi D_w}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_w}{\partial r} \right), \tag{D.2}
\]

where \( C_w \) is the VOC concentration in the aggregate aqueous solution, \( r \) is the radial coordinate in an aggregate, \( \phi \) is the aggregate porosity and \( D_w \) is the effective aggregate diffusivity of water/solid combination. In (D.2), we assume that while both
aqueous and solid phases exist in an aggregate, the diffusive flux is controlled only by the aqueous concentration gradient. For an aggregate of radius $a$,

$$
\overline{C}_a = \frac{3}{4\pi a^3} \int_0^a 4\pi r^2 C_a dr.
$$

(D.3)

It follows from (D.2)

$$
\frac{\partial \overline{C}_a}{\partial t} = \phi D_w \frac{\partial C_w}{\partial r} \bigg|_{r=a} \times 4\pi a^2 \times (4\pi a^3 / 3)^{-1},
$$

(D.4)

which is the total mass flux across aggregate surface per volume of aggregate. This verifies that the right-hand side of (D.1) has the meaning of mass transfer per bulk volume.

By assuming linear sorption isotherm, the local value of the total aggregate concentration $C_a$ is related to the local value of the aqueous phase concentration $C_w$ by

$$
C_a = [K_d (1 - \phi) \rho_s + \phi] C_w,
$$

(D.5)

where $K_d$ is the sorption partition coefficient and $\rho_s$ is the aggregate solid density. Therefore (D.2) can be rewritten as

$$
\frac{\partial C_w}{\partial t} = D_e \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_w}{\partial r} \right),
$$

(D.6)

where $D_e$ is the sorption-retarded effective aggregate diffusivity:

$$
D_e = \frac{\phi D_w}{K_d (1 - \phi) \rho_s + \phi}.
$$

(D.7)

In view of the relatively large air diffusivity, $C_g$ should be essentially uniform in the vicinity of an aggregate. In addition, equilibrium partition should prevail on an aggregate surface:

$$
C_w (r = a, X_i, t) = C_g (X_i, t) / H,
$$

(D.8)

where $H$ is the Henry’s law constant. As the microscale Peclet number $Pe = U_g a / D_g^*$,
where \( U_g \) is the scale for \( u \), is typically small in SVE operations, we ignore any film resistance on the aggregate surface. Assuming that initially the vapor and the aqueous phases are in equilibrium:

\[
C_g(X_i, t = 0) = C_{g0}(X_i), \quad (D.9)
\]

\[
C_w(r, X_i, t = 0) = C_{w0}(X_i) = C_{g0}(X_i)/H, \quad (D.10)
\]

we can solve the diffusion problem (D.6), (D.8) and (D.10) for a sphere (Carslaw and Jaeger, 1959, p. 233):

\[
C_w = -\frac{2}{a^2r} \sum_{n=1}^{\infty} (-1)^n e^{-\lambda_n t} \sin \left( \frac{n\pi r}{a} \right) \left\{ \frac{a^2}{n\pi} C_{w0} + \frac{n\pi D_e}{H} \int_0^t e^{\lambda_n t} C_g \, dt \right\}, \quad (D.11)
\]

where

\[
\lambda_n = \frac{n^2\pi^2 D_e}{a^2}. \quad (D.12)
\]

The average of \( C_w \) over volume of an aggregate then gives

\[
\overline{C}_w = \frac{3}{a^3} \int_0^a r^2 C_w \, dr
\]

\[
= \frac{6D_e}{a^2} \sum_{n=1}^{\infty} \left[ \frac{C_{w0} e^{-\lambda_n t}}{\lambda_n} + \frac{1}{H} \int_0^t e^{-\lambda_n (t-\tau)} C_g \, d\tau \right]
\]

\[
= \frac{C_g}{H} - \frac{6D_e}{a^2 H} \sum_{n=1}^{\infty} \frac{1}{\lambda_n} \int_0^t e^{-\lambda_n (t-\tau)} \frac{\partial C_g}{\partial \tau} \, d\tau, \quad (D.13)
\]

where in the second step integration by parts and (D.10) have been used. Hence, with (D.5), we may now calculate the right-hand side of (D.1) to obtain the effective vapor transport equation with an integral source term due to the vapor-aggregate phase exchange:

\[
\theta_g \frac{\partial C_g}{\partial t} + \nabla \cdot (\theta_g u C_g) - \nabla \cdot (\theta_g D_g^{*} \nabla C_g) = -\frac{6\phi D_w \theta_a}{a^2 H} \sum_{n=1}^{\infty} \int_0^t e^{-\lambda_n (t-\tau)} \frac{\partial C_g}{\partial \tau} \, d\tau. \quad (D.14)
\]

Equations (D.13) and (D.14) are the same as (2.82) and (2.84) respectively.
Appendix E

On the Danckwerts Boundary Conditions

In existing analyses of subsurface contaminant transport, the computational domain is often limited to the finite region which is originally affected by the spill or leakage (e.g., Valocchi, 1986; Rathfelder et al., 1991; Goltz and Oxley, 1994). In this finite domain, the transport equation is solved with the boundary conditions that the concentration gradient is zero at the flow outlet and the flux is zero at the flow inlet. Heuristic justifications of these boundary conditions, first introduced by Danckwerts (1953), for one-dimensional flow in laboratory columns have been discussed by Wehner and Wilhelm (1956) and Pearson (1659). In order to assess the realm of validity, we present below another derivation of these boundary conditions for a field scale transport in a radially horizontal flow.

We assume that initially the contaminant is confined within a cylindrical region \( r < r_c \), at the center of which is a pumping well of radius \( r_0 \). Let us denote the vapor concentration in the well by \( C_{g0} \) and that in the outer region \( (r > r_c) \) by \( C_{g1} \). At the two boundaries of the originally contaminated region, we require the continuity of concentration and flux:

\[
C_{g0} = C_g, \quad u_0 C_{g0} - D_{g0} \frac{\partial C_{g0}}{\partial r} = \theta_g \left( u C_g - D_g \frac{\partial C_g}{\partial r} \right) \quad \text{at } r = r_0, \quad (E.1)
\]
\[ C_{g1} = C_g, \quad uC_{g1} - D_g \frac{\partial C_{g1}}{\partial r} = uC_g - D_g \frac{\partial C_g}{\partial r} \quad \text{at } r = r_c, \]  
(E.2)

where \( u_0 \) and \( D_{g0} \) are respectively the radial air velocity and the air diffusivity in the well.

We first consider the flux continuity in (E.1). Clearly by flow continuity across the well screen or \( u_0 = \theta_g u \), the two advection terms cancel each other. Also by radial symmetry, the radial concentration gradient within the well is close to zero as long as the well radius \( r_0 \) is much smaller than the macro transport length scale \( L \) (i.e., \( r_0 \ll 1 \)). When this is true, the flux condition in (E.1) simply reduces to

\[ \frac{\partial C_g}{\partial r} = 0 \quad \text{at } r = r_0, \]  
(E.3)

which is the outlet Danckwerts boundary condition. Since \( r_0 \ll 1 \) is assumed, the above boundary condition is used in the present study.

To derive the inlet boundary condition, we consider the transport in the outer region:

\[ \frac{\partial C_{g1}}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (ruC_{g1}) - \frac{1}{r} \frac{\partial}{\partial r} \left( rD_g \frac{\partial C_{g1}}{\partial r} \right) = 0, \quad r > r_c, \]  
(E.4)

where the chemical phase change is ignored. The above transport equation can be approximated as quasi-steady when its time scale is much shorter than that in the inner region. In other words, when the following condition is satisfied:

\[ \frac{D_g}{U_1^2} \ll T = \frac{L}{U_g} \]  
(E.5)

where \( U_1 \) is the local velocity scale at \( r = r_c \), the transport equation (E.4) reduces to

\[ \frac{d}{dr} \left( ruC_{g1} - rD_g \frac{dC_g}{dr} \right) \approx 0. \]  
(E.6)

By virtue of a zero flux at infinity, the above equation implies that the flux throughout the outer region is zero. Then it follows from the flux continuity in (E.2) that

\[ uC_g - D_g \frac{\partial C_g}{\partial r} = 0 \quad \text{at } r = r_c, \]  
(E.7)
which is the inlet Danckwerts boundary condition. Noting that the local velocity scale $U_1$ is smaller than the global velocity scale $U_g$, we may write the condition (E.5) as

$$\left(\frac{U_1}{U_g}\right) \frac{L U_1}{D_g} \gg 1 \quad \text{or} \quad Pe_1 \gg \left(\frac{U_2}{U_1}\right) > 1 \quad (E.8)$$

where $Pe_1 = LU_1/D_g$ is the local Peclet number at the inlet. In short the inlet Danckwerts boundary condition is valid only when the local Peclet number is sufficiently larger than order unity. Using some typical values, one may estimate that while the global Peclet number can be large depending on the pumping rate, its local value at the inlet need not be much larger than 1. Therefore the Danckwerts condition at a finite radius is not used here. Instead, the problem domain is extended radially to infinity at which both the concentration and the flux are zero.
Appendix F

Asymptotic Expansion of the Integral Source Term

In this appendix we work out the asymptotic expansion of the integral on the right-hand side of (4.5) in Chapter 4 when the following condition is true:

\[ \hat{\lambda}_n = \lambda_n i = n^2 \pi^2 D_e \hat{i}/a^2 \gg 1 \quad (n = 1, 2, \cdots). \]  

(F.1)

By Laplace’s method, we first approximate the integral by restricting the integration to a narrow region surrounding the maximum of the exponent, \( \hat{\tau} = \hat{i} \), about which \( \partial C_g / \partial \tau \) can be replaced by its Taylor series. Then the integrals in the series are evaluated after extending the lower integration limit to \(-\infty\).

\[
\sum_{n=1}^{\infty} \int_0^t e^{-\hat{\lambda}_n (t-\tau)} \frac{\partial C_g}{\partial \tau} \, d\tau \\
= \sum_{n=1}^{\infty} \int_0^i e^{-\hat{\lambda}_n (i-\hat{\tau})} \frac{\partial C_g}{\partial \hat{\tau}} \, d\hat{\tau} \\
\sim \sum_{n=1}^{\infty} \int_{i-\epsilon}^{i} e^{-\hat{\lambda}_n (\hat{i}-\hat{\tau})} \left[ \frac{\partial C_g}{\partial \hat{t}} + (\hat{\tau} - \hat{i}) \frac{\partial^2 C_g}{\partial \hat{t}^2} + \cdots \right] \, d\hat{\tau} \quad \text{(for any small } \epsilon > 0) \\
\sim \sum_{n=1}^{\infty} \int_{-\infty}^{i} e^{-\hat{\lambda}_n (i-\hat{\tau})} \left[ \frac{\partial C_g}{\partial \hat{t}} + (\hat{\tau} - \hat{i}) \frac{\partial^2 C_g}{\partial \hat{t}^2} + \cdots \right] \, d\hat{\tau} \\
= \sum_{n=1}^{\infty} \frac{1}{\hat{\lambda}_n} \frac{\partial C_g}{\partial \hat{t}} - \sum_{n=1}^{\infty} \frac{1}{\hat{\lambda}_n^2} \frac{\partial^2 C_g}{\partial \hat{t}^2} + \cdots
\]

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\[
\frac{a^2}{\pi^2 D_e} \sum_{n=1}^{\infty} \frac{1}{n^2} \frac{\partial C_g}{\partial t} - \frac{a^4}{\pi^4 D_e^2} \sum_{n=1}^{\infty} \frac{1}{n^4} \frac{\partial^2 C_g}{\partial t^2} + \ldots
\]

\[
= \frac{a^2}{6 D_e} \frac{\partial C_g}{\partial t} - \frac{a^4}{90 D_e^2} \frac{\partial^2 C_g}{\partial t^2} + \ldots \quad \text{as } \lambda_n \gg 1.
\] (F.2)
Appendix G

Numerical Method of Solution for the Problem in Chapter 4

In Chapter 4, the flow and the transport problems are mathematically similar. Namely, the equations are radial in spatial dimension for the coarse layers, but vertical for the lens. Solutions in the inner coarse layers are coupled to those in the outer coarse layer and in the lens through the continuity conditions on the interfaces. As suggested by these features, we adopt an alternate-direction-iterative finite-difference scheme for both problems. An iterative scheme is required also because the flow equations are nonlinear. Omitting the standard details, we outline the solution scheme as follows.

To give better numerical resolution near the well, we change the radial coordinate by

\[ y = \ln(\hat{r}/\hat{r}_0) \]  \hspace{1cm} (G.1)

so that

\[ \hat{r} \frac{\partial}{\partial \hat{r}} \rightarrow \frac{\partial}{\partial y} \] and \[ \frac{1}{\hat{r}^2} \frac{\partial}{\partial \hat{r}} \left( \hat{r} \frac{\partial}{\partial \hat{r}} \right) \rightarrow \frac{1}{\hat{r}^2} \frac{\partial^2}{\partial y^2}. \]  \hspace{1cm} (G.2)

The coarse layers are linear segments:

\[ \Omega_1, \Omega_2 : \quad 0 = y_1 < y < y_b \] discretized into \( I_b - 1 \) equal intervals,

\[ \Omega_3 : \quad y_b < y < y_m \] discretized into \( I_m - 1 \) equal intervals, \hspace{1cm} (G.3)
where \( y = y_m \) corresponds to a large radial distance at which the far field boundary conditions are applicable within the time of the problem. On the other hand, the lens is a two-dimensional domain:

\[
\Omega_f : \quad 0 = y_1 < y < y_b, \quad \hat{F}_1(y) < \hat{\varepsilon} < \hat{F}_2(y), \quad (G.4)
\]

which is divided into \( I_b \) columns each of which is discretized into \( J_m \) equal intervals. The bottom and the top end points of each column in \( \Omega_f \) coincide respectively with the points in \( \Omega_1 \) and \( \Omega_2 \) with the same radial distance. The outer boundary points in \( \Omega_1 \) and \( \Omega_2 \) also coincide with the inner boundary point in \( \Omega_3 \).

Let the pressure or concentration be known everywhere at \( m \Delta \hat{t} \). Advancing the solutions to \( (m + 1) \Delta \hat{t} \) is carried out by the following steps. All individual one-dimensional equations are solved with a standard second-order implicit scheme of forward time, centered-space differences. The integral source terms are calculated with an approximate method described in Chapter 3.

1. Using the most recent quantities in \( \Omega_f \) for the interface terms, we first advance solutions by iterations in the three coarse layers satisfying the radial boundary and matching conditions. In each iteration the solutions in \( \Omega_1 \) and \( \Omega_2 \) are first obtained with the boundary value at \( \hat{r} = \hat{r}_b \) given by that of the last iterate in \( \Omega_3 \). The solution in \( \Omega_3 \) is then found with the flux at \( \hat{r}_b \) computed from the new iterates in \( \Omega_1 \) and \( \Omega_2 \). The iterations continue until satisfactory convergence is achieved. For the present study the iteration will stop when the relative difference between two consecutive iterates is less than \( 10^{-4} \) for all variables.

2. With the newly obtained solutions in \( \Omega_1 \) and \( \Omega_2 \) as the boundary values, we advance solutions in each column (except the one at the lens tip \( \hat{r} = \hat{r}_b \)) in the lens.

3. Repeat Steps 1 and 2 successively until satisfactory convergence of all solutions is achieved. The convergence criterion is the same as in Step 1.

By now the solution procedure is complete up to \((m + 1)\)th time step. The above
procedure is repeated for the next time step. The above scheme is applied to both
the flow and the transport problems. Nonlinearity in the flow equation is treated by
updating the pressure variable in the coefficients at each time of iteration.
Appendix H

Homogenization Theory for Aqueous Diffusion in an Aggregate With Trapped NAPL

H.1 Micro-cell and Physical Equations

As shown in Figure 5-1b, a microscale unit cell $\Omega$ within an aggregate is composed of the following domains: solid grains $\Omega_s$, immobile water $\Omega_w$, trapped NAPL $\Omega_o$, and residual air $\Omega_g$, separated by interfaces denoted by $\Gamma_{ws}$, $\Gamma_{wo}$ and $\Gamma_{go}$. We define the porosity of the aggregate as

$$\phi = (|\Omega_w| + |\Omega_o| + |\Omega_g|) / |\Omega|,$$  \hspace{1cm} (H.1)

and the fluid saturations as

\begin{align*}
\text{NAPL:} & \quad S_o = |\Omega_o| / (|\Omega_w| + |\Omega_o| + |\Omega_g|), \\
\text{water:} & \quad S_w = |\Omega_w| / (|\Omega_w| + |\Omega_o| + |\Omega_g|), \\
\text{air:} & \quad S_g = |\Omega_g| / (|\Omega_w| + |\Omega_o| + |\Omega_g|).
\end{align*}

(H.2)
Clearly the sum of the saturations equals unity: \( S_o + S_w + S_g = 1 \). The various phase fractions in a unit cell are therefore

\[
\frac{\Omega_s}{|\Omega|} = 1 - \phi \quad \text{for solid;}
\]
\[
\frac{\Omega_o}{|\Omega|} = \phi S_o \quad \text{for NAPL;}
\]
\[
\frac{\Omega_w}{|\Omega|} = \phi S_w \quad \text{for water;}
\]
\[
\frac{\Omega_g}{|\Omega|} = \phi S_g \quad \text{for air.} \tag{H.3}
\]

The equations for conservation of mass of component \( i \) in the different domains are:

\[
\frac{\partial C_{wi}}{\partial t} = D_{wi} \frac{\partial^2 C_{wi}}{\partial x_k \partial x_k} \quad \text{in } \Omega_w, \tag{H.4}
\]
\[
\frac{\partial C_{gi}}{\partial t} = D_{gi} \frac{\partial^2 C_{gi}}{\partial x_k \partial x_k} \quad \text{in } \Omega_g, \tag{H.5}
\]
\[
\frac{\partial C_{si}}{\partial t} = K_{ri} \left( K_{di} C_{wi}\mid_{\Gamma_{ws}} - C_{si} \right) \quad \text{in } \Omega_s, \tag{H.6}
\]

where \( D_{wi} \) and \( D_{gi} \) are respectively the diffusivities of component \( i \) in pure water and in pure air, \( K_{ri} \) is the desorption rate and \( K_{di} \) is the equilibrium sorption partition coefficient.

The boundary conditions along the interfaces are as follows. Assuming equilibrium partitions along the fluid interfaces, we may obtain from Raoult’s law:

\[
C_{wi} = \chi_i C_{wi}^{sat} \quad \text{on } \Gamma_{wo}, \tag{H.7}
\]
\[
C_{gi} = \chi_i C_{gi}^{sat} \quad \text{on } \Gamma_{go}, \tag{H.8}
\]

where \( C_{wi}^{sat} \) and \( C_{gi}^{sat} \) are respectively the saturation aqueous and vapor concentrations for pure component \( i \), and \( \chi_i \) is the mole fraction of component \( i \) in the NAPL mixture given by

\[
\chi_i = \frac{C_{ai}/M_i}{\sum_{j=1}^N C_{aj}/M_j} \tag{H.9}
\]

in which \( M_j \) are the molecular weights of the corresponding components. We also get
by relating the rate of mass change in trapped NAPL, vapor and sorbed phases to the aqueous flux along the corresponding interface:

\[
\frac{1}{|\Gamma_{wo}|} \frac{\partial}{\partial t} \left( \overline{C_{\alpha}} |\Omega_o| + \overline{C_{g|}} |\Omega_g| \right) = -D_{wi} \frac{\partial C_{wi}}{\partial x_k} n_k \quad \text{on } \Gamma_{wo}, \quad (H.10)
\]

and

\[
\frac{|\Omega_s| \rho_s}{|\Gamma_{ws}|} \frac{\partial \overline{C_{si}}}{\partial t} = -D_{wi} \frac{\partial C_{wi}}{\partial x_k} n_k \quad \text{on } \Gamma_{ws}, \quad (H.11)
\]

where the overbar denotes the average of the quantity over its local phase domain, and \( n_k \) is the unit normal vector to the interfaces directing away from the water phase.

H.2 Physical Scalings

1. Length Scales:
   
   Let \( \ell \) and \( \ell^a \) be the microscale and the aggregate length scales respectively. Their ratio

   \[
   \ell/\ell^a = \varepsilon \ll 1 \quad (H.12)
   \]

   will be used as the small perturbation parameter.

2. Time Scale:
   
   The time scale of interest \( T \) is that of aqueous diffusion across an aggregate:

   \[
   T = \ell^a/\ell^a \quad (H.13)
   \]

3. Diffusivities Ratio:
   
   As in previous studies, the following ratio is assumed:

   \[
   D_{wi}/D_g = O(\varepsilon^2) \quad (H.14)
   \]

4. Sorption Exchange Rate:
   
   Fast sorption/desorption between solid and aqueous phases (or \( K_r \gg T^{-1} \)) is
assumed. This is usually true for non-polar or hydrophobic compounds such as benzene and toluene. Specifically, we assume that

\[ K_r = O \left( \varepsilon^{-2} D_w / \ell^2 \right). \]  \hspace{1cm} (H.15)

5. Mass in NAPL:

Note that for any species the concentration in NAPL is always much higher than the aqueous and the vapor concentrations. For example,

\[ C_{wi} \sim X_i C_{wi}^{\text{sat}} = \frac{C_{wi}^{\text{sat}} / M_i}{\sum_{j=1}^{N} C_{oj} / M_j} C_{oi} \ll C_{oi} \]  \hspace{1cm} (H.16)

since the saturation aqueous molar concentration is typically three orders of magnitude smaller than the average molar concentration in the NAPL. For generality it is however desirable to consider a case in which the mass partitioned in the trapped NAPL is comparable to that in other phases. Therefore, we assume that

\[ C_{oi} S_o \sim C_{wi} S_w \sim C_{gi} S_g, \]  \hspace{1cm} (H.17)

which implies a relatively small NAPL saturation \( S_o \ll S_w \) in aggregates.

**H.3 Perturbation Equations**

Based on the above scalings, we may identify the relative order of magnitude of each term in the physical equations:

\[ \varepsilon^2 \frac{\partial C_{wi}}{\partial t} = D_{wi} \frac{\partial^2 C_{wi}}{\partial x_k \partial x_k} \quad \text{in } \Omega_w, \]  \hspace{1cm} (H.18)

\[ \varepsilon^4 \frac{\partial C_{gi}}{\partial t} = D_{gi} \frac{\partial^2 C_{gi}}{\partial x_k \partial x_k} \quad \text{in } \Omega_g, \]  \hspace{1cm} (H.19)

\[ \varepsilon^2 \frac{\partial C_{si}}{\partial t} = K_{ri} \left( K_{di} C_{wi} |_{\Gamma_{ws}} - C_{st} \right) \quad \text{in } \Omega_s, \]  \hspace{1cm} (H.20)
and in the boundary conditions:

\[ \varepsilon^2 \frac{1}{|\Gamma_{wo}|} \frac{\partial}{\partial t} \left( \overline{C}_{oi}|\Omega_o| + \overline{C}_{gi}|\Omega_g| \right) = -D_{wi} \frac{\partial C_{wi}}{\partial x_k} n_k \quad \text{on } \Gamma_{wo}, \quad (H.21) \]

\[ \varepsilon^2 \frac{|\Omega_s| \rho_s \frac{\partial C_{si}}{\partial t}}{|\Gamma_{ws}|} = -D_{wi} \frac{\partial C_{wi}}{\partial x_k} n_k \quad \text{on } \Gamma_{ws}. \quad (H.22) \]

Let us now obtain the perturbation equations by substituting the following expansions into the above equations:

\[ C \rightarrow C^{(0)} + \varepsilon C^{(1)} + \varepsilon^2 C^{(2)} + \cdots \quad (H.23) \]

and

\[ \frac{\partial}{\partial x_k} \rightarrow \frac{\partial}{\partial x_k} + \varepsilon \frac{\partial}{\partial x_k^a}, \quad (H.24) \]

where \( x_k^a \) are the coordinates on the aggregate scale.

### H.3.1 Leading Order Results

At this order, the transport equations (H.18)–(H.20) read

\[ 0 = D_{wi} \frac{\partial^2 C_{wi}^{(0)}}{\partial x_k \partial x_k} \quad \text{in } \Omega_w, \quad (H.25) \]

\[ 0 = D_{gi} \frac{\partial^2 C_{gi}^{(0)}}{\partial x_k \partial x_k} \quad \text{in } \Omega_g, \quad (H.26) \]

\[ 0 = K_{ri} \left( K_{di} C_{wi}^{(0)} \big|_{\Gamma_{ws}} - C_{si}^{(0)} \right) \quad \text{in } \Omega_s, \quad (H.27) \]

while the two flux conditions (H.21) and (H.22) give

\[ 0 = -D_{wi} \frac{\partial C_{wi}^{(0)}}{\partial x_k} n_k \quad \text{on } \Gamma_{wo}, \quad (H.28) \]

\[ 0 = -D_{wi} \frac{\partial C_{wi}^{(0)}}{\partial x_k} n_k \quad \text{on } \Gamma_{ws}. \quad (H.29) \]
We argue that the concentration gradient across the NAPL layer, because of its thinness, is so small that the concentration $C_{oi}$ is essentially constant, at least to the leading order, over the scale of a micro-cell. Then by virtue of above homogeneous transport equations and boundary conditions, we may infer that all concentrations are independent of the micro-scale coordinates, i.e.,

$$C_{oi}^{(0)} = C_{oi}^{(0)}(x_{k}, t), \quad C_{wi}^{(0)} = C_{wi}^{(0)}(x_{k}, t), \quad C_{gi}^{(0)} = C_{gi}^{(0)}(x_{k}, t), \quad C_{si}^{(0)} = C_{si}^{(0)}(x_{k}, t).$$

(H.30)

Furthermore, these concentrations may be related to one another using the equilibrium partition interface conditions (H.7), (H.8) and (H.27):

$$C_{wi}^{(0)} = \chi_{i}^{(0)} C_{wi}^{s} \quad C_{gi}^{(0)} = \chi_{i}^{(0)} C_{gi}^{s} = H_{i} C_{wi}^{(0)}, \quad C_{si}^{(0)} = K_{di} C_{wi}^{(0)},$$

(H.31)

where $H_{i} = C_{gi}^{s} / C_{wi}^{s}$ is the Henry’s law constant for component $i$, and

$$\chi_{i}^{(0)} = \frac{C_{oi}^{(0)} / M_{i}}{\sum_{j=1}^{N} C_{oj}^{(0)} / M_{j}}.$$

(H.32)

It will be more convenient if we can express $C_{oi}$ explicitly in terms of $\chi_{i}$. This is possible on assuming the NAPL being an ideal mixture of which the total volume is the sum of the partial volumes of the components:

$$\sum_{j=1}^{N} C_{oj} / \rho_{oj} = 1,$$

(H.33)

where $\rho_{oj}$ are the liquid densities of the pure components. With the above relationship, we may write for the leading order

$$C_{oi}^{(0)} = \frac{\chi_{i}^{(0)} M_{i}}{\sum_{j=1}^{N} \chi_{j}^{(0)} M_{j} / \rho_{oj}} = \frac{C_{wi}^{(0)} M_{i} / C_{wi}^{s}}{\sum_{j=1}^{N} C_{wj}^{(0)} M_{j} / (C_{wj}^{s} \rho_{oj})}.$$

(H.34)
H.3.2 First Order Results

At $O(\varepsilon)$, we only need to consider the equation and boundary conditions for $\Omega_w$:

\[
0 = D_{wi} \frac{\partial}{\partial x_k} \left( \frac{\partial C_{wi}^{(1)}}{\partial x_k} + \frac{\partial C_{wi}^{(0)}}{\partial x_k^a} \right) \quad \text{in } \Omega_w, \quad (H.35)
\]

\[
0 = -D_{wi} \left( \frac{\partial C_{wi}^{(1)}}{\partial x_k} + \frac{\partial C_{wi}^{(0)}}{\partial x_k^a} \right) n_k \quad \text{on } \Gamma_{wo}, \quad (H.36)
\]

\[
0 = -D_{wi} \left( \frac{\partial C_{wi}^{(1)}}{\partial x_k} + \frac{\partial C_{wi}^{(0)}}{\partial x_k^a} \right) n_k \quad \text{on } \Gamma_{ws}. \quad (H.37)
\]

Still at this order the aqueous diffusion is in a steady-state with no phase exchange between all other phases. The condition (H.36) implies that the total mass of component $i$ in the NAPL and in the residual air is conserved up to this order.

We may now represent $C_{wi}^{(1)}$ in terms of the global gradient of $C_{wi}^{(0)}$:

\[
C_{wi}^{(1)} = -A_l \frac{\partial C_{wi}^{(0)}}{\partial x_l^i} \quad (H.38)
\]

where $A_l(x_k, x_k^a)$ are $\Omega$-periodic cell functions governed by

\[
0 = \frac{\partial^2 A_l}{\partial x_k \partial x_k} \quad \text{in } \Omega_w, \quad (H.39)
\]

with the boundary condition

\[
\frac{\partial A_l}{\partial x_k} n_k = n_l, \quad \text{on } \Gamma_{wo} \text{ and } \Gamma_{ws}. \quad (H.40)
\]

H.3.3 Second Order Results

At $O(\varepsilon^2)$, the unsteady local change terms first appear in the aqueous diffusion equations and interface conditions:

\[
\frac{\partial C_{wi}^{(0)}}{\partial t} = D_{wi} \frac{\partial}{\partial x_k} \left( \frac{\partial C_{wi}^{(2)}}{\partial x_k} + \frac{\partial C_{wi}^{(1)}}{\partial x_k^1} \right) + D_{wi} \frac{\partial}{\partial x_k^a} \left( \frac{\partial C_{wi}^{(1)}}{\partial x_k} + \frac{\partial C_{wi}^{(0)}}{\partial x_k^a} \right), \quad \text{in } \Omega_w, \quad (H.41)
\]
\[
\frac{1}{|\Gamma_{wo}|} \frac{\partial}{\partial t} \left( C_{oi}^{(0)} |\Omega_o| + C_{gi}^{(0)} |\Omega_g| \right) = -D_{wi} \left( \frac{\partial C_{wi}^{(2)}}{\partial x_k} + \frac{\partial C_{wi}^{(1)}}{\partial x_k^a} \right) n_k \quad \text{on } \Gamma_{wo}, \quad (H.42)
\]
\[
\frac{|\Omega_s| \rho_s \partial C_{si}^{(0)}}{|\Gamma_{ws}|} \frac{\partial t}{\partial t} = -D_{wi} \left( \frac{\partial C_{wi}^{(2)}}{\partial x_k} + \frac{\partial C_{wi}^{(1)}}{\partial x_k^a} \right) n_k \quad \text{on } \Gamma_{ws}. \quad (H.43)
\]

By taking \( \Omega \)-average of (H.41) and using (H.38) and Gauss theorem, we obtain
\[
\phi S_w \frac{\partial C_{wi}^{(0)}}{\partial t} = \frac{\partial}{\partial x_k^a} \left[ \phi S_w (D_{wi}^*)_{kl} \frac{\partial C_{wi}^{(0)}}{\partial x_l^a} \right] + \frac{1}{|\Omega|} \iint_{\Gamma_{wo} + \Gamma_{ws}} D_{wi} \left( \frac{\partial C_{wi}^{(2)}}{\partial x_k} + \frac{\partial C_{wi}^{(1)}}{\partial x_k^a} \right) n_k d\Gamma \quad \text{in } \Omega_w, \quad (H.44)
\]
where
\[
(D_{wi}^*)_{kl} = D_{wi} \left( -\frac{|\Omega|}{|\Omega_w|} \left( \frac{\partial A_i}{\partial x_k} \right)_w + \delta_{kl} \right) \quad (H.45)
\]
is the effective aqueous diffusivity in the porous aggregate which is a function of the microstructure and the water content inside the aggregate.

The boundary terms on the right-hand side of (H.44) are evaluated using (H.42) and (H.43):
\[
\frac{1}{|\Omega|} \iint_{\Gamma_{wo}} D_{wi} \left( \frac{\partial C_{wi}^{(2)}}{\partial x_k} + \frac{\partial C_{wi}^{(1)}}{\partial x_k^a} \right) n_k d\Gamma = -\frac{\partial}{\partial t} \left( C_{oi}^{(0)} \frac{|\Omega_o|}{|\Omega|} + C_{gi}^{(0)} \frac{|\Omega_g|}{|\Omega|} \right) = -\frac{\partial}{\partial t} \left( \phi S_o C_{oi}^{(0)} + \phi S_g C_{gi}^{(0)} \right), \quad (H.46)
\]
\[
\frac{1}{|\Omega|} \iint_{\Gamma_{ws}} D_{wi} \left( \frac{\partial C_{wi}^{(2)}}{\partial x_k} + \frac{\partial C_{wi}^{(1)}}{\partial x_k^a} \right) n_k d\Gamma = -\frac{|\Omega_s| \rho_s \partial C_{si}^{(0)}}{|\Omega|} \frac{\partial t}{\partial t} = -(1 - \phi) \rho_s \frac{\partial C_{si}^{(0)}}{\partial t}. \quad (H.47)
\]

Putting back these boundary terms into (H.44) and assuming isotropy for the medium, we finally get the effective aqueous diffusion equation in an aggregate:
\[
\frac{\partial C_{oi}^{(0)}}{\partial t} = \frac{\partial}{\partial x_k} \left[ \phi S_w D_{wi}^* \frac{\partial C_{wi}^{(0)}}{\partial x_k^a} \right], \quad (H.48)
\]
\[305\]
where $C_{ai}(x_k^a, t)$ is the aggregate concentration, or the total mass of component $i$ per bulk volume of aggregate, given by

$$C_{ai}^{(0)} = \phi \left[ S_o C_{ai}^{(0)} + S_w C_{wi}^{(0)} + S_g C_{gi}^{(0)} + (1 - \phi) \rho_s C_{si}^{(0)}/\phi \right].$$

(H.49)

Using (H.31), (H.34) and the fact that $C_{gi} \ll C_{ai}$, we may express $C_{ai}^{(0)}$ solely in terms of $C_{wi}^{(0)}$:

$$C_{ai}^{(0)} = \phi (S_o \alpha_i + 1) \beta_i C_{wi}^{(0)}$$

(H.50)

where

$$\alpha_i = \frac{M_i/(C_{wi}^{sat} \beta_i)}{\sum_{j=1}^{N} C_{wj}^{(0)} M_j/(C_{wj}^{sat} \rho_{oj})},$$

(H.51)

and

$$\beta_i = S_w + (1 - S_w) H_i + (1 - \phi) K_{di} \rho_s / \phi.$$

(H.52)

For a spherical and homogeneous aggregate of radius $a$, the effective aqueous diffusion equation may be written in terms of the radial distance $r$ from the center as

$$\frac{\partial}{\partial t} [ (S_o \alpha_i + 1) C_{wi} ] = \frac{S_w D_{wi}^{*}}{\beta_i r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_{wi}}{\partial r} \right) \quad 0 < r < a \quad (i = 1, \ldots, N),$$

(H.53)

where the superscripts $(0)$ and $a$ have been omitted.
Appendix I

Numerical Method of Solution for the Problem in Chapter 5

Similar numerical schemes are used for the problems in §5.6 and §5.7. Here we explain the numerical steps only in terms of the radial flow problem considered in §5.7. For this problem, we anticipate rapid variations near the well and need better resolution for small \( \tilde{r}' \) in solving the macroscale problem. A transformed coordinate for the macro-radial distance is introduced:

\[
y = \ln(\tilde{r}'/\tilde{r}_w')
\]

(I.1)

so that the macroscale vapor transport equation (5.36) can be written as

\[
\frac{\partial \tilde{C}'}{\partial t} = -\frac{\partial}{\partial \tilde{r}} \left(S_o' \alpha_i' \tilde{C}'_{g_i} \right) - \frac{1}{\tilde{r}^2} \frac{\partial}{\partial \tilde{y}} \left( \tilde{r}' \tilde{u} \tilde{C}'_{g_i} \right) + \frac{1}{P_{e_i}} \frac{\partial^2 \tilde{C}'}{\partial \tilde{y}^2} - \xi_i \frac{\partial \tilde{C}_{ai}}{\partial t}.
\]

(I.2)

On summing the above equation for all components and using (5.40), we get

\[
\frac{\partial}{\partial t} \left(S_o' \sum_{i=1}^{N} \chi_{i0} \alpha_i' \tilde{C}'_{g_i} \right) = \sum_{i=1}^{N} \chi_{i0} \left\{ -\frac{1}{\tilde{r}^2} \frac{\partial}{\partial \tilde{y}} \left( \tilde{r}' \tilde{u} \tilde{C}'_{g_i} \right) + \frac{1}{P_{e_i}} \frac{\partial^2 \tilde{C}'_{g_i}}{\partial \tilde{y}^2} - \xi_i \frac{\partial \tilde{C}_{ai}}{\partial t} \right\}.
\]

(I.3)

For computational convenience, we also introduce the following change of variable
for the microscale aggregate diffusion problem:

\[ \dot{C}_{wi} = \psi / \hat{r} \]  

(I.4)

so that (5.42), (5.45)–(5.47) can be rewritten as

\[ \frac{\partial \psi_i}{\partial t} = -\frac{\partial}{\partial \hat{r}} (S_o \alpha_i \psi_i) + \sigma_i \frac{\partial^2 \psi_i}{\partial \hat{r}^2}, \]  

(I.5)

\[ \sum_{i=1}^{N} \chi_{i0} \psi_i = \hat{r}, \]  

(I.6)

\[ \psi_i = 0 \quad \text{at} \quad \hat{r} = 0; \quad \psi_i = \hat{C}''_{gi} \quad \text{at} \quad \hat{r} = 1. \]  

(I.7)

The aggregate concentration (5.48) is also rewritten as

\[ \dot{C}_{ai} = (S_o \alpha_i + 1) \psi_i / \hat{r}. \]  

(I.8)

Summing (I.5) for all components and using (I.6), we get

\[ \frac{\partial}{\partial \hat{r}} \left( S_o \sum_{i=1}^{N} \chi_{i0} \alpha_i \psi_i \right) = \sum_{i=1}^{N} \chi_{i0} \sigma_i \frac{\partial^2 \psi_i}{\partial \hat{r}^2}. \]  

(I.9)

The above problems are solved with an alternate-direction-iterative finite-difference scheme. With uniform discretizations, the grid points are located at \( y = (I - 1) \Delta y \) where \( I = 1, \cdots, I_m \) macroscopically and at \( \hat{r} = (J - 1) \Delta \hat{r} \) where \( J = 1, \cdots, J_m \) microscopically. Advancing the solutions from \( \hat{t} = n \Delta t \) to the new time \( (n + 1) \Delta t \) is achieved by iterations of the following steps:

1. The \((k + 1)\)th iterate of \((S'_o)_I^{n+1, k+1}\) is obtained from (I.3):

\[ (S'_o)_I^{n+1, k+1} = \left[ \left( S'_o \sum_{i=1}^{N} \chi_{i0} \alpha'_i \hat{C}'_{gi} \right)_I^n + \sum_{i=1}^{N} \chi_{i0} (ADS_i)_I^{n+1, k} \right] / \left( \sum_{i=1}^{N} \chi_{i0} \alpha'_i \hat{C}'_{gi} \right)_I^{n+1, k} \]  

(I.10)
where

\[(ADSi)^{n+1,k}_I = -\frac{\Delta t}{4\Delta y^2 r_f^2} \left[ (\hat{r}'\hat{u}\hat{C}'_{gi})_{I+1}^{n+1,k} - (\hat{r}'\hat{u}\hat{C}'_{gi})_{I-1}^{n+1,k} + (\hat{r}'\hat{u}\hat{C}'_{gi})_{I+1}^n - (\hat{r}'\hat{u}\hat{C}'_{gi})_{I-1}^n \right]
+ \frac{\Delta t}{2Pe_i\Delta y^2 r_f^2} \left[ (\hat{C}'_{gi})_{I+1}^{n+1,k} + (\hat{C}'_{gi})_{I-1}^{n+1,k} - 2(\hat{C}'_{gi})_{I}^{n+1,k} + (\hat{C}'_{gi})_{I+1}^n + (\hat{C}'_{gi})_{I-1}^n - 2(\hat{C}'_{gi})_{I}^n \right]
- \xi_i \left[ (\langle \hat{C}_{ai} \rangle)_{I}^{n+1,k} - (\langle \hat{C}_{ai} \rangle)_{I}^n \right]. \tag{I.11}\]

2. The \((k + 1)\)th iterate of \((\hat{C}'_{gi})_{I}^{n+1}\) is then obtained from (I.2):

\[(\hat{C}'_{gi})_{I}^{n+1,k+1} = (\hat{C}'_{gi})_{I}^{n} - (S_o)_{I}^{n+1,k+1} (\alpha'_i \hat{C}'_{gi})_{I}^{n+1,k}
+ (S'_o \alpha'_i \hat{C}'_{gi})_{I}^{n} + (ADSi)^{n+1,k}_I, \tag{I.12}\]

from which \((\alpha'_i)_{I}^{n+1,k+1}\) can be computed according to (5.37). It also updates the boundary value at \(\hat{r} = 1\) for \(\psi_i\) in the next two steps. Note that the above equation guarantees that \(\sum_{i=1}^N \chi_{i0} \hat{C}'_{gi}\) is always equal to the its initial value, which is prescribed to be unity.

3. The \((k + 1)\)th iterate of \((S_o)_{I,J}^{n+1}\) is obtained from (I.9):

\[\left(\sum_{i=1}^N \chi_{i0} \hat{C}'_{gi} \right)_{I,J}^{n+1,k} = \left[ \left(\sum_{i=1}^N \chi_{i0} \alpha_i \psi_i \right)_{I,J}^{n+1,k} + \sum_{i=1}^N \chi_{i0} \left(DFF_i\right)_{I,J}^{n+1,k} \right] / \left(\sum_{i=1}^N \chi_{i0} \alpha_i \psi_i \right)_{I,J}^{n+1,k}, \tag{I.13}\]

where

\[(DFF_i)_{I,J}^{n+1,k} = \frac{\sigma_i \Delta t}{2\Delta r^2} \left[ (\psi_i)_{I,J+1}^{n+1,k} + (\psi_i)_{I,J-1}^{n+1,k} - 2(\psi_i)_{I,J}^{n+1,k} + (\psi_i)_{I+1,J}^{n} + (\psi_i)_{I-1,J}^{n} - 2(\psi_i)_{I,J}^{n} \right]. \tag{I.14}\]
4. The \((k + 1)\)th iterate of \((\psi_i)_{I,J}^{n+1}\) is then obtained from (I.5):

\[
(\psi_i)_{I,J}^{n+1,k+1} = (\psi_i)_{I,J}^n - (S_o)_{I,J}^{n+1,k+1} (\alpha_i \psi_i)_{I,J}^{n+1,k} + (S_o \alpha_i \psi_i)_{I,J}^n + (DF_i)_{I,J}^{n+1,k},
\]

(I.15)

from which \((\alpha_i)_{I,J}^{n+1,k-1}\) can be computed according to (5.43). The aggregate concentration \((\hat{C}_{ai})_{I,J}^{n+1,k+1}\) is then calculated according to (I.8), whose mean value will be used in Steps 1 and 2 of the next iteration for an updated source term in (I.11). Again the above equation guarantees that \(\sum_{i=1}^N \chi_{ai} \psi_i\) is always equal to its initial value, which is prescribed to be \(\hat{r}\).

The above steps are repeated successively until the relative difference between two consecutive iterates is less than \(10^{-4}\) for all variables. For computations in the radial flow problem, the following discretizations are used: \(\Delta y = 0.05756\), \(\Delta \hat{r} = 0.02\), \(\Delta t = 0.001\), \(I_m = 81\) and \(J_m = 51\). We have found that the number of iterations required to march one time step is typically less than 5.
Bibliography


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