Homogenization theory applied to soil vapor extraction in aggregated soils

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The macroscale equations governing the convective diffusion of a volatile organic compound during soil vapor extraction in the vadose zone composed of aggregated soils 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-scaled media. 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 capillarity and viscous forces, (iii) the aggregates are much smaller than the macroscale, and (iv) diffusion in the aggregates is much weaker 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. © 1996 American Institute of Physics.

I. INTRODUCTION

Organic substances such as gasoline leaked into the subsurface can pose a long-term threat to the quality of groundwater. These compounds are often sufficiently soluble to render the groundwater undrinkable. The vapors of these compounds can migrate in the unsaturated zone to affect a far greater extent than the original spill site, by contaminating building basements or the atmosphere above the ground surface.

Soil vapor extraction (SVE) is the major technology of cleaning up unsaturated soils (vadose zone) contaminated with volatile organic compounds (VOC).1,2 An SVE system 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 As the contaminated air is withdrawn, the local chemical equilibrium is upset, inducing the transfer of contaminant from the dissolved phase, the non-aqueous phase liquid (NAPL) and the sorbed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.1–6 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 multi-component system, the macroscale effective transport equations for a nonreactive \( \alpha \)-component in the various phases, can be written in general form as follows.7–9 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, \( u \) 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; \( j=g,w,o \)):
  \[
  \frac{\partial}{\partial t} \left( \theta S_j c_j^\alpha \right) = -\nabla \cdot \left[ \theta S_j \left( c_j^\alpha \bar{u}_j + \bar{J}_j^\alpha \right) \right] + \sum_i I_{ji}^\alpha, \\
  \]
  \( i=g,w,o,s \);

- Solid phase:
  \[
  \frac{\partial}{\partial t} \left( \rho_b c_s^\alpha \right) = \sum_i I_{ji}^\alpha, \quad i=g,w,o. 
  \]

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

\[
I_{ji} = -I_{ij} \quad \text{and} \quad S_g + S_w + S_o = 1. 
\]

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.10 Since most subsurface environments are humid, direct sorptive exchange between vapor and solid may also be ignored.11 Different models have been proposed with regard to the description of the interphase transfer:

(i) **Local equilibrium model.** In early developments,10,12,13 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 air and NAPL by Raoult’s law, and that between sorbed solid and water by the sorption isotherm relationship. With these laws of partition, the four transport equations (1) and (2) can be summed to eliminate the interphase mass transfer terms to give a single equation for the concentration in one phase.

However, many vapor extraction experiments indicate that in the absence of liquid organic phase, the effluent con-
centration often shows very long tailing behavior.\textsuperscript{14,15} Vapor concentrations usually drop rapidly to a low level at the early stage of vapor extraction, but during a temporary shutdown, they are often found to increase again.\textsuperscript{16,17} 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.

(ii) Empirical first-order kinetic model. In the vadose zone, soils composed mainly of medium to fine grains tend to form aggregates which are surrounded by air-filled macropores. It is reasonable to assume that the micropore fluid velocity is negligible as compared to that in the macropores. Solute movement in the immobile region is dominated by molecular diffusion, while that in the mobile region is accomplished by advection and diffusion/dispersion. For nonvolatile solute transport in saturated soils, a typical one-dimensional formulation is given by van Genuchten and Wierenga\textsuperscript{18}

\begin{equation}
\theta_m \frac{\partial c_m}{\partial t} + \left( \theta_{im} + \rho_b K_d \right) \frac{\partial c_{im}}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial z^2} - u_m \theta_m \frac{\partial c_m}{\partial z},
\end{equation}

(4)

\begin{equation}
\left( \theta_{im} + \rho_b K_d \right) \frac{\partial c_{im}}{\partial t} = \alpha (c_m - c_{im}),
\end{equation}

(5)

where the subscripts $m$ and $im$ refer to mobile and immobile regions respectively, $c_{im}$ is average concentration in the im-

mobile region, $\theta$ is volume fraction of the region, and $D$ is the dispersion coefficient. The inter-phasal transfer is assumed to obey a first-order relation (5) with an empirical coefficient $\alpha$. This model is not justified theoretically and also lacks sufficient experimental support.

(iii) Aggregate diffusion model. A more basic model takes into account the details on the aggregate level or the microscale.\textsuperscript{19–23} Diffusion in an aggregate saturated by immobile water is described by a radial diffusion equation, and the concentration at the boundary equals that in the mobile region at the same macrosopic location. By assuming a soil matrix of spherical aggregates, one can solve for the micr-

oscale diffusion problem to get $c_{im}$ which can be used to determine the mass exchange rate $\partial c_{im}/\partial t$ where

\begin{equation}
\overline{c}_{im} = \frac{3}{a} \int_0^a r^2 c_{im} dr,
\end{equation}

(6)

in which $r$ is the radial coordinate, and $a$ is the aggregate radius. In this way, the empirical first-order relation (5) is avoided.

The radial diffusion model was originally developed by heuristic reasoning for mass and heat transfer in a liquid-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 Rosen,\textsuperscript{24} Pellett\textsuperscript{25} and Rasmussen and Neretnieks.\textsuperscript{26} More recently, Hornung\textsuperscript{27} has given a mathematical justification of the aggregate-diffusion model by the method of homogenization. Goltz and Roberts\textsuperscript{28} were the only authors to have applied the diffusion model to a three-dimensional transport problem. They stud-

ied analytically solute transport due to an instantaneous point source in aggregated soils in the presence of a uniform groundwater flow.

For one-dimensional VOC transport in the vadose zone, the spherical aggregate/diffusion model has been combined with the first-order kinetics hypothesis by Gierke et al.\textsuperscript{14} They also added a number of hypotheses requiring coefficients which are unavailable from existing experiments. Brusseau\textsuperscript{29} 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 also 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. Similar first-order kinetic relations have also been used by McCoy and Rolston\textsuperscript{30} 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.

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. It has been applied by us\textsuperscript{31} to compare with column tests where all the physical or chemical coefficients are either measured or reliably estimated.

In this work we aim to derive the governing equations for soil vapor extraction in aggregated soils, previously ob-

tained by heuristic arguments. The following qualitative assumptions are first made 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.

(2) Residual NAPL is not present in the soil matrix, or has already been volatilized into vapor phase. 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).

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

For computational simplicity, the microstructure is here assumed to be a periodic array of spherical aggregates whose size can vary only slowly over the macroscale. 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 shapes. Modification of the present theory can in principle be made by augmenting the numerical effort in solving the type of cell problems to be described.

II. SCALES ESTIMATES AND PHYSICAL PARAMETERS

For the idealized model just described, we wish to estab-

lish first the practical relevance of certain scaling assump-
We first let over the global length scale, $L$, and $l$ are the microscopic and macroscopic length scales respectively; their ratio $l/L = \epsilon \ll 1$ will be the small ordering parameter. Further let $U_g$, $D_g$ 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 $Re = U_g/l$. Typical air velocity in SVE operations is in the order of 0.1 mm/s. Assuming an aggregate size of $O(1-10)$ mm, and using $\nu = 0.15$ cm$^2$/s, we get $Re = O(10^{-2} - 10^{-3})$. Specifically we shall assume that

$$Re = O(\epsilon).$$

(b) Pore Péclet number $Pe = U_g/l$. Typical diffusivity in air $D_g$ is in the order of 0.1 cm$^2$/s, which is comparable to kinematic viscosity of air. Hence we shall take

$$Pe = O(Re) = O(\epsilon).$$

(c) Ratio of diffusivities $D_w/D_g$. Typical diffusivity of chemical compounds in pure water is in the order of $10^{-5}$ cm$^2$/s. Because of impedance by solid grains, the effective value in aggregate solution, $D_w$, can be as low as $O(10^{-7})$ cm$^2$/s. Therefore the ratio of diffusivities $D_w/D_g$ is $O(10^{-4} - 10^{-6})$, and we shall make the important assumption that

$$\frac{D_w}{D_g} = O(\epsilon^2).$$

(d) Time scales. On dimensional grounds there are three time scales in this transport problem: (i) time for diffusion through an aggregate, $L^2/D_w$; (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 assumptions (8) and (9) imply that all these time scales are comparable. We first let

$$T = \frac{l^2}{D_w}.$$ 

Then by $l = \epsilon L$ and assumption (9) it follows immediately that $T = O(L^2/D_g)$. Furthermore

$$\frac{L^2}{D_g} = \frac{L}{D_g} \frac{U_g}{U_g} = \frac{Pe}{\epsilon} \frac{L}{U_g}. $$

Therefore by condition (8) we also have $T = O(L/U_g)$. As numerical estimates, we take $D_w = 10^{-7}$ cm$^2$/s, then $T \sim 1$ day for $l = 1$ mm, and $T \sim 100$ days for $l = 1$ cm.

Assuming cubic packing, a microcell $\Omega$ is of cubic shape and linear dimension $l$ (Fig. 1). Centered in each cell is a spherical aggregate of radius $a$ which may vary slowly in space. Let the surface of the aggregate be $\Gamma_{ga}$ and be described mathematically by $F(x_i) = 0$. Also the aggregate domain $\Omega_g$ corresponds to $F(x_i) > 0$, and the gas domain $\Omega_a$ corresponds to $F(x_i) < 0$. Then the gradient of the function $F$ will give the normal vector to $\Gamma_{ga}$ 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

$$\langle f \rangle_g = \frac{1}{|\Omega_g|} \int \int \int_{\Omega_g} f d\Omega, \quad \text{and} \quad \langle f \rangle_a = \frac{1}{|\Omega|} \int \int \int_{\Omega_a} f d\Omega.$$ 

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.

III. AIR FLOW

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

$$\frac{\partial u_i}{\partial x_i} = 0,$$

and the momentum equation is

$$\rho u_i \frac{\partial u_j}{\partial x_j} = - \frac{\partial p}{\partial x_i} + \mu \frac{\partial^2 u_i}{\partial x_j \partial x_j} + \frac{\mu}{3} \frac{\partial^2 u_i}{\partial x_i \partial x_j},$$

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

$$\frac{pM}{R_g \Theta} = \rho.$$ 

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 0.2 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, the scale of pressure variation \( P \) is characterized by \( \mu LU_x^2/\ell^2 \) over the global length scale \( L \). In terms of the normalized variables (distinguished by a prime):
\[
 x_i = l x_i', \quad p = P p', \quad u_i = U_x u_i', \quad \rho = \frac{PM}{R_x \Theta} \rho',
\]
the dimensionless Navier-Stokes equations are
\[
 \frac{\partial p' u_i'}{\partial x_i'} = 0, \tag{17}
\]
\[
 \frac{\partial p'}{\partial x_i'} = \epsilon (\frac{\partial^2 u_i'}{\partial x_i' \partial x_j'} + \frac{1}{3} \frac{\partial^2 u_j'}{\partial x_i' \partial x_j'}) - \epsilon \Re p' u_i' \frac{\partial u_i'}{\partial x_j'}. \tag{18}
\]

Use has been made of (15) and the isothermal assumption so that \( p \sim \rho \). Since \( \Re \) has been assumed to be of order \( \epsilon \), the last term in (18) is of order \( \epsilon^2 \).

From here on let us return to physical variables but keep the ordering parameter for identification,
\[
 \frac{\partial p u_i}{\partial x_i} = 0, \tag{19}
\]
\[
 \frac{\partial p}{\partial x_i} = \epsilon \mu (\frac{\partial^2 u_i}{\partial x_i \partial x_j'} + \frac{1}{3} \frac{\partial^2 u_j'}{\partial x_i \partial x_j'}) - \epsilon^2 \rho u_i \frac{\partial u_i}{\partial x_j}. \tag{20}
\]

Let us introduce the local and global coordinates \( x_i \) and \( X_i = \epsilon x_i \), and the multiple-scale expansions
\[
 u_i = u_i^{(0)} + \epsilon u_i^{(1)} + \cdots, \quad p = p^{(0)} + \epsilon p^{(1)} + \cdots, \tag{21}
\]
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), one gets at the leading order \( O(\epsilon^0) \)
\[
 p^{(0)} = p^{(0)}(X_i), \tag{22}
\]
and
\[
 \frac{\partial u_i^{(0)}}{\partial x_i} = 0. \tag{23}
\]

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 (20) vanishes by virtue of (23). The resulting problem can be represented in terms of the global pressure gradient by
\[
 u_i^{(0)} = -\frac{K_{ij}}{\mu} \frac{\partial p^{(0)}}{\partial x_j}, \tag{24}
\]
\[
 p^{(1)} = -A_j \frac{\partial p^{(0)}}{\partial x_j} + \tilde{p}^{(1)}, \tag{25}
\]
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
\[
 \frac{\partial K_{ij}}{\partial x_i} = 0 \text{ in } \Omega_g, \tag{26}
\]
with the boundary conditions
\[
 K_{ij} = 0 \text{ on } \Gamma_{gu}, \tag{28}
\]
\[
 K_{ij} \text{ and } A_j \text{ are } \Omega - \text{periodic}, \tag{29}
\]
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 (24) gives Darcy’s law
\[
 \langle u_i^{(0)} \rangle_g = -\frac{\langle K_{ij} \rangle_g}{\mu} \frac{\partial p^{(0)}}{\partial x_j}. \tag{30}
\]

On averaging the \( O(\epsilon) \) continuity equation and using Gauss theorem, we get the leading order global continuity equation
\[
 \frac{\partial}{\partial X_i} (p^{(0)} \langle u_i^{(0)} \rangle_g) = 0. \tag{31}
\]

Equations (30) and (31) 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 (30) and (31) to yield the nonlinear equation for \( p^{(0)} \),
\[
 \frac{\partial}{\partial X_i} \left( \frac{K}{\mu} p^{(0)} \frac{\partial p^{(0)}}{\partial X_i} \right) = 0. \tag{32}
\]

So far \( K \) can still be a function of \( X_i \). If we further assume a homogeneous soil, \( K \) reduces to a constant and (32) can be simplified as
\[
 \frac{\partial^2 (p^{(0)})^2}{\partial X_i \partial X_j} = 0. \tag{33}
\]

Hence for a steady air flow in an isotropic and homogeneous porous medium, the leading order pressure \( p^{(0)} \) may readily be determined from (33) with appropriate global boundary conditions; the leading order specific discharge \( \langle u_i^{(0)} \rangle_g \) is then found from (30).

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 (31) would be replaced by
\[
 \frac{\partial}{\partial t} \frac{\partial (\theta_g p^{(0)})}{\partial t} + \frac{\partial}{\partial x_i} (p^{(0)} \langle u_i^{(0)} \rangle_g) = 0. \tag{34}
\]

With the help of (30), the time scale required to approach steadiness is readily seen to be
\[
 T_i = O \left( \frac{\theta_g \mu L^2}{K P} \right). \tag{35}
\]

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

A. Solute transport in air

We begin with the microscopic vapor transport equation

\[
\frac{\partial c_g}{\partial t} + \frac{\partial}{\partial x_i} (u_i c_g) = D_g \frac{\partial^2 c_g}{\partial x_i \partial x_i}.
\]  (36)

Normalizing \(x_i\) and \(u_i\) according to (16), and

\[c_s = c_g c_g', \quad t = (L/U_g) t',\]

where \(c_{g0}\) is a characteristic value for the vapor concentration, we may write (36) as

\[
\varepsilon \frac{\partial c_g'}{\partial t} + \frac{\partial}{\partial x_i} (u_i c_g') = \frac{1}{\varepsilon} \frac{\partial^2 c_g'}{\partial x_i \partial x_i}.
\]  (38)

Recall that the pore Péclet number \(Pe = O(\varepsilon)\) as estimated in (8). We may now return to physical variables but retain \(\varepsilon\) for ordering identification:

\[
\frac{\partial c_g}{\partial t} + \frac{\partial}{\partial x_i} (u_i c_g) = D_g \frac{\partial^2 c_g}{\partial x_i \partial x_i}.
\]  (39)

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

\[
0 = D_g \frac{\partial^2 c_g^{(0)}}{\partial x_i \partial x_i},
\]  (40)

\[
\frac{\partial}{\partial x_i} (u_i^{(1)} c_g^{(0)}) = D_g \left( \frac{\partial^2 c_g^{(1)}}{\partial x_i \partial x_i} + 2 \frac{\partial c_g^{(0)}}{\partial x_i} \right),
\]  (41)

\[
\frac{\partial c_g^{(0)}}{\partial t} + \frac{\partial}{\partial x_i} (u_i^{(1)} c_g^{(1)} + u_i^{(0)} c_g^{(0)}) + \frac{\partial}{\partial X_i} (u_i^{(0)} c_g^{(0)})
\]

\[
= D_g \frac{\partial}{\partial x_i} \left( \frac{\partial c_g^{(2)}}{\partial x_i} + \frac{\partial c_g^{(1)}}{\partial x_i} \right) + D_g \frac{\partial}{\partial X_i} \left( \frac{\partial c_g^{(1)}}{\partial x_i} + \frac{\partial c_g^{(0)}}{\partial x_i} \right).
\]  (42)

B. 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

\[
c_a = (1 - \phi) \rho_s c_s + \phi c_w,
\]  (43)

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

\[
c_s = K_d c_w,
\]  (44)

where \(K_d\) is the sorption partition coefficient. Then (43) may be written as

\[
c_a = [K_d (1 - \phi) \rho_s + \phi] c_w.
\]  (45)

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

\[
\frac{\partial c_a}{\partial t} = \phi D_w \frac{\partial^2 c_w}{\partial x_i \partial x_i}.
\]  (46)

Substituting (45) for \(c_a\), the diffusion equation becomes

\[
\frac{\partial c_w}{\partial t} = D_e \frac{\partial^2 c_w}{\partial x_i \partial x_i},
\]  (47)

where \(D_e\) is the diffusivity in an aggregate effectively retarded by sorptive exchange:

\[
D_e = \frac{\phi D_w}{K_d (1 - \phi) \rho_s + \phi}.
\]  (48)

By (9), it follows that

\[
\frac{D_e}{D_g} = O(\varepsilon^2).
\]

Following similar normalization procedures as for the vapor transport equation, we may show that both sides of (47) are of the same order, as expected. Introducing multiple-scale expansions \(c_w = c_w^{(0)} + \cdots\), the leading order equation is clearly

\[
\frac{\partial c_w^{(0)}}{\partial t} = D_e \frac{\partial^2 c_w^{(0)}}{\partial x_i \partial x_i}.
\]  (50)

C. Microscale boundary conditions

Boundary conditions on gas-aggregate interface \(\Gamma_{ga}\):

(a) Continuity of flux: In terms of physical variables,

\[
D_g \frac{\partial c_g}{\partial x_i} n_i = \phi D_w \frac{\partial c_w}{\partial x_i} n_i,
\]

where

\[
n_i = \frac{\partial F/\partial x_i}{\partial F/\partial x_i},
\]

is the unit normal vector to \(\Gamma_{ga}\) directing into the aggregate. Note that by (9) the right-hand side of (51) is of order \(\varepsilon^2\) 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 macroporosity is allowed to vary slowly in space. After expanding for \(c_g\), \(c_w\) and \(x_i\), we obtain the following boundary conditions

\[
D_g \left( \frac{\partial c_g^{(0)}}{\partial x_i} + \frac{\partial c_g^{(1)}}{\partial X_i} \right) \frac{\partial F}{\partial x_i} + D_g \frac{\partial c_g^{(0)}}{\partial X_i} \frac{\partial F}{\partial X_i} = 0,
\]  (53)

\[
D_g \left( \frac{\partial c_g^{(2)}}{\partial x_i} + \frac{\partial c_g^{(1)}}{\partial X_i} \right) \frac{\partial F}{\partial x_i} + D_g \frac{\partial c_g^{(1)}}{\partial X_i} \frac{\partial F}{\partial X_i} + D_g \frac{\partial c_g^{(0)}}{\partial X_i} \frac{\partial F}{\partial X_i} = 0.
\]  (54)

(b) Partition: On the aggregate level, local equilibrium dominates along the gas-water interface as a result of the
high gas molecular velocity.\textsuperscript{36} 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,

$$H = \frac{c_g^{(m)}}{c_w} (m = 0, 1, 2, \ldots) \text{ on } \Gamma_{ga}. \quad (56)$$

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, $c_g^{(m)}$ ($m = 0, 1, 2, \ldots$) are $\Omega$-periodic.

D. Effective transport equations on the macroscale

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

\textit{O(1):} From (40) and (53), it is obvious that

$$c_g^{(0)} = c_g^{(0)}(X_i, t). \quad (57)$$

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

\textit{O($\epsilon$):} By (57) and (23), (41) now becomes

$$0 = D_g \frac{\partial^2 c_g^{(1)}}{\partial x_i \partial x_j}. \quad (58)$$

Since $c_g^{(1)}$ satisfies the linear boundary condition (54), we let

$$c_g^{(1)} = -N_i \frac{\partial c_g^{(0)}}{\partial x_i}, \quad (59)$$

which implies a canonical boundary value cell problem for $N_i(x, X_i)$:

$$\frac{\partial^2 N_i}{\partial x_i \partial x_j} = 0, \quad (60)$$

subject to the boundary conditions

$$\frac{\partial N_i}{\partial x_i} \frac{\partial F}{\partial x_j} = \frac{\partial F}{\partial x_i} \text{ along } \Gamma_{ga}. \quad (61)$$

Furthermore $N_i$ must be $\Omega$-periodic along the cell boundaries. Once $N_i$ are solved, the first-order correction $c_g^{(1)}$ may be determined in terms of $\partial c_g^{(0)} / \partial x_i$ from (59).

\textit{O($\epsilon^2$):} We first find $\Omega$-average of (42). 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\textsuperscript{32}

$$\frac{\partial f_i}{\partial x_i} = \frac{\partial}{\partial x_i} \langle f_i \rangle_g + \frac{1}{|\Omega|} \int_{\Gamma_{ga}} \int_{\Gamma_{ga}} \frac{\partial F}{\partial x_i} d\Gamma, \quad (62)$$

where $f_i$ is any vector in $\Omega_g$. This result is essentially the same as the spatial averaging theorem in the method of volume averaging.\textsuperscript{33,39} In particular for all convection-related terms which are proportional to $u_i$, the surface integral on the right-hand side of (62) vanishes because of zero velocity at the aggregate boundary. For these terms microscale averaging and macroscale differentiation can be interchanged. With (62), we average (42) over the $\Omega$-cell and obtain after using Gauss theorem and substituting (59),

$$\frac{\partial c_g^{(0)}}{\partial t} + D_g \frac{\partial}{\partial x_i} \langle (u_i^{(0)})_g c_g^{(0)} \rangle = \frac{\partial}{\partial x_i} \left[ D_g \left( -\left( \frac{\partial N_i}{\partial x_i} \right)_g + \theta_g \delta_i \right) \frac{\partial c_g^{(0)}}{\partial x_i} \right] + I_{ga}. \quad (63)$$

where $\theta_g = [\Omega_g/|\Omega|] \text{ is the macroporosity, } \delta_i$ is the Kronecker delta, and

$$I_{ga} = \frac{1}{|\Omega|} \int_{\Gamma_{ga}} D_g \left[ \frac{\partial c_g^{(2)}}{\partial x_i} + \frac{\partial c_g^{(1)}}{\partial x_i} \right] \frac{\partial F}{\partial x_i} d\Gamma \quad (64)$$

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

We next take $\Omega$-average of (50) and use also Gauss theorem to obtain

$$\frac{\partial c_g^{(0)}}{\partial t} = -\frac{1}{|\Omega|} \int_{\Gamma_{ga}} D_e \frac{\partial c_w^{(0)}}{\partial x_i} \frac{\partial F}{\partial x_i} d\Gamma. \quad (65)$$

Since $D_e$, $D_w$ and $\phi$ are independent of microscale coordinates, the right-hand side of (65) is equal to $- (D_e / (\phi D_w)) I_{ga}$ by virtue of the boundary condition (55). Therefore the source term can be expressed as

$$I_{ga} = \frac{\phi D_w \theta_a}{D_e} \frac{\partial c_w^{(0)}}{\partial t}, \quad (66)$$

Substituting $I_{ga}$ from (66) into (63), we obtain

$$\frac{\partial c_g^{(0)}}{\partial t} + \frac{\partial}{\partial x_i} \left( \theta_g u_i^{(0)} c_g^{(0)} \right) - \frac{\partial}{\partial x_i} \left( \theta_g (D_g^{*})_{il} \frac{\partial c_g^{(0)}}{\partial x_i} \right) = -\frac{\phi D_w \theta_a}{D_e} \frac{\partial c_w^{(0)}}{\partial t}, \quad (67)$$

where

$$u_i^{(0)} = \langle u_i^{(0)} \rangle_g / \theta_g \quad (68)$$

is the effective air seepage velocity in which $\langle u_i^{(0)} \rangle_g$ can be found from Darcy’s law (30), and

$$(D_g^{*})_{il} = \frac{\partial N_i}{\partial x_i} / \theta_g + D_g \delta_{il} \quad (69)$$

is the effective air diffusivity in the unsaturated soil matrix. It can be shown that the tensor $(D_g^{*})_{il}$ is symmetric and positive definite for any microstructure.\textsuperscript{41} Note from the cell problem (60)–(61) that $N_i$ depends only on the cell geometry, but not the flow. It follows that $(D_g^{*})_{il}$ is a function of the aggregate structure only but not the flow. In other words the hydrodynamical dispersion is relatively unimportant by

virtue of (8). This has been pointed out previously by Johnson et al.,13 Gierke et al.,14 and Brusseau.29
To find the source term on the right-hand side of (67), we first find \( c_w^{(0)}(x_i, t) \) from (50) and (56) where \( c_g^{(0)} \) is uniform in a local cell. For the simple geometry of spherical aggregates, the problem reduces to

\[
\frac{\partial c_w^{(0)}}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_w^{(0)}}{\partial r} \right),
\]

(70)

with the boundary condition

\[
c_w^{(0)}(r=a, X_i, t) = c_g^{(0)}(X_i, t)/H,
\]

(71)

and the initial concentration is a function of global coordinates only

\[
c_w^{(0)}(r, X_i, t=0) = c_w(0)(X_i).
\]

(72)

Solution for (70)–(72) can be found from Carslaw and Jaeger41

\[
c_w^{(0)} = -\frac{2}{a r} \sum_{n=1}^{\infty} (-1)^n \exp(-\lambda_n t) \sin \left( \frac{n \pi r}{a} \right)
\times \left\{ \frac{a^2}{n^2 \pi^2 c_w^{(0)} + \frac{n \pi D_e}{H} \int_0^t \exp(\lambda_n \tau) c_g^{(0)} d\tau} \right\},
\]

(73)

where

\[
\lambda_n = \frac{n^2 \pi^2 D_e}{a^2}.
\]

(74)

The \( \Omega_{a}\)-average of \( c_w^{(0)} \) is

\[
\langle c_w^{(0)} \rangle = \frac{3}{a} \int_0^a r^2 c_w^{(0)} dr = \frac{6 D_e}{a^2} \sum_{n=1}^{\infty} \exp(-\lambda_n t) \left[ \frac{c_w^{(0)}}{H} \right] \lambda_n
\times \left( \frac{c_w^{(0)}}{H} \right) \int_0^t \exp(\lambda_n \tau) c_g^{(0)} d\tau \right].
\]

(75)

Differentiating (75) with respect to time, and integrating by part, we get

\[
\frac{\partial c_w^{(0)}}{\partial t} = \frac{6 D_e}{a^2} \sum_{n=1}^{\infty} \exp(-\lambda_n t)
\times \left( \frac{c_w^{(0)}}{H} \right) \int_0^t \exp(\lambda_n \tau) \frac{\partial c_g^{(0)}}{\partial \tau} d\tau
\right].
\]

(76)

where \( c_w^{(0)}(X_i, t=0) = c_w^{(0)}(X_i) \) 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 \( c_w^{(0)} = c_w^{(0)}/H \) and the two terms inside the parentheses in (76) cancel each other. Finally substitution of (76) into (67) gives the macrotransport equation for the vapor phase solute

\[
\frac{\partial c_g^{(0)}}{\partial t} + \frac{\partial}{\partial X_i} \left( \theta_g u_i \frac{\partial c_g^{(0)}}{\partial X_i} \right) = -\frac{6 \phi D_w \theta_a}{H \gamma_g} \sum_{n=1}^{\infty} \int_0^t \exp(-\lambda_n (t-\tau)) \frac{\partial c_g^{(0)}}{\partial \tau} d\tau.
\]

(77)

In summary, one first finds \( p^{(0)} \) from (32) or (33), \( \langle u_i^{(0)} \rangle \) from (30), and then solves for \( c_g^{(0)} \) from (77) and \( c_w^{(0)} \) from (75). 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.19,20 and others cited before. Theoretically it is an extension of Hornung27 for diffusion of nonvolatile solute in saturated porous media.

E. Normalization and dimensionless parameters

Let us further assume that the soil matrix is isotropic and homogeneous so that \( (D_e)_{ij} \) reduces to \( D_e \delta_{ij} \) 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 prime):

\[
c_g^{(0)} = c_g^{(0)}/H, \quad c_w^{(0)} = \frac{(c_w^{(0)}/H) c_w^{(0)}}{H}, \quad X_i = L X_i',
\]

(78)

\[
t = (L/H) t', \quad u_i^{(0)} = u_i^{(0)}/H,
\]

the normalized forms of (77) and (75) are

\[
\frac{\partial c_g^{(0)}}{\partial t'} + \frac{\partial}{\partial X_i'} \left( \theta_g^{(0)} u_i^{(0)} \frac{\partial c_g^{(0)}}{\partial X_i'} \right) = -6 \xi \sigma \int_0^t \exp(-\lambda_n (t'-\tau')) \frac{\partial c_g^{(0)}}{\partial \tau'} d\tau',
\]

(79)

\[
\frac{\partial c_w^{(0)}}{\partial t'} + \frac{\partial}{\partial X_i'} \left( \theta_g^{(0)} u_i^{(0)} \frac{\partial c_w^{(0)}}{\partial X_i'} \right) = -\int_0^t \exp(-\lambda_n (t'-\tau')) c_g^{(0)} d\tau',
\]

(80)

where

\[
\xi = \frac{\phi D_w \theta_a}{H \gamma_g}, \quad \sigma = \frac{D_e L}{a^2 U_g}, \quad \lambda_n' = n^2 \pi^2 \sigma.
\]

(81)

(82)

(83)

(84)

Physically \( \xi \) 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:

\[
\frac{c_w^{(0)}}{c_g^{(0)}} = \frac{(\phi D_w / D_e) (c_w^{(0)}/H) \theta_a}{\phi D_w \theta_a / H D_e \gamma_g} = \xi,
\]

(85)
where in the first step use has been made of (45) 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.

V. LIMITING CASES

A. 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 (70) for $c_w$, the aggregate effective diffusion time scale can be estimated as

$$T_a = O \left( \frac{a^2}{D_e} \right) = O \left( \frac{a^2 (K_p (1 - \phi) \rho_s + \phi)}{D_w} \right).$$

(86)

The vapor concentration $c_v$ 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 $T_g > T_a$ which is equivalent to $\sigma > 1$, the aggregate diffusion reaches the steady state almost instantly. Then condition (71) holds not only on the boundary but throughout an aggregate, i.e.,

$$c_w^{(0)} (r, X_i, t) = c_w^{(0)} (X_i, t)/H, \quad 0 \leq r \leq a, \quad t > 0,$$

(87)

which implies local equilibrium between $c_w^{(0)}$ and $c_g^{(0)}$ macroscopically. When this is true, (67) can be simplified as

$$R \frac{\partial c_v^{(0)}}{\partial t} + \frac{\partial}{\partial X_i} \left( D_g^{(0)} \frac{\partial c_v^{(0)}}{\partial X_i} \right) = 0,$$

(88)

where $R$ is the retardation factor

$$R = 1 + \frac{\phi D_w \theta_g}{H D_e \theta_g} = 1 + \xi.$$

(89)

As a mathematical confirmation, we note that $\lambda_n = n^2 \pi^2 \sigma > 1$ when $\sigma > 1$. The integral on the right-hand side of (79) may be approximated by considering contributions from the neighborhood of $\tau' = t'$, according to Laplace’s method. Thus

$$\text{RHS(79)} = -6 \xi \sigma \sum_{n=1}^{\infty} \int_0^{t'} \exp \left[ -\lambda_n \left( t' - \tau' \right) \right] \frac{\partial c_v^{(0)}}{\partial \tau'} d \tau'$$

$$\approx -6 \xi \sigma \sum_{n=1}^{\infty} \int_0^{t'} \exp \left[ -\lambda_n (t' - \tau') \right] d \tau'$$

$$\approx -6 \xi \sigma \sum_{n=1}^{\infty} \frac{1}{\lambda_n}$$

$$= -\frac{6 \xi}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} = -\xi \frac{\partial c_v^{(0)}}{\partial t},$$

(90)

which gives (88) also.

B. Small $\xi$ with $\sigma \approx O(1)$

If the Henry’s law constant is so large that $\xi \approx 1$, very little amount of VOC is partitioned in the aggregates. Then the right-hand side of (79) becomes negligible as compared to the left-hand side as long as $\sigma \approx O(1)$; the vapor transport equation is reduced to

$$\frac{\partial c_g^{(0)}}{\partial t} + \frac{\partial (\bar{u} c_g^{(0)})}{\partial X_i} - \frac{1}{\rho c c_g^{(0)}} \frac{\partial^2 c_g^{(0)}}{\partial X_i^2} = 0,$$

(91)

which is independent of $\sigma$. While the normalized aqueous concentration can be calculated from (80) and still depends on $\sigma$, the physical value of $c_w^{(0)}$ is small compared to $c_g^{(0)}$, though it may be unacceptably high to meet the water quality standard.

VI. CONCLUDING REMARKS

In this paper we have given a mathematical derivation of 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. (9)]. In the more general case there is a mixture of air and water in the macropores; the problem must be dealt with as a multiphase flow, and is not treated here. The method of homogenization is used in order to identify the range of validity of the theory. For computational simplicity all aggregates are assumed to be uniform spheres. The derived effective equations on the macroscale are Darcy’s law and the continuity for a compressible gas, and (77) 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.

In a separate paper, $^{31}$ we have applied the deduced effective equations to SVE with unidirectional and radial flows. In the first case the theory with just three dimensionless parameters has been successfully compared to existing experiments in a column where physical and chemical coefficients are either measured or reliably estimated. Further extension to porous media with three scales (aggregates, layers, and macroscale) will be reported in the future.

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$^{3}$D. J. Wilson, A. N. Clarke, and J. H. Clarke, “Soil clean up by in-situ


