Review of Recent Insights on Physical Behavior of Gases in Porous Media : Theoretical and experimental Investigations on Density Driven Gas Flow

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Abstract

Under natural conditions, forces such as gravity, temperature, and pressure gradients in the soil coupled with diffusive fluxes will control the fate of gaseous contaminants. The assumptions underlying the basic equations of diffusive and advective gas transport processes in soil are discussed. To test the traditional equations for gas transport, laboratory experiments were conducted to explore the transport of a dense gas (freon-113) through columns of air-dry Oso-Flaco sand with a large concentration of freon-113 maintained at the inlet to the columns. Gas densities (concentrations) were monitored at the inlet and the outlet and within the columns during transport. Significant differences in fluxes and density profiles were observed for the three primary flow directions (horizontal, vertically upward, vertically downward) at high source densities. Numerical models based on the standard Darcy-Fickian transport equation did not fit the measured fluxes. Slip flow was found to be significant relative to Darcy advective flow, but did not account for the discrepancy between model simulations and data. Further theory development was necessary in order to ascertain why the standard equations did not adequately describe the diffusive and advective transport processes for dense gases. New equations governing the transport of gaseous chemicals in porous media were derived by applying the method of volume averaging to the point equations for mass and momentum flux. The form of the new transport parameters provide possible explanations for discrepancies between experimental and numerical modeling results for systems where neither diffusive nor advective driving forces dominate.

Key words : dense gas, gaseous contaminant, slip flow, diffusive and advective gas transport, volume averaging technique

Introduction

An understanding of the transport of gas-phase chemicals in porous media is important in determining the fate of many soil and vadose zone gases and contaminants. Numerous physical and chemical properties and the way these properties interact and vary through time and space will control gas-phase contaminant transport. Gas-phase fluxes in the vadose zone will generally be controlled by some combination of driving forces due to gravity and gradients in pressure, temperature, and concentration. Physical and chemical parameters such as permeability, porosity, diffusion, and sorption coefficients will exert control over the magnitude of the fluxes of interest.

Modeling of gas transport in situations of environmental concern has generally been accomplished by utilizing equations that have been successfully employed to describe liquid transport processes. Liquids and gases will, for

example, behave differently in their interactions with the solid-phase in porous media. This becomes quite clear in examining the assumptions which underlie Darcy's Law, the standard liquid phase advective velocity expression. Darcy's Law is based on the assumption that velocity at the pore walls is equal to zero. In the gas phase, however, if transport occurs in the region where neither advection nor diffusion is dominant, this assumption will be invalid. The form of the advective velocity expression may need to be altered to account for the non-zero velocity at the pore walls (slip velocity). The slip velocity accounts for only one of a number of factors that must be examined in order to arrive at a thorough understanding of the physics of gas transport in porous media.

The objectives of this study were to examine the validity of the traditional gas-phase transport equations for porous media and to explore any modifications that must be made to the equations based on an in-depth examination of the assumptions which underlie the traditional equations. Transport experiments were conducted and compared with the output of a numerical model based on traditional and new transport equations.

Physics of Gas Transport

Diffusion velocities of gas mixtures in soil are related to each other in a complex manner dependent upon the mole fraction of each gas, the molar fluxes of each gas, and the binary diffusion coefficient of each gas pair. Curtiss and Hirschfelder (1949) gave the general equations for steady transport of a multicomponent mixture of gases, based on gas kinetic theory. If gravity effects are ignored or diffusion occurs only horizontally (and diffusion occurs for vertical distances no greater than $100\,\mathrm{m}$), the well-known Stefan-Maxwell (SM) equations provide the theoretical framework for diffusion of gases in soils. The SM equations (Amali and Rolston, 1993) are :

$$\sum_{j=1, j\neq i}^{v} \frac{y_i J_j - y_j J_i}{D_{ij}} = -\frac{P}{RT}\frac{dy_j}{dx} \qquad [1]$$

where J_j is the molar flux density [moles/(soil area x time)] for species j, y_j is the vapor mole fraction for species j, D_{ij} is the effective binary diffusion coefficient in soil of species i in j (or vice versa), *P is the total gas mixture pressure (Pa)*, T is the mixture temperature ($^\circ$K), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and x is the spatial coordinate.

Fick's law for diffusion is a restrictive case of the SM equations. Jaynes and Rogowski (1983) concluded that Fick's law would result in incorrect estimations of mass distributions and mass fluxes for systems containing more than two vapor components when the concentrations of the diffusing species are not negligible compared to the bulk phase gas. Amali and Rolston (1993) showed that if the total mole fraction of volatile organic chemical (VOC) vapors in air exceeded about 0.05, Fick's law fluxes deviated from the true diffusive flux for each species by up to 5%. This indicated that the total mole fraction of the diffusing species also needs to be considered in addition to the requirement of Leffelaar (1987) that the binary diffusion coefficients of the diffusing species must be sufficiently different for multicomponent effects to be observed.

Thus, Fick's law is generally applicable for only a few special cases. One of these cases is for the diffusion of a trace gas in a binary mixture, meaning that the mole fraction of the tracer gas is small. The second special case is for diffusion of two gases in a closed system (total pressure remains constant). In this case, neither gas needs to be in trace amounts. Therefore, if Fick's law is to be used as the basis for any method of measuring the soil gas diffusivity, the method should satisfy one or more of these conditions.

Assuming that the special case conditions are met, Fick's law is given by

$$\frac{M_g}{At} = f_g = -D_p\frac{\partial C_g}{\partial x} \qquad [2]$$

where M_g is the amount of gas diffusing (g gas),

A is the cross-sectional area of the soil (m^2 soil), t is time (s), f_g is the gas flux density (g gas m^{-2} soil s^{-1}), C_g is concentration in the gaseous phase (g gas m^{-3} soil air), x is distance (m soil), and D_p is the soil-gas diffusion coefficient (m^3 soil air m^{-1} soil s^{-1}). The unsteady diffusion of a gas, which is nonreactive (physically, biologically, and chemically), is described by the combination of Fick's law (Eq. [2]) and the continuity equation

$$f_a \frac{\partial C_g}{\partial t} = D_p \frac{\partial^2 C_g}{\partial x^2} \qquad [3]$$

where f_a is the soil-air content (m^3 air m^{-3} soil).

For cases where external forcing occurs causing pressure gradients or driving forces due to density differences, advective processes need to be considered in addition to the diffusive processes given by Eq. [2] and [3]. The traditional equations for diffusive and advective gas-phase mass and momentum conservation in a binary system can be represented, in one dimension as (Altevogt *et al.,* 2003 a)

$$\text{Mass:} \quad \underbrace{\left[f_u + \rho_{bulk} \frac{aQ}{(1+a\rho_F)^2} \right]}_{\text{Retardation Coefficient}} \frac{\partial \rho_F}{\partial t} = \frac{\partial}{\partial z}$$

$$\underbrace{\left[\rho D_P \frac{\partial \omega_F}{\partial z} \right]}_{\text{Fickian Diffusive Flux}} - \frac{\partial}{\partial z} \underbrace{[\rho_F v_z]}_{\text{Advective Flux}} \qquad [4]$$

$$\text{Momentum:} \quad v_z = - \underbrace{\frac{K_z}{\mu} \left[\frac{dP}{dz} + \rho g \right]}_{\text{Darcy Velocity}} + \underbrace{\left[\frac{D_p \frac{d\omega_F}{dz}}{\omega_F + \alpha} \right]}_{\text{Slip Velocity}} \quad [5]$$

where ρ_{bulk} is the bulk density of the soil (kg soil/m^3 soil), a and Q are measured adsorption/desorption rate constants for the Langmuir isotherm (m^3 gas/kg freon and kg freon/kg soil, respectively), ρ_F is density of the tracer gas (kg freon/m^3 gas), t is time (s), z is distance (m soil), ρ is total gas phase density (kg gas/m^3 gas), ω_F is mass fraction of the tracer gas (kg freon/kg gas), v_z is total advective velocity (m^3 gas m^{-2} soil s^{-1}), μ is mixture viscosity (Pa s), K_z is permeability (m^3 gas/m soil), P is total gas

phase pressure (Pa), g is gravitational acceleration (m/s^2), and α is a factor in the slip velocity expression. Adsorption of the gas can be described by a Langmuir isotherm. The Darcy velocity term takes into account an advective component due to differences in gas density. The slip velocity term arises from the non-equimolar flux for gases that are not in trace amounts and have very different diffusion coefficients.

Materials and Methods

Experiments were conducted in an apparatus consisting of a stainless steel cylinder packed with Oso-Flaco sand with large chambers on either end. The volumes of the inlet and outlet chambers were 31 and 16.3 L, respectively, and were constructed of 3-mm thick stainless steel. The soil cylinder was 0.40 m long with an I.D. of 77 mm. Freon-113 (1,1,2 Trichloro- 1,2,2 triflouroethane) was utilized as the tracer gas due to its relatively high molecular weight and vapor pressure. Table 1 presents the physical and chemical properties of

Table 1 Physical and chemical characteristics of the experimental system

Packed Column Properties	
Bulk Density	1.57 g soil/m^3 soil
Permeability	2.74×10^{-11} m^3 gas/m soil
Oso-Flaco Sand Properties	
Mineral Density	2.61 g soil/m^3 soil particles
Mean Pore Diameter	5.3×10^{-5} m gas
Chemical Properties	
Freon 113	
Molecular Weight	187.39 g/mol
Vapor Pressue	0.44 atm (4.45×10^4 Pa)
Viscosity	1.03×10^{-5} Pa s
Binary Soil Gas Diffusion Coefficient	1.3×10^{-6} m^3 gas m^{-1} soil s^{-1}
"Air"	
Molecular Weight	28.81 g/mol
Viscosity	1.86×10^{-5} Pa s

the experimental system. All parameters were measured independently.

Experiments were run in a 25℃ constant temperature room. Experiments were initiated by injecting a measured amount of liquid freon into the vented inlet chamber and allowing it to vaporize. A plunger connecting the chamber to the soil cylinder was kept closed until the freon had fully vaporized and its concentration had stabilized. The plunger was then pulled and freon was allowed to enter the soil. During transport experiments, gas samples were taken with $50\,\mu L$ gas sampling syringes (Hamilton) through mininert (VICI Inc.) ports located along the soil cylinder and in the inlet and outlet chambers and analyzed on a gas chromatograph. Experiments were conducted in three separate configurations : vertically upward (inlet at the bottom of the system), vertically downward (inlet at the top), and horizontally. For more information on the experiments, see Altevogt *et al.* (2003 a, 2003 c).

Results and Discussion

Comparison of Numerical Modeling Output with Experimental Data

Figure 1 presents model output plotted with measured data for a vertically downward transport experiment conducted at an approximate inlet freon-113 density of 1.86 mg/mL. Figure 1 a contains the results for flux at the soil

column outlet. Fig. 1b compares the measured freon density profiles at 5 and 25 cm from the inlet chamber with model output. In both figures, it is clear that the traditional transport equations (Eqs. [4] and [5]) are far from adequate for describing experimental data. It should be noted that many previous studies might have missed this result due to the use of fitted dispersion coefficients. It should be noted that these equations do not include a mechanical dispersion term. The highest velocity encountered in all of our experiments was 6.2×10^{-4} m/s. Utilizing this value along with the mean pore diameter (estimated from mean particle size) and diffusion coefficient from Table 1 yields a Peclet number of 0.025. This is the maximum value of the Peclet number that was encountered, and it lies well below the criteria value of 1 (Aris 1956, Bear 1988, Auriault and Adler 1995). This means that mechanical dispersion will be negligible for all of the flow regimes of interest in this study. The slip velocity was accounted for only by utilizing the expression in Eqs. [4] and [5].

Volume Averaged Transport Equations

Based on the poor fit of the traditional equations to the experimental data, additional theoretical analysis was conducted. The fully coupled equations derived in the volume averaging work of Altevogt *et al.* (2003 b) can be represented as
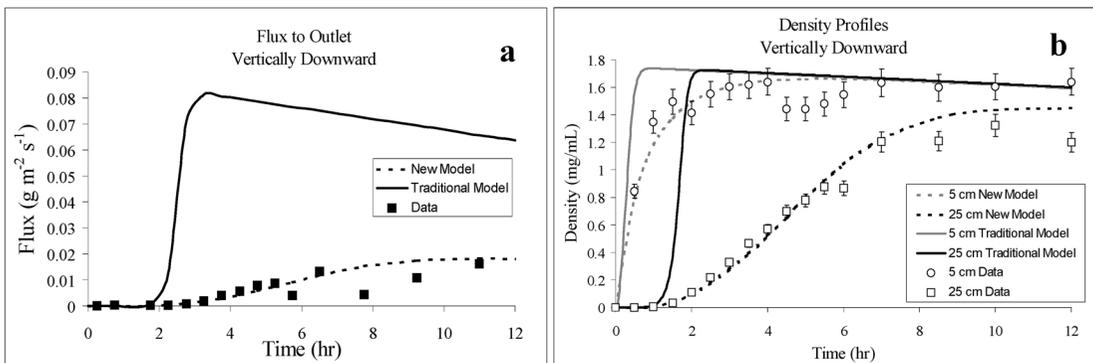

Fig. 1 Comparison of data and numerical models for vertically downward data. Flux to the outlet chamber (a) and density profiles (b). $q = 0.65$ for new model output.

Mass :

$$\underbrace{\left[f_u + \rho_{bulk}\,\frac{aQ}{(1+a\rho_F)^2}\right]}_{\text{Retardation Coefficient}} \frac{\partial\rho_F}{\partial t} = \frac{\partial}{\partial z}$$

$$\underbrace{\left[\rho D_P \frac{\partial\omega_F}{\partial z}\right]}_{\text{Fickian Diffusive Flux}} - \underbrace{\frac{\partial}{\partial z}\left[\rho_F v_z\right]}_{\text{Traditional Advective Flux}} + \frac{\partial}{\partial z}$$

$$\underbrace{\overbrace{q}^{\substack{\text{Coupled}\\\text{Closure}\\\text{Variable}\\\text{Estimate}}}\rho_F\ v_z}_{\substack{\text{Newly Derived}\\\text{Slip Coupling}\\\text{Term}}} \qquad [6]$$

Momentum :

$$v_z = -\underbrace{\frac{K_z}{\mu}\left[\frac{dP}{dz} + \rho g\right]}_{\text{Darcy Velocity}} + \underbrace{\left[\frac{D_p\,\frac{d\omega_F}{dz}}{\omega_F + \alpha}\right]}_{\text{Slip Velocity}} +$$

$$\underbrace{\left[\left(\frac{\rho_{bulk}aQ}{(1+a\rho_F)^2}\right)\left(\frac{\omega_F - 1}{\rho_F + \rho\alpha}\right)\frac{\partial\rho_F}{\partial t}\right]}_{\text{Sorptive Velocity}} \qquad [7]$$

The term q appears in Eq. [6] as a result of the order of magnitude estimate (Altevogt *et al.*, 2003 b) that the slip coupling term will be a linear function of the species density within the range $0.1 < q < 10$. Differences between Eqs. [4] and [5] and Eqs. [6] and [7] lie in the reduction in magnitude of the advective flux and the inclusion of a sorptive contribution to the velocity, both of which arise directly from microscale coupling of the mass and momentum equations. Equations were solved using a one-dimensional finite difference numerical technique.

The newly derived mass and momentum equations fit the data remarkably well with a fitted q value of 0.65. This value of $q = 0.65$ was equally applicable to cases of upward and horizontal transport (not shown). The model output from the new transport equations with $q = 0.65$ provides a very good match to the data. This corresponds well with our estimate that q should be of the order $0.1 < q < 10$. In order to obtain an exact expression for the slip coupling term in Eq. [6], it will be necessary to fully solve the coupled closure equations presented in Altevogt *et al.* (2003 b).

It must be noted that due to the high molecular mass of freon-113 relative to that of "air", the value of α will be minimized and the effects of slip magnified. For species with smaller differences in molecular mass, the value of the slip velocity will be greatly reduced. Secondly, freon-113 adsorbs weakly to the Oso-Flaco sand used in these studies as compared with other organic chemical/porous media combinations. Thus, the values of sorptive velocity will undoubtedly be higher in many situations.

Summary

Comparison of simulations using the traditional transport equations with data from column experiments using a dense gas (freon-113) clearly show that these equations are not adequate for describing transport of volatile chemicals in the region where neither diffusion nor advective processes dominate. Sensitive measurement of pressure within the soil column (Altevogt *et al.*, 2003 a) showed that the interaction between the non-equimolar diffusive flux and advection due to gravity produces significant pressure gradients within the soil that differ depending on flow direction. Newly derived transport equations, using volume averaging techniques, gave additional terms arising directly from microscale coupling of the mass and momentum equations. Simulations using the newly derived equations compared remarkably well with data. Further research is needed on the coupling term to evaluate the physical significance and degree of transferability to other systems.

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多孔質体中におけるガスの物理的挙動と密度流に関する洞察

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要　　旨

　自然条件下にある土壌では，重力勾配，温度勾配，圧力勾配などの力が拡散フラックスと関連してガス状汚染物質の消長をつかさどる。本論文では土壌中における移流拡散のガス輸送過程を記述する基礎方程式の各項の仮定について議論する。従来のガス輸送方程式を検証する目的で，砂カラム中の高比重ガス（フレオン-113）の輸送を詳細に調べる実験を行った。風乾した砂カラムの入口を高濃度に保ち，実験中のカラム出入口とカラム内のガス密度（濃度）を連続測定した。その結果，高密度では，水平・鉛直上向き・鉛直下向きの 3 方向で，フラックスと密度分布が大きく異なることが観察された。この実験結果は，標準的な輸送方程式による数値モデルでは再現できなかった。スリップ流が移流と比べて重要であることがわかったが，それを考慮しただけでは数値計算と実験結果の矛盾を説明できなかった。そこで，質量と運動量フラックスについて体積平均法をミクロスケールに適用することにより，多孔質体中におけるガス状汚染物質の輸送を支配する新しい方程式を誘導した。この方程式による数値モデルは高比重ガスの実験結果を良好に再現できることがわかった。

Dr. Rolston 講演に関する質疑

質問：

　提案された式の中に見られる slip coupling 項の q の値は，結論では変数として取り扱うとのことだが，御報告では定数として取り扱っていたように思うが，それでよいのか。

Rolston（カリフォルニア大）：

　前半では，下方へのガス移動について，これまでの式と新しい式との適合度の違いを示すための計算を行ったが，その場合には q は定数として取り扱った。この時の密度の高いガスの下方への移動は重力項のみによるものとした。一方，後半では新しい式の実際の現象への適用について検討したが，この場合に q は 0.1〜10 の数オーダー変化することになる。実験では二つのガスの相対濃度差が生じるように種々初期条件を与えて行ったため移流速度は少なくとも 2 オーダー，ガス濃度ではもっと大きな変化が生じたものと思われる。ただ，ガス濃度は実験中絶えず変化していたため，シミュレーションでは q はその平均値を用いている。

質問：

　新しいモデルでは，これまでのモデルとの違いが非定常状態では大きく，定常状態では小さくなると言えるのか。

Rolsoton：

　ガス移動のカラム実験においてはそれを判定するのは難しい。というのは，inlet 部でガス濃度が高く，outlet 部が 0 でガスが移動しているという状態から実験を開始するため，それから定常状態にまで持っていくというのは事実上不可能だ。ガス濃度は常に変化しており，カラム内どの点においても全て同じ濃度になるいわゆる平衡状態という意味での定常状態を実験で作り出すことは不可能といえる。

質問：

　水分量が飽和に近づくと q は 0 に近づいていくのか。

Rolston：

　水分量は関係ない。ここでいう飽和度とはガスの飽和程度を意味している。いま，一方のガスの相対濃度（C/C_0）が 0 に近づくということは，もう片方のガスの相対濃度が 1 に近づくことであり，これは単一ガス系となることを意味している。この場合には，今問題にしている 2 相ガス系の拡散や slip velocity の影響は全くなくなり，これまでの濃度差による拡散と圧力差による移流のみで表現できる現象となってしまう。q への影響は決して水分量ではない。なお，実験はかなり低い水分の一定条件下で行っている。

質問：

　それでは水分量増加によってどのようなことが起こるのか。

Rolston：

　水分が低下することによって，まず生じるのは拡散係数の低下であり，同様に通気性も低下することになる。この結果，ガス移動の移流，拡散画分が大幅に低下することになる。

質問：

　q への影響はないのか。

Rolston：

　水分変化に伴い変化するような要素は q の中には含まれていない。ただ，強いて言えば，水分の増加によって q は 0 へと近づいていき，結果として新たな式はこれまでの式に近づいていくことになる。

<div align="right">（文責：井上　久義）</div>