

Demonstration of the Discrepancies of Fick's Law and the Dusty Gas Model Predictions of Steady State Gaseous Fluxes in Soils with Small Pore Sizes

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Abstract: - Models for gas phase mass transport into natural soils have been frequently developed based on Fick's model (FM) and the dusty-gas model (DGM) and several studies have been reported to validate these models with experimental data for specific systems. It was concluded that the dusty-gas model is the most appropriate model to simulate gas transport phenomena into porous media, yet FM is still widely used because it does not require numerical solutions whereas the DGM does. Not to mention that in certain situations FM may provide a good approximation of the dusty-gas model, except in the case, but not limited to, of small pore sizes where only the DGM is recommended. This is due to the fact that Knudsen diffusion becomes more significant and must be considered. The DGM considers Knudsen diffusion and Fick's Law does not. These situations are encountered in any given soil profile because an increase in the soil moisture content changes both the air filled porosity, the pore sizes, and its shape, and thus may change the dominant diffusion mechanism. This paper presents simple scenarios to illustrate the discrepancies between the predictions of FM and the DGM for steady state gaseous fluxes from groundwater table towards the surface. Results indicate that for soils with very small pore sizes, the DGM always predicts higher fluxes.

Key-Words: - Steady State Flux; Fick's law; Dusty Gas Model; Moisture Content; methane; TCE; benzene; Pore Size

1 Introduction

The transport of gaseous components through porous media has been extensively studied over the years as described in many references [1, 2, 3, 4, 5, 6, and 7]. In general, mass transport of components inside porous media can be described using either the Fick's model (FM) or the dusty-gas model (DGM) as explained in [1, 2, 3, 4, 5, 6, and 7]. Both FM and the DGM are mass transport equations taking into account, molecular diffusion and the effect of a finite pressure gradient. The key feature of the DGM differs from that of FM in that the flux ratio in DGM depends on the square-root of gas molecular weight and it incorporates Knudsen Diffusion. Although the DGM is superior to FM in its capability to predict the fluxes inside porous media [8, 9, and 10] FM is more frequently used because it allows explicit analytical expressions to be derived for fluxes.

Soil pore size is one of the key parameters used to evaluate mass transport models in natural soils. This is because an appropriate mass transport model for large pore size may be not suitable for small pore size. When pore size is reduced, the Knudsen diffusion becomes predominant due to the decreasing capability of gas to diffuse inside the porous structure. It is obvious that pore size has no effect with using the FM, which is to be expected since Knudsen diffusion is not taken into consideration. DGM, in contrast, incorporates the Knudsen diffusion and the fluxes estimated from DGM should be equal to or higher than those obtained from the FM [11, 12, and 13].

For a given soil profile, soil moisture content reduces the volume of soil gas available for gaseous transport and changes the tortuosity and pore sizes. Generally an increase in the soil moisture content

decreases the pore sizes because part of the void space will be filled by water. At higher saturations, the reduction reaches a point where Knudsen diffusion has more impact on the overall diffusion rate even for soils with large pore size when dry [14, and 15]. Many correlations have been developed to estimate the effective binary diffusion coefficients based on the air filled porosity [16, and 17]. Yet the quantification of these effects is not straight forward and will be evaluated using the following examples.

Consequently, the objective of this paper is to evaluate the discrepancies in the gaseous fluxes predictions of FM and DGM for different soils conditions with variable pore sizes and air-filled porosities.

2 Model Development

For a single component, the mass transport equation can be written as

$$\frac{\varepsilon}{RT} \frac{\partial(y_i P)}{\partial t} = -\nabla \cdot N_i + r_i \text{ (mol m}^{-3} \text{ s}^{-1}\text{)} \quad (1)$$

where: ε represent the porosity; R is the gas constant; T is the temperature; y_i is the mole fraction of gas i ; P is the total pressure; t is the time; and N_i the rate of mass transport into porous media; and r_i is the rate of reaction inside the porous medium. The term on the left-hand side is valid when unsteady state is approached. The first and second terms on the right-hand side represent the diffusion rate and the rate of reaction inside the porous medium. For this study it is assumed that the diffusion process is at steady state and that the reactions take place at the boundaries rather than throughout the porous medium. Therefore, within the unsaturated vadose zone, only the first term on the right-hand side is significant, eqn. (1) therefore, becomes

$$\nabla \cdot N_i = 0 \quad (2)$$

The rate of mass transport, N_i , generally depends on the operating conditions (reactant concentration, temperature and pressure) and the microstructure of material (porosity, tortuosity and pore size). Two models were used to develop expressions for N_i : Fick's, and the dusty-gas models.

2.1 Fick's model (FM)

FM is the simplest form used to describe the transport of components through the gas phase and within porous media. The general form of this model for isobaric conditions is given by [1, 2, and 3]:

$$N_i = -\frac{D_i^{\text{eff}}}{RT} \frac{\partial(y_i P)}{\partial z} \quad (i = 1, \dots, n) \quad (3)$$

where D_i^{eff} the effective diffusivity of species i , and z is the vertical spatial coordinate.

2.2 Dusty-Gas Model (DGM)

The DGM takes into account Knudsen diffusion. It is assumed from this model that pore walls consist of giant molecules ('dust') uniformly distributed in space. These dust molecules are considered to be a dummy, or pseudo, species in the mixture. The general form of the DGM for isobaric conditions is given by [1, 2, and 3]:

$$\frac{N_i}{D_{i,k}^{\text{eff}}} + \sum_{j=1, j \neq i}^n \frac{y_j N_i - y_i N_j}{D_{ij}^{\text{eff}}} = -\frac{P}{RT} \frac{dy_i}{dz} \quad (4)$$

Summing eqn. (4) over the n species leads to the Graham's law of diffusion in gaseous mixtures [2]:

$$\sum_{i=1}^n N_i \sqrt{M_i} = 0 \quad (5)$$

where M_i is the molecular weight of component i . For two binary component systems eqn.(4) becomes:

$$\frac{N_1}{D_{1,k}^{\text{eff}}} + \frac{y_2 N_1 - y_1 N_2}{D_{12}^{\text{eff}}} = -\frac{P}{RT} \frac{dy_1}{dz} \quad (6)$$

Rearranging eqn. (6) gives,

$$N_1 \left(\frac{1}{D_{1,k}^{\text{eff}}} + \frac{y_2 - y_1 N_2/N_1}{D_{12}^{\text{eff}}} \right) = -\frac{P}{RT} \frac{dy_1}{dz} \quad (7)$$

Because $y_2 = 1 - y_1$ and $N_2/N_1 = -\sqrt{M_1/M_2}$

(Graham's law), N_1 can be written as follow:

$$N_1 = -\frac{P}{RT} \left[\frac{1 - \alpha y_1}{D_{12}^{\text{eff}}} + \frac{1}{D_{1,k}^{\text{eff}}} \right]^{-1} \frac{dy_1}{dz} \quad (8)$$

where

$$\alpha = 1 - \left(\frac{M_1}{M_2} \right)^{1/2} \quad (9)$$

Substituting eqn. (8) into eqn. (2) gives:

$$\frac{d^2 y_1}{dz^2} + \frac{\alpha}{D_{12}^{eff}} \left[\frac{1 - \alpha y_1}{D_{12}^{eff}} + \frac{1}{D_{1,k}^{eff}} \right]^{-1} \left(\frac{dy_1}{dz} \right)^2 = 0 \quad (10)$$

Eqn. (10) is in the form of an ordinary differential equation, which can be solved by using the two following initial conditions:

$$\text{IC.1:} \quad y_1|_{z=0} = y_{1, \text{saturation}} \quad (11)$$

$$\text{IC.2:} \quad y_1|_{z=\text{surface}} = 0 \quad (12)$$

3 Calculations and Examples

These examples are designed to simulate the steady state vertical transport of a gas from a source depth into sandy and clayey soils. It is assumed that the gas is generated at a depth equal to the depth of the water table, L, and transported to the surface due to diffusion only (no convective fluxes are considered). The gases considered in this study are methane, benzene, and trichloroethylene diffusing into air. These gases have been chosen because they are common contaminants and their molecular masses almost equally range from 16 to 131.4 g/mole. The air has been treated as one stagnant component that fills the soil pores. Benzene and TCE are assumed to have their saturated vapor pressures at the depths of the water table and zero pressure at the ground surface. Methane is assumed to have a molar fraction of 40% at the depth of the water table (the rest is air, i.e. = 60%) and zero molar fraction at the surface. Two soil profiles are considered, the first consists of homogeneous crushed Monterey dune sand and the other consists of Kaolinite clay. These soils have been chosen because they represent cases with large and small pore sizes (Kaolinite has an extremely small pores). For the purpose of comparison, the air filled porosity is assumed the same for both soils (=0.3). Crushed Dune Sand has an average diameter of 0.013 cm, average pore radius of 2.26 E-03 cm, porosity of 0.315, residual saturation of 0.015, and bulk density of 1.60 g/cm³. Kaolinite has an average pore radius of 9.0E-05 cm [17]. For each case, the steady state diffusive flux is

calculated using equations (3) and (10) for different groundwater depths, L, ranging from 100 to 1200 cm. Details of the calculation procedure and data needed for these examples are summarized in Table (1). The calculations were done using a straight forward program and sample results are presented in Fig 1 given below.

Table 1 Summary of Data for the Examples

General Data		
Temperature = 25 °C = 298.2 °K		Atmospheric Pressure = 101.3 kPa
Thermodynamic Properties of the Contaminants		
Chemical	Molecular Weight (g/mole)	Vapor Pressure, P° (kPa)
Trichloroethylene	131.4	9.9
Benzene	78.1	12.7
Methane	16.04	40.32
Air	28.97	101.3
Soil Data		
	Monterey Crushed Dune Sand	Kaolinite Clay
Average Pore Radius, r' (cm)	2.26 E-03	9.0E-05
Air Filled Porosity	0.3	0.3

Analysis indicated that the greatest differences in the predictions of the DGM for the clay profile from the predictions for the sand profile is for methane as shown in Fig. 1 below.

4 Discussion and Conclusions

Mass transport models based on FM and DGM were developed to predict the steady state gaseous diffusive fluxes in unsaturated vadose zone. There are a variety of differences between the models. First of all, the FM does not include the Knudsen diffusion term to account for pore size. Secondly, the equimolar counter diffusion is assumed to determine the flux ratio in FM. By contrast, the flux ratio in the dusty-gas model is calculated from the ratio of the square-root of the gas molecular weight. This is derived from Graham's law of diffusion. Finally,

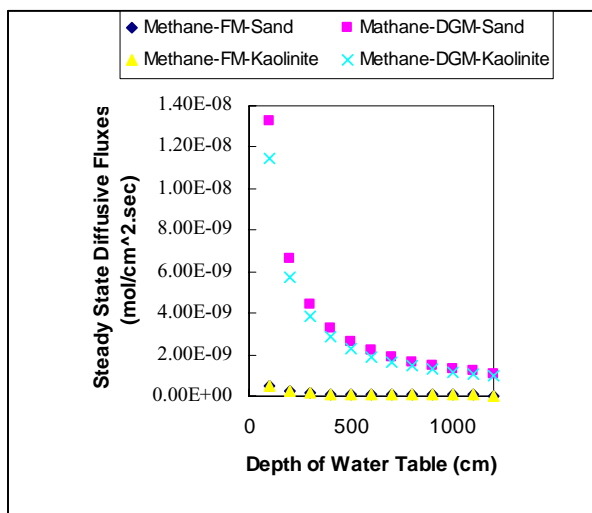


Fig. 1 Comparison of the Prediction of FM and DGM for Methane Steady State Fluxes in Kaolinite and Monterey Sand.

FM can be derived analytically while the DGM requires a numerical solution. For the examples considered in this study, the following points can be made:

For all the compounds considered, the DGM predicts larger steady state fluxes than the predicted fluxes based on FM. The difference is profound at shallow depths to the water table. The percent difference may reach up to two orders of magnitude.

FM predicts the same fluxes for the crushed Monterey sand and the Kaolinite clay. This is because the effective diffusion coefficient is adjusted based on the air filled porosity and no term is provided to account for the pore radius. However, the DGM predictions for sandy soils are larger than that for clayey soil at the same air-filled porosity (larger pore radius). This is an advantage that the DGM can provide.

The greatest differences in the predictions of the DGM for the clay profile from the predictions for the sand profile are for methane. This is so because Knudsen diffusion coefficient is inversely proportional to the molar mass of the diffusing gas and methane has the smallest mass among the gases considered (larger Knudsen flux).

In this analysis, air is considered as one component for the purpose of comparing the two models since Fick's law can not handle multicomponent analysis while the DGM can. This assumption is somewhat justified since the diffusion coefficients of the gases considered into air are very close to those into nitrogen and oxygen. Not to mention that for multicomponent systems with the DGM a set of complicated equations may be obtained and the solution may need an elaborate numerical analysis.

In general, the DGM is preferred to FM for systems with small pore sizes or natural soils with high moisture contents, as well as multicomponent analysis.

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