

Review of Enhanced Vapor Diffusion in Porous Media

Stephen W. Webb and Clifford K. Ho
Sandia National Laboratories
Albuquerque, New Mexico 87185

ABSTRACT

Vapor diffusion in porous media in the presence of its own liquid has often been treated similar to gas diffusion. The gas diffusion rate in porous media is much lower than in free space due to the presence of the porous medium and any liquid present. However, enhanced vapor diffusion has also been postulated such that the diffusion rate may approach free-space values. Existing data and models for enhanced vapor diffusion, including those in TOUGH2, are reviewed in this paper.

INTRODUCTION

Gas diffusion in porous media is generally significantly smaller than in free space due to the presence of the porous medium. The flow area for gas-phase diffusion is reduced by the presence of the solid particles, by the presence of any liquid, and by the fact that the flow path for diffusion in a porous medium is more tortuous than in free space. Using Fick's law, gas diffusion in a porous media may be expressed as

$$F_i = -\tau\phi S_g D_{12} \rho_g \nabla \omega_i = -\beta D_{12} \rho_g \nabla \omega_i \quad (1)$$

where D_{12} is the free-space diffusion coefficient at the pressure and temperature of interest. The product of the tortuosity coefficient, τ , the porosity, ϕ , and the gas saturation, S_g , is often referred to as the porous media factor, β . The porous media factor, β , is always less than 1, and gas diffusion in a porous medium is usually much lower than in free space.

In contrast, it has been postulated that diffusion of a condensible vapor in the presence of its liquid may be considerably enhanced compared to gas diffusion rates and may approach or exceed free-space values. (In the present discussion, *gas* refers to a non-condensable inert gas under the conditions of interest, or air. *Vapor* refers to the gas phase which may have a liquid phase present, or water vapor). The mechanisms for such an enhancement are postulated to occur at the pore scale and include local condensation and evaporation at isolated liquid "islands" within the porous medium, and an increased temperature gradient in the gas phase compared to the average temperature gradient in the equivalent porous medium. Enhanced vapor diffusion was first considered by Philip and deVries (1957) for soils. Jury and Letey (1979) estimated that the value of β is of the order 1.0 resulting in considerable

enhancement of vapor diffusion compared to gas diffusion. When β equals 1.0, diffusion is not affected by the porous medium at all and is equal to the value for free-space diffusion. Enhanced vapor diffusion is commonly assumed in soil science but has seen limited use in engineering applications.

Ho and Webb (1998) reviewed enhanced vapor diffusion and came to the conclusion that, while enhanced vapor diffusion may exist, there is no direct evidence to support it. Only indirect evidence exists, where the enhancement has been inferred from other measurements such as moisture content or heat flux. As part of their review, Ho and Webb recommended additional modeling and experiments at multiple length scales. Subsequent to the review by Ho and Webb (1998), which was actually conducted in early 1996, a number of modeling and experimental studies have been conducted. The current status of enhanced vapor diffusion is considerably more advanced than in 1996 due to these investigations, which are continuing.

PORE-SCALE ANALYSIS

It is instructive to review the pore-scale analysis presented by Ho and Webb (1998). Ho and Webb used a pore-scale model, which is depicted in Figure 1, to estimate the steady-state mass flow of water vapor in various pore-scale transport paths. The first path considered (A-A) is flow through the liquid island due to water vapor condensation and evaporation, which is a postulated mechanism for enhanced vapor diffusion. The second path (B-B) in Figure 1 is due to Fickian diffusion around the liquid island.

The mass flux for path (A-A) through the liquid island was based on an energy balance, which was performed on the surface of the liquid island exposed to the hotter side. The latent heat of condensation added to the liquid island was balanced by heat conduction through the liquid island. For path (B-B), Fick's law was used to evaluate the mass flux. Properties for

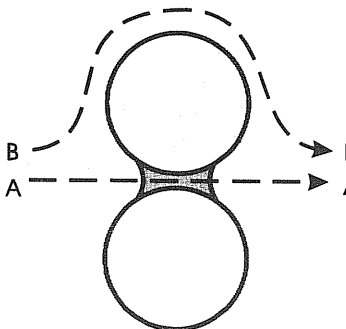


Figure 1
Pore-Scale Transport Paths
(A-A) Enhanced Vapor Diffusion
(B-B) Fickian Diffusion

water at 20°C were used.

The results from this simple pore-scale model indicate that net water vapor mass transfer through the liquid islands may be about an order of magnitude higher than water vapor transport around the liquid island by Fickian diffusion, or

$$\frac{m_{v,liquid\ island}}{m_{v,Fickian\ diffusion}} \sim 10 \quad (2)$$

While the existence of these mechanisms remains to be experimentally demonstrated, the possibility exists based on this simple analysis.

ENHANCEMENT FACTORS

Before reviewing the various models and data, some terms need to be defined and clarified. There are a number of different enhancement factors and models. The two types of enhancement factors are a mechanistic enhancement factor, η , which is the enhancement of the vapor diffusion rate compared to the gas diffusion rate, and the porous media factor, β , which is relative to diffusion in free space. The two factors are simply related by the gas diffusion values of tortuosity, porosity, and gas saturation, or

$$\beta = \tau \phi S_g \eta \quad (3)$$

In addition, there are various vapor diffusion models which use the enhancement factors in different ways. As mentioned earlier, enhanced vapor diffusion was first considered by Philip and deVries (1957) for soils. Their vapor diffusion equation is

$$F_v = - D_{atm} v \tau \phi S_g \nabla \rho_v \quad (4)$$

which is essentially the same as equation (1) earlier. The term v is a mass-flow factor term which is equal to the ratio of the total pressure to the air partial pressure. This term will be assumed equal to 1.0 and will not be included in the equations given below. Philip and deVries (1957) separated the vapor diffusion flux into temperature gradient and moisture gradient components by defining the vapor density gradient as a function of temperature and moisture content, or

$$\nabla \rho_v = h \frac{d\rho_0}{dT} \nabla T + \rho_0 \frac{dh}{d\theta} \nabla \theta \quad (5)$$

where h is the relative humidity and ρ_0 is the saturated vapor density. The resulting equation is

$$F_v = - D_{T,v} \nabla T - D_{\theta,v} \nabla \theta \quad (6)$$

where

$$D_{T,v} = D_{atm} \tau \phi S_g h \frac{d\rho_0}{dT} \quad (7)$$

$$D_{\theta,v} = D_{atm} \tau \phi S_g \frac{g\rho_v}{RT} \frac{d\Psi}{d\theta} \quad (8)$$

and Ψ is the capillary pressure. (Note that Philip and deVries, 1957, ignored the dependence of h on temperature as corrected by Nakano and Miyazaki, 1979). Per Philip and deVries (1957), enhancement of the vapor diffusion rate is only attributed to the thermal gradient term, so

$$D_{T,v,enh} = \eta D_{atm} \tau \phi S_g h \frac{d\rho_0}{dT} \quad (9)$$

or

$$D_{T,v,enh} = \beta D_{atm} h \frac{d\rho_0}{dT} \quad (10)$$

If there is no temperature gradient, the model of Philip and deVries (1957) predicts that enhanced vapor diffusion will not occur. This model has been used by numerous investigators including Milly (1984), Shurbaji and Phillips (1995), and Nassar and Horton (1997) among others.

The question of only applying the enhancement factor to the thermal gradient term is due to the perceived dominance of the temperature gradient on the proposed mechanisms for enhanced vapor diffusion. Pore-scale modeling and some ongoing experiments, to be discussed later, contradict this temperature-only dependence as enhanced vapor diffusion is seen even if no temperature gradient is imposed. Milly (1997, personal communication) also speculated that the enhancement factor may apply to the other terms, although he only applied it to the thermal gradient in his analyses.

Gu et al. (1998) used another form of the vapor diffusion equation by including the Soret effect, or

$$F_v = - \tau \phi S_g (D_{12} \rho_g \nabla \omega_v + D_{Soret} \nabla T) \quad (11)$$

and any enhancement factor is applied to both terms, or

$$F_v = - \tau \phi S_g (\eta D_{12} \rho_g \nabla \omega_v + \eta D_{Soret} \nabla T) \quad (12)$$

This relationship was used to derive an enhancement factor for their data. Note that only about 5-8% of the vapor diffusion rate was attributed to the Soret effect (Gu et al., 1998).

Due to the different enhanced vapor diffusion equations, any values from the Gu et al. data can not be directly compared to data or models that are based on the Philip and deVries approach. It is anticipated that the values from Gu et al. (1998) should be smaller than those factors for the Philip and deVries model, simply because the equation used by Gu et al. (1998) applies the enhancement to the total vapor density gradient, not just the thermal component.

EXPERIMENTAL DATA

A large number of experiments related to enhanced vapor diffusion exist in the soil science and engineering literature; Ho and Webb (1998) list a number of them. However, vapor diffusion rates were not directly measured. In soil science experiments, the vapor diffusion rate was inferred from total water flow (liquid plus vapor) and/or the thermal conductivity - heat flux data. In the engineering literature, the drying rate is often of most interest, which is strongly influenced by the heat and mass transfer coefficients at the drying surface, which are unknown. A discussion of some of the problems with inferring vapor diffusion rates from these data is given by Ho and Webb (1998).

Most of the inferred values of enhanced vapor diffusion, such as Cary (1965) who deduced vapor movement from total water movement, are at discrete values for different average temperatures and moisture contents. No continuous variation of a parameter, such as the moisture content, was performed. The data from Cass et al. (1984) are significantly different. Their data, which inferred vapor diffusion rates from thermal conductivity information, give a continuous variation in the vapor diffusion rate, and the enhancement, as a function of moisture content at different temperatures. Their empirical fit, which is discussed later, is also important because it considers the behavior of the enhancement factor at various moisture content limits.

Cass et al. (1984) present their data as a mechanistic enhancement factor, η , and as a porous media factor, β , based on the Philip and deVries approach. Figure 2 gives the fits of η and β provided by Cass et al. (1984) for their two soils (lysimeter sand and Portneuf Silt Loam) at various temperatures. The mechanistic enhancement factor, η , increases rapidly from a value of around 1.0 for all-gas conditions (zero saturation), reaching a value of about 8-15 for a saturation of about 0.15 to 0.40; the value then slowly increases thereafter. The porous media factor, β , starts out at approximately the porous media factor for all-gas conditions, increases to a maximum of 2 to 4 at a saturation of about 0.15 to 0.40, and decreases thereafter to 0.0 at full liquid saturation.

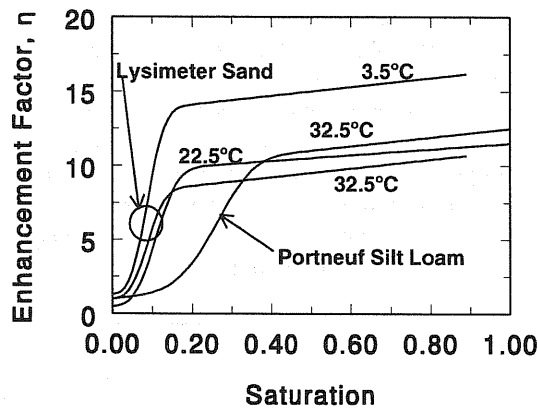


Figure 2a

Cass et al. (1984) Enhancement Factors, η

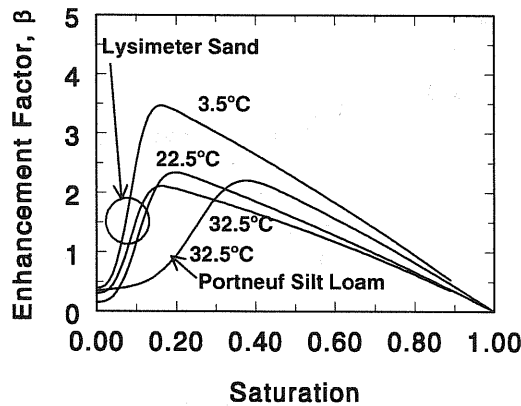


Figure b

Cass et al. (1984) Enhancement Factors, β

Other data, as tabulated by Jury and Letey (1979), consist of 38 values at various conditions from five different investigations. They based their enhancement factors on the Philip and deVries model. Water content information is given for less than half the data. The values of β range from 0.72 to 3.8, with an average value of 1.83 ± 0.79 .

As noted earlier, all the above enhancement data are inferred. Recently, three different experimental investigations have been initiated to directly measure enhanced vapor diffusion at three different scales.

Experiments are underway at New Mexico Tech to measure vapor diffusion at the pore scale. The experimental setup consists of an individual pore, or two pores in parallel, with a concentration gradient across the pore(s); no temperature gradient is imposed. The concentration gradient is enforced by boundaries of pure water and a brine solution. The liquid in the pore is a mixture of the water and brine solutions. Mass changes in the reservoirs are used to evaluate the vapor diffusion rates. Preliminary results indicate significant enhancement of vapor diffusion rates if a liquid island is present in the pore (T. Silverman, personal communication, 1998).

At Sandia National Laboratories, enhanced vapor

diffusion is being studied in a rough-walled analog fracture using alcohol as the fluid. Light transmission methods are used to characterize the aperture field and measure liquid phase structure as a function of time within the fracture plane. Boundary conditions are imposed to yield constant vapor concentrations at the upstream (1.0) and downstream (0.0) edges of the fracture. These experiments are currently underway (R.J. Glass, Jr., personal communication, 1998).

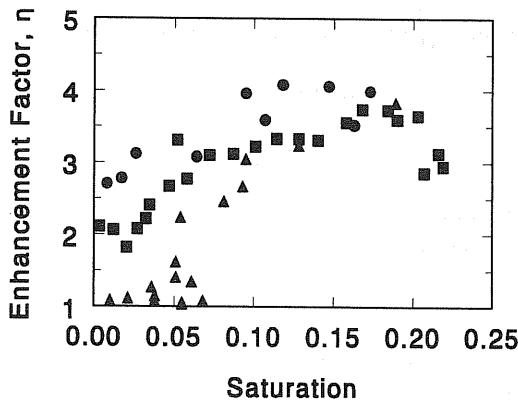


Figure 3a

Gu et al. (1998) Enhancement Factor (η) Data

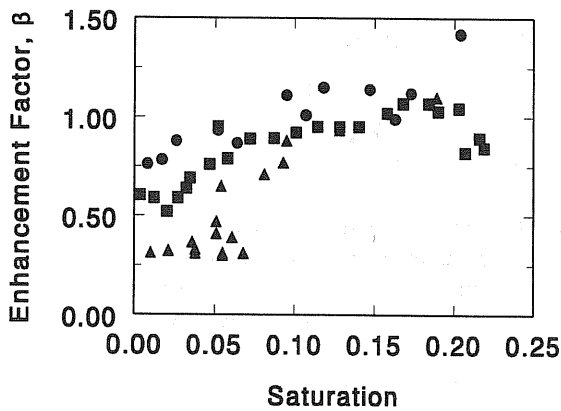


Figure 3b

Gu et al. (1998) Enhancement Factor (β) Data

Finally, at Washington State University, enhanced vapor diffusion has been measured in a packed bed of glass beads. The boundary conditions ranged from a concentration gradient under isothermal conditions, to combined concentration and temperature gradients, to drying conditions with only an imposed temperature gradient. Vapor fluxes are measured by a mass balance at the inlet and outlet reservoirs as well as the mass in the porous media packed bed. The data from the first series of experiments are given in Figure 3 (Gu et al, 1998); the various symbols represent different experiments. The mechanistic enhancement factor, η , increases from about 1.0 to a value approaching 4-5 at a saturation of 0.20; similarly, β increases from a value of about 0.5 at zero saturation to a value greater than

1.0 at higher saturations. The trends are in general agreement with the inferred data for Cass et al., although the values are typically lower. Differences are probably due to the different enhanced vapor diffusion equation used in each investigation as discussed above.

EMPIRICAL MODELS

There are a number of empirical models used to describe enhanced vapor diffusion. All the models, except that in TOUGH2 (Pruess, 1991), are based on the Philip and deVries (1957) assumption that enhanced vapor diffusion is only due to a thermal gradient.

The first empirical model for enhanced vapor diffusion was developed by Philip and deVries (1957) considering the difference in the temperature gradient in the gas phase compared to the average bulk temperature gradient, and the movement of vapor through isolated liquid islands. Jury and Letey (1979) modified the Philip and deVries (1957) model by considering the thermal conductivity of the vapor and liquid phases which changes the temperature gradient term. Cary (1979) developed another model, again based on the temperature gradient approach.

Cass et al. (1984) present curve fits to their data in the form

$$\eta = A + BS_f - (A - D)\exp[-(CS_f)^E] \quad (13)$$

and, β can be calculated from

$$\beta = \tau \phi S_g \eta \quad (14)$$

Their values of A, B, C, D, and E are given in Table 1.

Table 1. Cass et al. Curve Fit Coefficients

	A	B	C	D	E
Lysimeter Sand, 3.5°C	13.5	3	10	1.3	3
Lysimeter Sand, 22.5°C	9.5	2	8	0.5	3
Lysimeter Sand, 32.5°C	8.0	3	10	1.0	3
Portneuf Silt Loam, 32.5°C	9.5	3	3.5	1.0	4

As reported by Globus and Gee (1995), Campbell (1985) proposes a fit which is presumably based on the Cass et al. (1984) data, which is

$$\eta = 9.5 + 6\theta - 8.5\exp[-[(1 + 2.6f^{-1/2})\theta]^4] \quad (15)$$

where θ is the moisture content (ϕS_g), and f is the clay fraction content.

Finally, TOUGH2 allows for the use of a constant

value of β as input. In this case,

$$\eta = \frac{\beta}{\tau \phi S_g} \quad (16)$$

The factors in TOUGH2 are based on equation (1) and any enhancement is applied to the total diffusion rate.

The value of β from the various models are compared in Figure 4. Note that Cass et al. (1984) did a similar comparison for their correlation and the models of Cary (1979) and Jury and Letey (1979). The prediction of Cary (1979) is taken from the Cass et al. (1984) plots. Where needed, the tortuosity is set equal to 0.66 (Penman, 1940) as done by Philip and deVries (1957) and Cass et al. (1984). As can be seen, none of the models, other than the correlation of Cass et al. (1984) and the fit of Campbell (1985), adhere to the dramatic variation in the porous media factor at low liquid saturations, where enhanced vapor diffusion is most important. Equally disheartening, the models do not follow the appropriate behavior at low liquid saturations such that the value of β should go to the all-gas value at all-gas conditions.

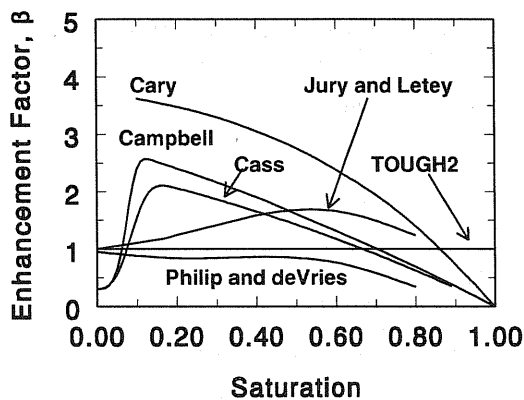


Figure 4
Model Comparison

MODELING STUDIES

As part of the enhanced vapor diffusion investigation being conducted at Sandia, pore-scale modeling has been performed using TOUGH2. Details of the model are discussed in more detail by Webb and Ho (1998). Significant enhancement of vapor diffusion up to an order of magnitude has been calculated under a concentration gradient (no temperature gradient) as shown by Webb and Ho (1997). These results indicate that enhancement may occur without a temperature gradient, contrary to the model of Philip and deVries (1957). Temperature gradient results for the pore-scale model are presented by Webb (in. prep) which indicate that the concentration gradient may dominate temperature gradient effects. In addition, Webb (1998) has shown that enhancement factors are equivalent for

steady-state vapor diffusion and transient drying conditions, which has important modeling implications.

The original enhancement results of Webb and Ho (1997) were presented as enhancement as a function of liquid island length. These results are converted to enhancement as a function of model saturation for comparison to other information. The results from the single pore and the pore network are shown on Figure 5. The single pore results are considered to be the maximum enhancement factor because the liquid islands would be uniformly distributed among the pores. The pore network model with a single liquid island is the minimum enhancement factor. Note that the porosity of the model is 0.322.

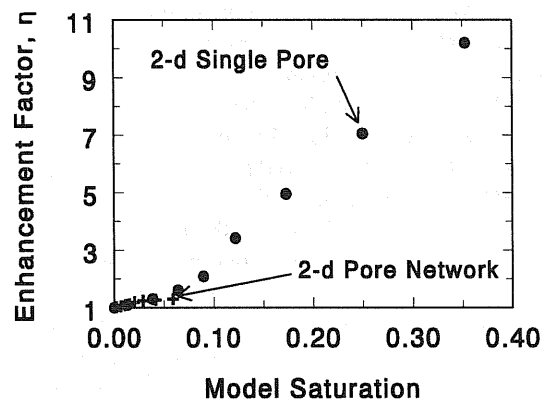


Figure 5
Pore-Scale Model Results (Webb and Ho, 1997)

The enhancement factor is applied to the total vapor diffusion rate similar to Gu et al. (1998). The calculated enhancement factor is in qualitative agreement with the data and model of Cass et al. (1984), and reasonable qualitative and quantitative agreement with Gu et al. (1998). The enhancement factor starts out as 1.0 which slowly increases until a saturation of about 0.05. The factor then increases rapidly, reaching a value of about 5.5 at a saturation of 0.20. This agreement may be fortuitous given the simplifications in the pore-scale model. As noted by Ewing and Gupta (1993), pore-scale modeling is a "useful concept rather than a physical reality". Further modeling studies should be conducted to investigate the effect of various model parameters on the results.

The above results indicate that if TOUGH2 were used at the pore scale, and individual liquid islands are included, enhanced vapor diffusion could be directly calculated. However, this amount of detail is impossible in practical applications, and continuum models with average enhancement factors must be used. The present enhanced vapor diffusion function in TOUGH2 does not agree with the expected variation as shown in Figure 4. A function similar to Cass et al. (1984) or Campbell (1985) would seem to be more appropriate.

DISCUSSION AND CONCLUSIONS

Enhanced vapor diffusion in the presence of its own liquid should be treated differently than air diffusion. Due to pore-level effects, vapor diffusion is enhanced relative to air diffusion rates. Even though this enhancement was inferred in previous studies, new information confirms the existence of enhanced vapor diffusion through direct measurements.

The existing models for enhanced vapor diffusion are based on the theory of Philip and deVries (1957), in which the enhancement is only due to temperature gradient effects. If there is no temperature gradient, there is no enhancement. Preliminary data and pore-scale modeling studies indicate that vapor diffusion is enhanced even if there is no temperature gradient, indicating that the theory and model of Philip and deVries may need to be revised.

Most of the existing models do not exhibit adequate behavior, especially at low liquid saturation. The exceptions to this behavior are the correlations of Cass et al. (1984) and Campbell (1985). Unfortunately, the enhancement factors are based on the model of Philip and deVries (1957), so the values may need to be revised. Nevertheless, these correlations are the best models to date. If the enhancement is applied to the entire vapor diffusion flux, as is tentatively recommended, the correlations of Cass et al. (1984) or Campbell (1985) should provide an upper bound of the enhancement factor, η .

NOMENCLATURE

D_{atm}	atmospheric diffusion coefficient
D_{soret}	Soret diffusion coefficient
D_T	temperature diffusion coefficient
D_{12}	binary diffusion coefficient
F	mass flux
h	relative humidity
m_v	vapor mass transfer rate
S	saturation
v	mass-flow factor
β	porous media factor
η	enhancement factor
ρ	density
τ	tortuosity coefficient
ϕ	porosity
ω	mass fraction
θ	moisture content
Ψ	capillary pressure

Subscripts

enh	enhanced
g	gas
i	gas i
l	liquid
v	vapor
0	saturated value

ACKNOWLEDGMENTS

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000 as part of a Sandia LDRD Project on Enhanced Vapor-Phase Diffusion in Porous Media. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

This study was stimulated by the paper by Y.W. Tsang and K. Pruess, "Modeling Studies of Gas Movement and Moisture Migration at Yucca Mountain, Nevada," presented at the TOUGH Workshop, September 13-14, 1990.

REFERENCES

- Campbell, G.S., 1985, "Soil Physics with BASIC," Elsevier, Amsterdam, as referenced by Globus and Gee.
- Cary, J.W., 1965, "Water Flux in Moist Soil: Thermal Versus Suction Gradients," *Soil Science*, 100:168-175.
- Cary, J.W., 1979, "Soil Heat Transducers and Water Vapor Flow," *Soil Sci. Soc. Am. J.*, 43:835-839.
- Cass, A., Campbell, G.S., and Jones, T.L., 1984, "Enhancement of Thermal Water Vapor Diffusion in Soil," *Soil Sci. Soc. Am. J.*, 48:25-32.
- Ewing, R.P., and Gupta, S.C., 1993, "Modeling percolation properties of random media using a domain network," *Water Resour. Res.*, 29:3169-3178.
- Globus, A.M., and Gee, G.W., 1995, "Method to Estimate Water Diffusivity and Hydraulic Conductivity of Moderately Dry Soil," *Soil Sci. Soc. Am. J.*, 59:684-689.
- Gu, L., Ho, C.K., Plumb, O.A., Webb, S.W., 1998, "Diffusion With Condensation and Evaporation in Porous Media," AIAA/ASME Joint Thermophysics and Heat Transfer Conference, Albuquerque, NM.
- Ho, C.K., and Webb, S.W., 1998, "A Review of Porous Media Enhanced Vapor-Phase Diffusion Mechanisms, Models, and Data - Does Enhanced Vapor-Phase Diffusion Exist?" *J. Porous Media*, 1:71-92.
- Jury, W.A., and Letey, Jr., J., 1979, "Water Vapor Movement in Soil: Reconciliation of Theory and Experiment," *Soil Sci. Soc. Am. J.*, 43:823-827.
- Milly, P.C.D., 1984, "A Simulation Analysis of Thermal Effects on Evaporation From Soil," *Water Resour. Res.*, 20:1087-1098.
- Nakano, M., and Miyazaki, T., 1979, "The Diffusion and Nonequilibrium Thermodynamic Equations of Water Vapor in Soils Under Temperature Gradients," *Soil Science*, 128:184-188.
- Nassar, I.N., and Horton, R., 1997, "Heat, Water, and Solute Transfer in Unsaturated Porous Media: I-Theory Development and Transport Coefficient Evaluation," *Trans. in Porous Media*, 27:17-38.
- Philip, J.R., and deVries, D.A., 1957, "Moisture Movement in Porous Materials under Temperature Gradients," *Trans., Am. Geophys. Union*, Vol. 38, No. 2, pp. 222-232, p. 594.
- Penman, H.L., 1940, "Gas and Vapour Movements in Soil: I. The Diffusion of Vapours in Porous Solids," *J. Agric. Sci. (England)*, 30:347-362.
- Pruess, K., 1991, *TOUGH2 - A General-Purpose Numerical Simulator for Multiphase Fluid and Heat Flow*, LBL-29400, Lawrence Berkeley Laboratory.
- Shurbaji, A.-R.M., and Phillips, F.M., 1995, "A numerical model for the movement of H_2O , $H_2^{18}O$, and 2H_2O in the unsaturated zone," *J. Hydrology*, 171:125-142.
- Webb, S.W., and C.K. Ho, 1997, "Pore-Scale Modeling of Enhanced Vapor Diffusion in Porous Media," *Proceedings of the ASME Fluids Engineering Division*, FED-Vol. 244, pp. 457-468.
- Webb, S.W., 1998, "Pore-Scale Modeling of Transient and Steady-State Vapor Diffusion in Partially-Saturated Porous Media," 1998 AIAA/ASME Joint Thermophysics and Heat Transfer Conference, Albuquerque, NM, June 15-18.
- Webb, S.W., in prep., "Temperature Gradient Effects in Vapor Diffusion in Partially-Saturated Porous Media."
- Webb, S.W. and C.K. Ho, 1998, "Pore-Scale Modeling Using TOUGH2," TOUGH Workshop '98, Lawrence Berkeley Laboratory, May 4-6, 1998.