Reply to comment by Michael D. Novak on “Evaporation from soils under thermal boundary conditions: Experimental and modeling investigation to compare equilibrium and nonequilibrium based approaches”

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1. Introduction

[1] This reply is written in response to Dr. Michael Novak’s comments on our paper entitled “Evaporation from soils under thermal boundary conditions: Experimental and modeling investigation to compare equilibrium and nonequilibrium based approaches.” We appreciate the effort by Dr. Novak to look critically at the paper. We hope that this response will help to resolve some of the issues raised by Dr. Novak and to better communicate our approach and contributions to the reader. There are two main aspects to Dr. Novak’s comments. First, Dr. Novak disagrees with the assumptions and formulations of the nonequilibrium based modeling approach that we present in the paper. In his comments, an alternative approach has been presented and we agree that it has merit. We encourage him to pursue his approach both numerically and experimentally. However, the merit in his approach does not make our approach invalid. For every problem, there are often many different numerical and theoretical approaches that may be pursued, developed and applied. Second, Dr. Novak disagrees with portions of our paper. We think this is due to the misinterpretation of many key aspects of our paper. As a result, Dr. Novak comes to the unsupported conclusion that our approach and paper are not correct. From his comments, it is clear to us that we need to provide further clarification on some of the details of the approach. However, it is also evident from reviewing Dr. Novak’s comments that he did not clearly follow the paper and the particular approach we presented in order to make definite conclusions on its merits and validity.

2. On the Validity of the Local Equilibrium Assumption

[2] Dr. Novak used Milly’s [1982] simple argument to test for the validity of the local equilibrium assumption during the column experiment in the work of Smits et al. [2011]. Milly’s [1982] scaling argument states, as also outlined by Dr. Novak,

$$\frac{\tau_v}{\tau_f} = \frac{1}{\theta_g D_v},$$

(1)

where $\tau_v$ and $\tau_f$ are the characteristic times for vapor diffusion and environmental forcing, respectively ($\ell$ is a pore length scale (m), $q$ is the infiltration rate (m s$^{-1}$), $\theta_g$ is the porosity (m$^3$ m$^{-3}$ soil), and $D_v$ is the molecular diffusivity (m$^2$ s$^{-1}$). By applying Milly’s approach for the water infiltration to the evaporation experiment in the work of Smits et al. [2011], Dr. Novak does some calculations to demonstrate that “equilibrium is expected at all depths throughout the experiment.”

[3] Equation (1) is actually the well-known dimensionless Peclet number (Pe). The Peclet number (or Milly’s [1982] argument) shows the relative effect of advection (numerator) with respect to diffusion processes (denominator) within a scale of $\ell$ (here, Novak used the mean grain size). The lower the Pe (<1), the more dominant the diffusion processes and vice versa. The value of Pe has nothing to do with the characteristic time for reaction between liquid and gas phases or phase change of water molecules from one phase to the other, and the Pe number cannot be used to draw conclusions about the justification of local equilibrium. Smits et al. [2011] already demonstrated that the vapor diffusion was dominate over vapor advection in their system [Smits et al., 2011, Figure 8]. However, Dr. Novak’s argument does not support his statement that “equilibrium is expected at all depths throughout the experiment.”

[4] A more formal approach to derive the dimensionless numbers characterizing the relative importance of different mass transfer processes during vapor transport in soil is warranted. The 1-D advection-diffusion equation for vapor transport in soil with a nonequilibrium mass transfer reaction can be expressed as

$$\frac{\partial (\phi S_p \rho_v w_v)}{\partial t} + \frac{\partial}{\partial z} \left( \phi \rho_g w_v - D_v \frac{\partial w_v}{\partial z} \right) = k \theta_g \rho_g \frac{RT}{M_w} (w_{eq} - w_v),$$

(2)

where $w_v$ is the mass fraction of water vapor in the gas phase, $w_{eq}$ is the mass fraction of the water vapor under equilibrium in the gas phase, $\rho_g$ (M L$^{-3}$) is the density of...
the gas phase, \( \phi \) is the porosity, \( S_g \) is the volumetric gas saturation, \( q_g \) is the Darcy velocity of the gas phase, and \( D_o \) as defined in the work of Smits et al. [2011], is the effective diffusivity of the water vapor in the gas phase. In equation (2), \( R \) is the universal gas constant, \( T \) is the temperature, and \( M_w \) is the molecular weight of water. The right hand side of equation (2) represents the nonequilibrium mass transfer of water vapor between the gas phase and the liquid phase. The kinetic rate coefficient \( k_{o \theta}RT/M_w (w_{eq} - w_v) \) (i.e., mass transfer rate in the units of mass per unit volume of gas per unit time) is multiplied with the volumetric gas content \( \theta_g = \phi S_g \) to write the expression in consistent units of the left-hand side of the equation (mass per unit total volume of the porous medium per unit time) [Choi and Corapcioglu, 1997]. Introduction of such a nonequilibrium mass transfer relationship to the model is not an empirical approach as Dr. Novak states, but rather based on the Hertz-Knudsen equation (HKE) derived from the kinetic theory of gases [Hertz, 1882; Knudsen, 1915; Schrage, 1953; Ytrehus and O sting, 1996; Badam et al., 2007]. (Note that the HKE assumes water vapor molecules are ideal gases not attracting rigid spheres. Also, the velocity of the condensing and evaporating molecules is described by the Maxwellian distribution with zero mean). The HKE represents the net evaporation at a liquid-vapor interface, and under thermal equilibrium conditions, the net evaporative mass transfer is shown to be proportional to the difference between the actual vapor mass pressure and the equilibrium vapor pressure. Smits et al. [2011] called the term denoted by \( k_{o \theta}RT/M_w \) in equation (2) as the effective mass transfer coefficient, \( k_{eff} (T^-) \). The effective mass transfer coefficient is known to be a function of the specific interfacial area \( (L^-) \) (i.e., the interfacial area per volume) between the gas phase and the liquid phase in porous media. However, evaluating the interfacial area is challenging because of the complexity of the interfacial geometry between the phases. Thus, the specific interfacial area is commonly described either by assuming a simplified geometry for the phase configurations [Shahraeeni and Or, 2010] or by using nondimensional expressions [Geller and Hunt, 1993]. For applications to realistic soil systems, both of these approaches involve a fitting procedure for matching the developed theoretical expressions to experimental data. Due to lack of data and complex geometry of the actual pore space and the fluids, by following [Bixler, 1985; Zhang and Datta, 2004], Smits et al. [2011] used an empirical relationship for the effective mass transfer coefficient as \( k_{eff} = b(\theta_w - \theta_{wr})RT/M_w \) where \( b \) is an empirical fitting parameter, \( \theta_w \) is the volumetric water content and \( \theta_{wr} \) is the residual water content. The multiplication of the effective water content \( (\theta_w - \theta_{wr}) \) and \( b \) by Bixler [1985] is an empirical factor used for representing the phase change in the soil that is assumed to be limited by the effective water content. Based on this representation, the effective mass transfer coefficient approaches zero as the effective water content approaches zero. We accept and state in the paper that the way we introduce \( k_{o \theta} \) into the model involves an empirical coefficient; it is not possibly to exactly represent the reactions as we do not know the interfacial description of phases/soil grains. We discuss in the paper’s conclusions that further research is required in order to properly understand mass transfer processes.

[5] By defining dimensionless time and distance variables as

\[
t' = \frac{tD_o}{F}, \quad z' = \frac{z}{l}, \quad \rho' = \frac{\rho o}{\rho R},
\]

where \( l \) as defined above is a characteristic length (L), \( t \) is time (T), \( z \) is the distance (L), \( D_o \) is a reference diffusivity of water vapor in soil \( (L^2T^{-1}) \), and \( \rho_o \) is a reference density of the gas phase; a nondimensional formulation of the vapor transport equation in 1-D with the nonequilibrium mass transfer reaction [e.g., Smits et al., 2011, equation (6)] can be expressed as

\[
\partial(S_g \rho' w_v)/\partial t' + \partial (\text{Pe} \rho' w_v - D' \rho' \partial w_v/\partial z') = Da \rho' (w_{eq} - w_v),
\]

where

\[
\text{Pe} = \frac{q_g l}{D_o \phi}, \quad Da = \frac{k_{eff} l^2}{D_o \phi}, \quad D' = \frac{D_o}{D_o \phi}.
\]

As opposed to Dr. Novak’s argument above, the Damkohler number (Da) is the appropriate dimensionless number that compares the characteristic time for transport and the characteristic time for the reaction or phase change, [Bahr and Rubin, 1987; Brussaard, 1992; Lichtner, 1998; Niessen and Hassanzadeh, 2009]. Note that the diffusive transport as shown in the work of Smits et al. [2011] is much more dominant (~4 orders of magnitude greater) than the advective transport (i.e., \( Pe \ll 1 \)). Generally if the Da number \( \gg 1 \), the local equilibrium assumption is justified. If we make some calculations, similar to those of Dr. Novak’s calculations (above) based on the same length scale and the same reference diffusivity and the fitted parameter \( b \) value outlined in the work of Smits et al. [2011] \( (b = 2.1e^{-2} \text{ m}^2 \text{ s}^{-1}) \), we obtain a Da number maximum of less than 0.04 for the considered range of temperatures (22–70°C) and effective water contents (0.3–0). As the characteristic scale increases, the Da number increases. For instance, a of 1 cm results in a maximum Da of ~14. Clearly, increasing \( k_{eff} \) increases the Da number, resulting in faster phase change. Da approaches a maximum close to the saturation value of the water content, and thus the equilibrium is expected close to the saturated water content.

3. Vapor Transport in Soil Under Nonequilibrium and Equilibrium Conditions

[6] The equilibrium assumption has never been tested at the REV scale; no data is available to show its validity. In addition, Smits et al. [2011] discusses how the equilibrium assumption is called into question by experiments on liquid/gas phase change in porous media suggesting that establishment of equilibrium is not instantaneous [Bénét and Jouanna, 1982; Ruiz and Bénét, 2001; Chamharmi et al., 2003; Chamharmi et al., 2008; Bénét et al., 2009]. The equilibrium assumption is an approximation of natural processes in an attempt to simplify a system. In other words, the assumption is tied to the time scale that is of interest. The occurrence of nonequilibrium, on the other hand, is in
fact a natural process. Questioning or attempting to improve upon the representation of the phase change in soil, irrespective of if it could be considered negligible or not, can only be explored by implementing nonequilibrium based approaches. This has been our attempt; we are not promoting the use of nonequilibrium assumption in all situations. In the experiments reported in our paper, we did not make any measurement to test for the occurrence of nonequilibrium, however, in our analysis we did not assume equilibrium (a simplification) of a nonequilibrium (more realistic) process. Rather, we presented an alternative way to model the system that has more flexibility to represent the measurements than the so called “equilibrium model.” It is our hope that showing different ways to mathematically represent the problem of water vapor transport will motivate other researchers to experimentally test for local equilibrium in soil.

[7] It is important to note that Smits et al. [2011, Figure 12] presented the concentration of vapor as the mass of water vapor per unit volume of soil. This is obtained by multiplying the predicted vapor concentration in the gas phase by the volumetric gas content. Thus, in addition to the small discrepancy between the estimations of the water content distribution from the two models (the single-phase equilibrium model estimates faster drainage), the two models predict two different equilibrium vapor concentrations, which together resulted in the nonequilibrium-model-predicted vapor concentration exceeding the equilibrium-model-predicted vapor concentration value at some depths in the soil in Figure 12. In the REV scale, the equilibrium-based single phase model shows a significant vapor pressure lowering effect (i.e., \( \exp \left[ -\frac{p_c m_w}{(\rho_w RT)} \right] \) < 1, where \( p_c \) is the capillary pressure in the two-phase nonequilibrium model, and it is equivalent to negative water pressure in the single-phase equilibrium model), while the nonequilibrium model shows almost none (i.e., \( \exp \left[ -\frac{p_c m_w}{(\rho_w RT)} \right] \approx 1 \)).

[8] As Smits et al. [2011, Figure 10] showed, the equilibrium-based model shows an unrealistic jump (compared to measured values) in water pressure (relative to atmospheric gauge pressure) at any portion of the soil as soon as that portion starts drying, while the nonequilibrium prediction of water pressure nicely match the measured values. The pressure jump in the equilibrium-based model occurs because of the negative evaporative flux (measured from the experiment) applied to both liquid water and water vapor assigned to the top boundary condition in the single phase (pressure-based) formulation of the equilibrium-based model. The form of the equilibrium formulation and the approach developed by Philip and deVries [1957] allows total water (liquid and vapor) to leave the system. However, in reality, only the water vapor can leave the system. Since there is no explicit mechanism in the model (or numerical trick) to prevent liquid water flux going out of the column, the negative flux term forces the water pressure to drop to unrealistically low (negative) values as the water evaporation continues. As a result, the vapor pressure lowering term becomes significant (<1), which reduces the equilibrium vapor concentration of the single-phase equilibrium-based model compared to the equilibrium concentration value of the nonequilibrium model. Therefore, the formulation of the problem by separating the water vapor from liquid water phase is more appropriate as done by the nonequilibrium model formulation. As a conclusion, we state in the work of Smits et al. [2011] that the nonequilibrium model formulation is superior to the equilibrium-based model formulation in the paper because in the nonequilibrium-based model, (1) the solution appears more stable and smoother compared to the equilibrium-based model, (2) the boundary conditions are easier to implement, and (3) the nonequilibrium based model represents the experimental data (evaporation rate, water content, and water pressure) under the conditions tested in the laboratory better than the equilibrium-based model in the paper.

[9] Dr. Novak points out that gas phase resistance should be taken into account in the comparison of equilibrium/nonequilibrium model results. In this reply, although we knew that the results would not change significantly, we incorporated the effect of gas phase pressure into the equilibrium-based model formulation. Essentially, the equilibrium model involves two pressure equations (for liquid and gas) and one heat equation, whereas the nonequilibrium model involves two pressure equations, one heat equation and one advection-diffusion equation for water vapor in the gas phase. The boundary conditions are as explained in the work of Smits et al. [2011]. As done in the work of Smits et al. [2011] for the single-phase equilibrium model, the top boundary condition for the water component in the two-phase equilibrium model here is also assigned based on the derivative of the measured weight of the column during drying. Note that the dissolution of air in water was neglected in both models. Figure 1 compares the predictions of the vapor concentration from the two-phase equilibrium model (dashed lines) and the two-phase nonequilibrium model (solid lines). Different than Figure 12 in the work of Smits et al. [2011], we present the vapor concentration in Figure 1 as mass of water vapor per unit

![Figure 1. Comparison of the two-phase nonequilibrium and equilibrium model results, presenting the water vapor concentrations in the gas phase. The dashed lines represent the equilibrium model results and the solid lines represent the nonequilibrium model results.](image-url)
volume of the gas phase, $C_{w(g)}$ (M L$^{-3}$). (Note that the results in Figure 1 are essentially equivalent to Figure 12 in the work of Smits et al. [2011].) $C_{w(g)}$ predicted by the two-phase nonequilibrium model appears always less than $C_{w(g)}$ predicted by the two-phase equilibrium model.

4. Boundary Conditions for the Equilibrium/Nonequilibrium Models

[10] The soil/atmosphere boundary can be conceptualized as two adjacent domains with completely different dynamics (for instance, Darcy’s law is not applicable above the ground surface, and it is only applicable in the soil water zone in the subsurface). At the interface between the atmosphere and the soil surface, it can be assumed that there is a transition zone where the gas flow dynamics may be controlled by a flow regime between Darcy’s law and Navier-Stokes. As a result of the processes occurring within this transition zone, mass transfer characteristics also change as vapor transports from inside the soil, through this zone and into the atmosphere. Since we cannot model gas flow accurately in this zone based on Darcy’s law (or, since we did not model this zone explicitly), we have to make assumptions about the mass transfer processes between the soil and the atmosphere. Therefore, we used the boundary layer approximation theory and assumed that the mass transfer into the atmosphere is driven by the difference between the bulk water vapor concentration of gas in the soil and the bulk water vapor concentration of the atmosphere, and a rate coefficient that has transition zone-specific properties as well as component-specific properties (i.e., water vapor). This is not “double counting” as Dr. Novak states.

[11] Smits et al. [2011] did not impose evaporative flux (measured based on the column weight) as a boundary condition in the nonequilibrium model. For the nonequilibrium based formulation, either water vapor concentration or water vapor flux (based on soil surface resistance) was assigned as the top boundary condition, using the relative water vapor flux (based on soil surface resistance) as either the Dirichlet boundary condition or the Neumann boundary condition in both models for testing their abilities to estimate the evaporation rate. This test showed that the nonequilibrium-based model significantly over predicted the cumulative evaporation at late times.

[12] Dr. Novak criticizes using only a flux boundary condition at the top boundary for the equilibrium-based model as both the Dirichlet and the Neumann boundary conditions are implemented in the nonequilibrium model. Theoretically, it is possible to calculate water pressure at the top in the equilibrium-based model from Kelvin’s equation (assuming equilibrium and atmospheric gas phase pressure) and the relative humidity measurements. However, this quickly results in enormous negative pressure values and pressure gradients as mentioned in section 3 of this reply, and as a result, the numerical convergence cannot be maintained. Implementing a time-dependent vapor flux boundary condition is much better option for the equilibrium-based pressure formulation than the Dirichlet boundary condition.

5. Additional Comments

[13] Some of the calculations that Dr. Novak outlines in his comment paper are consistent with our paper and support the case for nonequilibrium phase change to be investigated in more detail. We hope that by investigating different ways to formulate the phase change, this will encourage other researchers to mathematically and experimentally investigate the equilibrium assumption, helping to progress science further. We would like to thank Dr. Novak for his comments and hope that this reply clears up some of the misinterpretations about our paper.

References


