A soil-water retention function that includes the hyper-dry region through the BET adsorption isotherm

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Abstract

Most existing full-range soil-water retention functions extend standard capillary pressure curves into the dry region to zero water content at a finite matric pressure. A description of dryness is commonly taken as oven-dry conditions given by a matric suction of about $10^9$ Pa at zero liquid saturation. However, no finite pressure can be exerted by a zero amount of water, so a possibly more realistic situation necessarily implies that as water content approaches zero, suction tends to infinity. In this study we propose a full-range water retention function that takes advantage of the physical consistence of the Brunauer-Emmett-Teller (BET) adsorption isotherm to describe the very dry end, and preserves the capillary behavior of the classical Brooks and Corey function in the wet range. The transition from capillary to adsorption mechanisms is accounted for by a generalization of the Bradley’s isotherm. Tests on seven widely studied soil data sets show that the experimental water retention curves are well fitted by the proposed retention model. In order to test the present approach, our simulations were compared to experimental data, for water transport under dry conditions, found in the literature. The present model was also compared with a recently proposed extended retention function in a hypothetical experiment designed to test the influence of predicted soil humidity on solute volatilization. These comparisons showed that, under severe dryness, the water dynamics is well described by the proposed model. Moreover, in these conditions the retention function determines the soil humidity, to which solute volatilization calculations can be very sensitive.
1. Introduction

Simulation of water flow and chemical transport in the vadose zone requires soil-water retention (SWR) models. These are mathematical descriptions of the relationship between matric suction and water content. The two most frequently used SWR models have been those proposed by Brooks and Corey [1964] (BC) and van Genuchten [1980] (VG). Their popularity is due to their ability to fit water retention experimental data in the wet region, where it is often expected that most flow occurs, and owing to the fact that they can also be readily combined with conductivity models [e.g., Burdine, 1953; Mualem, 1976] in order to yield analytic expressions for relative permeability.

Application of BC and VG functions is generally unsuitable for the very dry range (matric pressure < -1.5 MPa) [Nimmo, 1991; Ross et al., 1991]. In fact, one of the disadvantages of the traditional water retention models is that they do not allow water content to be below the "residual water content parameter", an assumption that is physically unrealistic [Nimmo, 1991; Groenevelt and Grant, 2004]. This may imply little or no difficulty for some applications, such as wetland studies or humid region agriculture, but others, including water flow and solute transport in arid and semi-arid regions, require a more realistic representation of the hydraulic characteristics over the whole range of saturation. For the fine-textured media the high-suction range can be relevant even when water content remains high.

Empirical extensions for the dry range have been given by several authors. Ross et al. [1991] modified the Campbell [1974] SWR model to extend the retention curve to dryness. They compared their model with the original equation of Campbell, which was extrapolated to oven-dry conditions, finding that the new function fitted experimental data better than the original equation. Campbell et al. [1993] showed that their simple linear relationship for the water sorption isotherm [Campbell and Shiozawa, 1992] fits experimental data as well as the
more complex model of Fink and Jackson [1973]. Rossi and Nimmo [1994] (RN) presented a sum and a junction model, both based on a power law function complemented with a logarithmic function in the dry range. The sum model adds these two components, while the junction model matches them. In both models the continuity of the function and its derivative is assured. Good agreement between both models and seven sets of experimental water retention data was obtained. Fayer and Simmons [1995] proposed replacing the residual water content in the BC and van Genuchten functions with the simple water adsorption equation given by Campbell and Shiozawa [1992]. Morel-Seytoux and Nimmo [1999] (MS-N) extended the BC model into the high suction range using the Rossi and Nimmo [1994] junction model. Webb [2000] presented a method to extend classical retention functions to zero liquid saturation, without the need to refit the experimental data as in other approaches [Rossi and Nimmo, 1994]. Groenevelt and Grant [2004] proposed a model that covers the complete retention curve, expressed in terms of the pF scale previously introduced by Schofield [1935]. These authors fitted their model to a variety of soils, finding good agreement between experimental data and their SWR function over the whole range of saturation. As Rossi and Nimmo [1994] have pointed out, one of the advantages in having a full-range model of water retention is that it can reliably extrapolate the water retention curve beyond the driest measured point, which can help save measurement time at high suctions. However, although these new whole range approaches give a more accurate representation in the dry end, they have the disadvantage of allowing water content to be zero at finite suction [Rossi and Nimmo, 1994; Morel-Seytoux and Nimmo, 1999; Groenevelt and Grant, 2004]. For laboratory conditions (e.g., oven drying at 105º-110 ºC in a room at 50% relative humidity), zero water content is defined as oven dryness, which corresponds to a finite suction, generally taken as ~10³ MPa. Although in most applications and from the practical point of view it is difficult to perceive differences in the calculated soil behavior at very high, but finite, matric
suctions, the theory of the thermodynamic equilibrium states that as absolute dryness is approached, the matric suction must tend to infinity [e.g. Baggio et al., 1997].

In an effort to provide a full-range SWR function that overcomes these difficulties, Tuller et al., [1999] and Or and Tuller, [1999] proposed a pore space representation (angular pore space model) that accommodates both capillarity and adsorptive processes on internal surfaces. This alternative approach enables consideration of individual contributions of capillary and adsorptive components to soil water matric pressure through the whole range of saturation, and even satisfies the condition of zero water content at infinite suction. However, its implementation in a numerical transport model is cumbersome and many parameters need to be fitted for a particular soil.

While the new full-range functions provide improved representations of the SWR characteristic, their use and evaluation in numerical transport models has been limited. So far the study of Andraski and Jacobson [2000] seems to be the one that has explicitly tested the performance of a full-range water-retention function. These authors altered the UNSAT-H numerical model [Fayer and Jones, 1990] to incorporate the Rossi and Nimmo [1994] water-retention function. Then they compared field measured and simulated water and heat transport in a layered soil during a period of 3.85 years. Their results showed that simulations using the RN approach compared favorably with those using the traditional BC model and that RN function can improve the prediction of water potentials in near-surface soils, particularly under dry conditions.

It is well known [Chiou and Shoup, 1985; Chen et al., 2000a and 2000b; Chen and Rolston, 2000] that chemical sorption on nearly dry soils (saturations lower than 0.1) is greatly influenced by relative humidity. Therefore, it is expected that a physically accurate description of the moisture behavior in a very dry soil could also help improve chemical and water transport simulations. In particular, an appropriate description of the SWR under hyper-
dry conditions is important for water behavior to be accurately predicted at and near the soil surface. Estimating evaporation and recharge rates can, therefore, be critical [e.g. Scanlon et al., 2003; Agam and Berliner, 2006]. Another area in which a SWR function extended to dryness can be useful is the remediation of volatile organic compounds by soil vapor extraction or venting strategies. When these techniques are used, water movement and competitive sorption between hydrocarbon and water vapors take place simultaneously [Batterman et al., 1995]. The description of these phenomena may potentially be important near the upper surface of the soil, in the vicinity of air injection wells, and in arid environments [Yoon et al., 2003]. This function can also play an important role in the area of materials science, where porous materials need to function under very dry conditions [e.g. Gawin et al., 2002; Schrefler, 2004]. The available extended SWR functions are not always able to describe the soil-water state in very dry conditions. For instance, Goss and Madliger [2007] found that the Rossi-Nimmo retention function does not satisfactorily fit their experimental data. For practical purposes, they fitted the data with a third-order polynomial, although they recognized that the type of function they chose has no mechanistic meaning [Goss and Madliger, 2007].

In this paper, a robust and physically meaningful full-range SWR function is proposed. In addition of accommodating the BC functionality in the wet range of the curve, this proposed function is in accordance with the Brunauer-Emmett-Teller (BET) adsorption isotherm in the dry range. A smooth transition from pure adsorption to pure capillarity is accomplished by a generalization of Bradley’s isotherm. To assess the accuracy and suitability of the present approach, we implemented the new water retention function in a transport model, and checked its performance in a water transport, and water and chemical transport numerical simulations.
2. Soil-Water Retention Model

We constructed our proposed SWR function for the whole range of suctions by linking three individual functions for specific suction ranges, much like the two-parameter junction model approach of Rossi and Nimmo [1994]. Three ranges are differentiated through the transition matric pressures, $P_1$ and $P_2$ (Pa), which define the transition between capillary-adsorptive and adsorptive-hyperadsorptive behavior. The individual functions are the Brooks-Corey function, (from saturation to $P_1$), a generalization of Bradley’s adsorption isotherm (from $P_1$ to $P_2$), and the BET adsorption isotherm (from $P_2$ to infinite suction). Note that in the wet region, the relationship between the matric pressure $P$ (Pa) and the volumetric water content $\theta_w$ can be taken from any retention function that has proved to be acceptable in the region. In this study we have considered the original BC model for simplicity. Unlike Rossi and Nimmo [1994] who adopted a parabolic correction near saturation, we considered the conventional BC including the air-entry pressure at saturation. This parabolic correction, or more elaborate proposals such as MS-N, can be used if a detailed description near saturation is needed.

Whereas in the wet range the SWR curve is the expression of capillary forces, in the dry range, adsorption dominates the relationship between water content and the forces that hold this water in its condensed state. Water adsorption onto soils has been studied by different authors [Puri et al., 1925; Orchiston, 1952; Chiou and Shoup, 1985; Valsaraj and Thibodeaux, 1988; Rhue et al., 1989; Pennell et al., 1992; Amali et al., 1994; Ruiz et al., 1998; Chen et al., 2000; de Seze et al., 2000] and it has been shown that it can be described by the conventional BET isotherm [Valsaraj, 1995]. This adsorption isotherm is written here as

\[
\frac{\theta_w}{\theta_{wm}} = \frac{Bx}{(1-x)(1+(B-1)x)}
\] (1)
where

$$\theta_{wm} = W_m (1 - \varepsilon) \rho_s / \rho_w$$

(2)

is a pseudo-volumetric water content at monolayer capacity. Also in (2), $\rho_s$ (kg/m³) is the density of the solid-soil phase, $\rho_w$ (kg/m³) is the density of the water, and $\varepsilon$ (m³/m³) is the porosity. The mass monolayer capacity $W_m$ (kg/kg) and $B$ are characteristic BET isotherm parameters and $x$ is the relative humidity of the air-soil. $W_m$, the surface index, is the mass of water required to cover the surface completely as a monolayer, while $B$ is the index of the average net heat of adsorption in the first layer [Orchiston, 1952]. In the absence of osmotic pressure effects, the relative humidity is related to the matric pressure according Kelvin's equation [e.g. Bear and Batchmat, 1991]

$$x = \exp \left( \frac{P \hat{V}_w}{RT} \right)$$

(3)

where $\hat{V}_w$ (m³/mol) is the liquid molar volume of water, $R$ is the universal gas constant (Pa m³/K mol) and $T$ (K) is the temperature. If osmotic pressure effects are present, equation (3) can be modified to include them. This can be done, for instance, using the more general thermodynamic-based relationship given by Burns et al. [2000a, 2000b], which describes the influence of free dissolved salts on water vapor pressure and liquid pressure in unsaturated soils.

The matric pressure definition can be extended to include adsorption considering
as Baggio et al. [1997] suggested, where $\Delta h$ (J/mol) is the enthalpy difference between water vapor in the gas-phase and the condensed or adsorbed liquid-phase, excluding the latent enthalpy of vaporization. Adopting this definition, matric pressure and Kelvin’s equation can be applied in SWR curves in the range of low water contents [Gawin et al., 2002; Schrefler, 2004]. Note that in the present model the water content is counted from absolute dryness, although most experimental data in the literature are based on the water content set at zero at a matric suction of $\sim 10^3$ MPa, where some water molecules are still present in the soil.

Our proposal is to use equations (1) and (3) as the part of the SWR curve applicable in the "dry" region. Using this approach, water adsorption onto soils and soil-water characteristic curves at low moisture content will be described by the same mechanism and formulation.

Altogether, there are three different regions to be considered throughout the range of the retention curve: (i) a reliable function at high water content where the capillary mechanism is dominant. For purposes of simplicity, in this study we have used the power law relationship proposed by Brooks and Corey [1964],

$$\theta_w = \epsilon, \ P \geq P_b$$  \hspace{1cm} (5a)

$$\frac{\theta_w - \theta}{\epsilon - \theta_r} = \left(\frac{P}{P_b}\right)^{-\lambda}; \ P_1 \leq P \leq P_b$$  \hspace{1cm} (5b)

(ii) a logarithmic behavior at low and medium water contents where multilayer adsorption progressively dominates capillary forces.
\[ \ln(-P) = a + b\theta_w + c\theta_w^2 + d\theta_w^3; \quad P_2 \leq P \leq P_1 \] (6)

and (iii) a final adsorption region described by the BET isotherm as given in equations (1)-(3) for \( P < P_2 \).

When \( c \) and \( d \) are zero, equation (6) reduces to the Bradley’s adsorption isotherm [Bradley, 1936], which has been demonstrated to be in good agreement with experimental data [e.g. Orchiston, 1952]. Indeed, the extension of this equation to dryness was the basic assumption used by Rossi and Nimmo [1994] to develop their model.

To apply the present model for a given soil, the BET isotherm parameters \((W_m, B)\) and the Brooks and Corey parameters \((P_b, \theta_r, \lambda, \epsilon)\) must be known or fitted. This is an acceptable number of parameters considering that two different phenomena are described by the same curve. Available experimental data of water adsorption on various soils [e.g., Orchiston, 1952; Amali et al. 1994; de Seze et al., 2000] shows that BET equation (1) gives a good representation up to \( x = 0.3 \). This is a reasonable value which is based on the study by de Seze et al. [2000], who note that for \( x > 0.5 \) the BET isotherm over-predicts the experimental data.

On the other hand, most hydraulic retention models, including BC and VG, fit the experimental data reasonably well at least up to the “permanent wilting point”. Generally, the permanent wilting point is assumed to be at a suction of 1.5 MPa, although in reality plant water stress depends on plant, soil and atmospheric conditions [Cassel and Nielsen, 1986]. Therefore, as a general rule, we have assumed that equation (6) for intermediate behavior is valid between the junction matric pressure \( P_2 = -162 \) MPa (at 20 °C), corresponding to a relative humidity of \( x_2 = 0.3 \), and the junction matric pressure \( P_1 = -1.5 \) MPa. Thus, the remaining unknown parameters \((a, b, c, d)\) can be calculated from the conditions that ensure continuity of \( \theta_w \) and its first derivative at \( P_1 \) between (5) and (6), and at \( P_2 \) between (6) and
Designating by $\theta_{w1}$ and $\theta_{w2}$ the volumetric water content at each matching point, these continuity equations are expressed as

\begin{align}
 a + \theta_{w1}b + \theta_{w1}^2c + \theta_{w1}^3d &= \ln(-P_1) \\
 b + 2\theta_{w1}c + 3\theta_{w1}^2d &= -\frac{1}{\lambda(\theta_{w1} - \theta_r)} \\
 a + \theta_{w2}b + \theta_{w2}^2c + \theta_{w2}^3d &= \ln(-P_2) \\
 b + 2\theta_{w2}c + 3\theta_{w2}^2d &= \frac{(1-x_2)^2 [1+(B-1)x_2]^2}{\theta_{im}Bx_2 \ln(x_2) [1 + (B-1)x_2^2]} 
\end{align}

Of course, the junction matric pressures $P_1$ and $P_2$ may be taken as fitting parameters. However, we have preferred to fix them, because this keeps the model simple and because the experimental data available supports these values.

A list of experimental water adsorption BET parameters in soils taken from the literature is given in Table 1. It is apparent that these parameters are soil dependent, with a range of values given by $0.04 \text{ mg/g} \leq W_m \leq 39.8 \text{ mg/g}$ and $5 \leq B \leq 128.07$. In the absence of experimental data, one could take as a first estimate the average of the values listed in Table 1, which are $W_m = 13.4 \text{ mg/g}$ and $B = 23.8$. The parameters $\lambda$, $\theta_r$, $\varepsilon$ and $P_b$ of the BC retention curve are also soil dependent. Fortunately, there are procedures for estimating these parameters from other, more easily measurable, soil properties. For instance, Rawls and Brakensiek [1989] gave the average BC parameter values for the different soil textural classes in addition to correlations for estimating these BC parameters from porosity and the clay and sand percentages.
However, when experimental data is available, the normal procedure we propose consists of two steps. First, one has to fit the BET adsorption isotherm (parameters $W_m$, $B$) in the range of relative humidity below $x_2 = 0.30$ through the common procedure described by other authors [e.g. Chen et al., 2000a; de Seze et al., 2000]. The second step is to fit the set of parameters ($\lambda$, $\theta$, $\varepsilon$, $P_b$) minimizing the global error of the piecewise SWR function, with the set of parameters ($a$, $b$, $c$, $d$) determined by solving the linear system of equations (7). In the majority of cases, porosity is a measured parameter, which reduces to three the number of BC parameters to be fitted. The present piecewise water retention curve was fitted to six data sets from Campell and Shiozawa [1992] and one data set from Schofield [1935]. The same data sets were used by Rossi and Nimmo [1994] and Morel-Seytoux and Nimmo [1999] to check their models. Figure 1 shows good agreement between the present SWR curve and the corresponding soil experimental data set. In this figure, the horizontal dashed lines define the locations of matching points at $P_1$ and $P_2$. To fit the BC parameters logarithmic transformation was used to provide variance homogeneity. The objective function of the optimization was the square of the root mean square error (RMSE)

\[
\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left[ \log(-M_i) - \log(-P_i) \right]^2}
\]  

(8)

where $M_i$ and $P_i$ are measured and predicted values of the matric pressure, respectively, and $N$ is the total number of measurements. The Generalized Reduced Gradient algorithm [Lasdon et al., 1978] was used to minimize the objective function, equation (8). The fitting parameters for each soil obtained by the strategy described above are given in Table 2. Additionally, we have included in Table 3 the $R^2$ values for the BET fit, the RMSE (Eq. 8), and the maximum and average $\theta_w$ discrepancies between the present approach and the experimental data.
calculated in the range of matric pressure lower than -1.5 MPa. For comparison, the MS-N model fits were also included in Figure 1. Below \( P_1 \), both models apparently fit the experimental data equally well. Close to saturation, the MS-N model uses a third order polynomial. Then it is not surprising that for some soils, as the L -Soil (Figure 1f), MS-N fits the experimental data better than BC. A major difference between the present model and other approaches is the behavior of the curve as \( \theta_w \) tends to zero. Whereas most of the other full-range functions have the limiting suction value of \( \approx 10^3 \) MPa (taken as oven dryness), the present proposal tends to infinite suction in accordance with adsorption theories. It should be noted that this limiting suction value of \( 10^3 \) MPa, taken for Morel-Seytoux and Nimmo [1999], can not be regarded as universal, contrary to what Groenevelt and Grant [2004] state. For instance, for soil #7 (Rothamsted) of the data set used by Morel-Seytoux and Nimmo [1999] they had to change the limiting suction value to \( 5 \times 10^3 \) MPa to conveniently fit the retention curve, and Chen et al. [2000] fitted a Bradley’s isotherm to their experimental data of adsorption of water on Yolo silt loam soil, at 24.5 ºC, obtaining a limiting suction of \( 1.7 \times 10^3 \) MPa. For most practical purposes the logarithmic law, expressed in the form of the Bradley’s isotherm, represents the state of the soil system in the dry end very well. However, it has the inconvenience of predicting a non-physical situation of finite matric pressure at zero water content. It should be borne in mind that this is a “fictitious” zero water content, since it has been defined as the water content present while the relative humidity in the soil is 1%, achieved by setting a given combination of temperature and relative humidity in the laboratory [Schofield, 1935; Groenevelt and Grant, 2004]. One of the advantages of the present approach is that it overcomes this inconsistency, because in the very dry range the BET adsorption isotherm governs the relationship between matric pressure and water content. Another advantage of the present approach is that it captures the correct water retention behavior in very dry conditions, as shown in Figure 2. In this figure, saturation, defined as
\( S = \theta_w / \varepsilon \), is presented versus \( x \), in the range of relative humidities lower than 100%, for L-
Soil and Royal soils (see Figure 1e-f). For comparison, the present approach, the MS-N model
and the experimental data are included. The representation of the water retention curve on the
BET scale shows that, for these soils, the MS-N retention model significantly underestimates
water saturation while the present approach fits the experimental data well.

Note that for all soils in Figure 1 the proposed SWR shows an abrupt change in the
present retention function near 10^3 MPa (\( x = 0.0007 \)), coinciding with the experimental oven-
dryness suction. It should be noted that below this \( x \) value, the BET isotherm can be well
approximated by the straight line \( \theta_w = B\theta_{wm}x \). This behavior is very similar to the behavior
shown by the modification to the Rossi-Nimmo two-parameter junction model proposed by
Grant and Sletten [2002]. These authors stated that for the soils studied by Campbell and
Shiozawa [1992], the relationship proposed by Rossi and Nimmo [1994] for the dry end
differs from the actual behavior of these soils, for which water content was an exponential
function of capillary pressure. Accordingly, Grant and Sletten [2002] suggested a
modification based on the relation between water vapor pressure and the nominal adsorbed
water thickness. It is interesting to note that they recognized a shortcoming in this relation: it
calculates a minute, but nonzero, water content at infinite capillary pressure.

### 3. Testing the soil-water retention function in transport models

In order to test the accuracy of present approach, we have incorporated the new SWR
function in a water and chemical transport numerical simulator. A suitable simulation scenario
must involve very low water content conditions, for which BET adsorption mechanism
governs the relationship between matric pressure and moisture. The testing exercise is divided
into two parts. In section 3.1, we first present the governing equations used in the water
transport model and details of the numerical implementation. Then, we use this model and our SWR function to simulate one of the experiments of Chen et al. [2000b] for initial low water content. This experiment involved the continuous evaporation of a soil column under atmospheric conditions of varying relative humidity. Therefore, at least close to the soil surface where evaporation occurs, the soil was expected to reach conditions of very low liquid content ($S < 0.10$), for which SWR will be dominated by the BET branch of the present approach (Eq. (1)). Finally, in section 3.2, we present the solute transport governing equations and then the simulation of a hypothetical experiment of water evaporation leading to very dry conditions in the soil, followed by the volatilization of an ethanol-contaminated layer. The behavior of the present model is compared to the MS-N retention function in order to demonstrate that under severe dryness conditions the present approach can also help improve chemical transport and volatilization simulations.

### 3.1. Water transport simulation

#### 3.1.1. Governing equations and numerical implementation

The unsaturated soil system considered consists of liquid ($l$), gas ($g$) and solid ($s$) phases. When deriving the transport model equations, we assume that (i) the soil system is under isothermal conditions, (ii) the water is in equilibrium in all phases at all times, (iii) the advection in the gas-phase is negligible an (iv) spatial variations are only considered in $z$ direction (depth). The mass-conservation equation for water can be described by [Silva and Grifoll, 2007]

$$\frac{\partial}{\partial t}(\theta_w \rho_w + \theta_g \rho_g) = -\frac{\partial}{\partial z} (\rho_w q_l + J_{wg})$$  \hspace{1cm} (9)
where $\rho_w$ (kg/m$^3$) is the liquid water density, $\theta_i$ (m$^3$/m$^3$) is the volumetric fraction of phase $i$ ($i = w, g$), $\rho_v$ (kg/m$^3$) is the water vapor density, and $q_l$ (m/s) is the specific discharge of the liquid-phase, which is given by the generalized Darcy’s law [Bear and Bachmat, 1991]

$$q_l = -\frac{k}{\mu_w} \left( \frac{\partial P}{\partial z} - \rho_w g \right)$$

(10)

In equation (10), $k$ is the intrinsic permeability of the soil (m$^2$), $g$ (m/s$^2$) is the gravity acceleration, $k_{rw}$ is the relative permeability (dimensionless) and $\mu_w$ (kg/m-s) is the dynamic viscosity of water. The diffusive mass flux of water vapor, $J_{Wg}$, is expressed as [Bear and Bachmat, 1991]

$$J_{Wg} = -\theta_g D_{Wg} \frac{\partial \rho_v}{\partial z}$$

(11)

where $D_{Wg}$ (m$^2$/s) is the effective water vapor diffusion coefficient in the air within the porous medium. The tortuosity was calculated using Millington and Quirk’s first model as recommended by Jin and Jury [1996]. The water vapor density was calculated assuming ideal gas behavior and correcting for the curvature effect of the gas-liquid interface, as stated by Kelvin’s equation [Bear and Bachmat, 1991]

A dynamic boundary condition at the surface was set to accommodate the evaporation flux, $N_{W0}$ (kg/m$^2$ s). This flux was calculated by considering a mass transfer limitation from the soil surface to the bulk atmosphere [Brutsaert, 1975; Grifoll and Cohen, 1994]
\[ N_{w0} = k_{w0}(\rho_{wbk} - \rho_{v0}) \]  

(12)

where \( k_{w0} \) (m/s) denotes the atmosphere-side mass transfer coefficients for water, \( \rho_{wbk} \) (kg/m\(^3\)) is the background water vapor density in the atmosphere, while \( \rho_{v0} \) (kg/m\(^3\)) is the water vapor density at the soil surface. The boundary condition at the bottom was set as zero flux of water.

The governing partial differential equation for water transport (Eq. 9) was discretized spatially and temporally in algebraic form using the finite volume method with a fully implicit scheme (backward Euler) for time integration [Patankar, 1980]. The non-linear discretized governing equation was solved for the matric pressure using the multivariable Newton-Raphson iteration technique [Kelley, 1995], with a finite difference approximation of the Jacobian coefficient matrix [Kelley, 1995; Press et al., 1986-1992] and the numerical algorithm described by Silva and Grifoll [2007]. The total soil depth of the simulation domain was set equal to 20 cm. The grid was set uniform with a grid spacing of \( \Delta z = 0.1 \) cm, and the time step was allowed to vary without exceeding a maximum time step of 144 s as in Chen et al. [2000b] and Chen and Rolston [2000].

3.1.2. Numerical simulation of water transport under severe dryness conditions

The water transport model described above and the present soil-water function were used to simulate the LW2, a low initial water content experiment performed by Chen et al. [2000b]. In this experiment, a soil column of about 20 cm length was subject to a continuous evaporation condition at surface. The relative humidity of the sweep gas alternately changed from wet to dry conditions (dry N\(_2\), with relative humidity 0%; wet air, with relative humidity 97%). The evaporation experiment consisted of five periods: a first wet air period, from 0 to
147.1 h; a first dry N₂ period, from 147.1 to 268.6 h; a second wet air period, from 268.6 to 387.1 h; a second dry N₂ period, from 387.1 to 501.4 h and a third and last wet air period, from 501.4 to 625.7 h. The soil was Yolo silt loam, for which the water adsorption BET parameters are [Chen et al., 2000a]: $B = 128.07$ and $W_m = 15$ (mg/g). Because the lack of explicit experimental data in the work of Chen et al. [2000b], we used their fitted retention curve and the experimental adsorption data given by Chen et al. [2000a] to fit our retention function, with an estimated porosity of $\varepsilon = 0.52$. The fitting parameters and the assessment of its accuracy are shown in Tables 2 and 3, respectively. Figure 3 shows the present retention curve fitted by the procedure described in section 2, together with the experimental water adsorption data and the Campbell retention curve obtained by Chen et al. [2000b] for saturations below 0.2. Above $S = 0.2$ (not shown) and with $\theta_r = 0$ both Campbell and BC are the same expressions and, as a result of the fit, they almost coincide for this Yolo silt loam. For $P_1 > P > P_2$ both Campbell and the present model fit the experimental data well. However, for $P < P_2$ only the proposed SWR follows the experimental data trend and values.

The molecular diffusion coefficient for water vapor in air and N₂ at 25 ºC, and the mass-transfer coefficient of water vapor at the soil surface were taken from Chen et al. [2000b]. The relative permeability was calculated according to Campbell’s model [Campbell, 1974] with the parameters given by Chen et al. [2000b].

Figure 4a shows the measured evolution of the water remaining in the soil and the values calculated using Campbell and present model. The weight variation is fairly well predicted by the water transport model using any of the retention curves, with a maximum difference of 1.3% between data and simulation results. This coincidence is not surprising when one considers that the region below $P_2$ of the SWR is only attained close to the surface and for short periods of time (see below). Figure 4b shows the measured and simulated volumetric liquid content profile at the end of the experiment. Below a depth of 5 cm the
calculated and measured values were very similar. Between the surface and a depth of 5 cm, matric pressures were high enough to show some $\theta_w$ differences between both the calculated curves. In this close-to-the-surface region, it seems that the present proposal describes most of the experimental profile better, although the value measured at the surface shows a change in tendency that is not predicted by the Campbell curve or the present proposal. The origin of this discrepancy is not known, but it should be taken into account that it is more difficult to measure water content near the soil surface, where steep gradients of the different variables in this zone develop more easily.

For the same experiment, the dynamics of the volumetric water content at two depths is shown in Figure 5. The calculated volumetric water contents followed the general trend of measured water content using any of the two SWR models, but did not perfectly match the experimental data, particularly in the near-surface soil region. Note that TDR measurements give an average value of volumetric water content between the rods. For the measurements at the nominal depth of 1 cm, the two-probe TDR rods were 1 cm apart. Then, assuming a rod diameter of 3 mm (~1/8”), the water content measured at 1 cm depth will be an average value between 0.35 and 1.65 cm. In Figure 5, the solid lines that represent the calculated water content evolution at 0.35 and 1.65 cm should encompass the reported experimental values at 1 cm of nominal depth. It can be seen that the experimental data is within this band during the wet air periods, but most of the values lie outside it during the dry N$_2$ periods. At the depth of 10 cm, the volumetric water content was measured by a TDR with rods that were 2 cm apart. Figure 5 shows that these two calculated lines and the experimental data practically coincide during the first wet air and dry N$_2$ periods. After the first dry N$_2$ period, the calculated lines start to deviate one from the other, reaching a maximum difference of 8.3% at the end of the simulation. Despite this difference, the experimental data are encompassed by the two calculated lines representing the nominal depth of the TDR probe. This illustrative figure
shows how the mechanism that dominates the water retention at any time and some depths varies during the simulation. For this Yolo silt loam, a water content of 0.027 (m³/m³) corresponds to the matching point below which BET adsorption dominates, while between this water content and \( \theta_{w_1} = 0.114 \) m³/m³ (\( P_1 = -1.5 \) MPa) the generalized Bradley's isotherm governs water retention. Above \( \theta_{w_1} \) there is the capillary region.

Figure 5 shows that during the dry N₂ periods, the simulated water content near the soil surface enters the BET adsorption region, which indicates that this nearly dry region is attainable under natural evaporation conditions. In addition, in the experiments of Chen et al. [2000b] they measured the relative humidity at surface and at various depths, and their measurements show that relative humidities at the surface were well below 30% during the dry N₂ periods. This indicates that at least at the surface the water content is governed by adsorption mechanisms that are well described by the proposed water retention curve.

It is worth noting that Gee et al. [1992] measured matric pressures in three soil samples of different textures taken from sites near Richland, WA. They reported matric pressures ranging from -204 to -264 MPa on the surface (0 to 1 cm). All these values are well within the BET region of the proposed SWR model (\( P_2 < -162 \) MPa), which suggests that there is a need for SWR models that provide a detailed description of the region of very low matric pressures, at least in arid regions and close to the surface.

3.2. Water and Chemical transport simulation

It is well known [Chiou and Shoup, 1985; Chen et al., 2000a, 2000b; Chen and Rolston, 2000] that chemical sorption on soils is greatly influenced by relative humidity. Therefore, a physically accurate description of how moisture behaves in a very dry soil is also expected to improve chemical transport and volatilization simulations. Transport models of
highly sorbing solutes in the vadose zone assume that the solid-gas and solid-liquid equilibrium relationships for chemicals are influenced by the fraction of the solid surface area not covered by water molecules.

3.2.1. Governing equations and numerical implementation

The chemical equilibrium relationships between the solid and fluid phases were calculated according to the proposal by Chen et al. [2000a], who considered that organic chemicals in soils are adsorbed onto water-solid and air-solid interfaces and dissolved in the soil solution. In this approach, the chemical concentration at the solid-fluid interfaces is affected by the fraction of the surface area not covered by water molecules, $\eta$, which depends on the relative humidity of the air-soil phase, $x$. The fraction $\eta$ can be calculated by considering that the water vapor sorption follows the BET model [Hill, 1946; Chen et al., 2000a]

$$\eta(x) = \frac{1 - x}{1 - x + B_x}$$ (13)

The chemical transport equation is given by [Silva and Grifoll, 2007]

$$\frac{\partial C_{sm}}{\partial t} = -\frac{\partial}{\partial z} \left( J_i + J_s + q_i C_i \right)$$ (14)

where $C_{sm}$ (kg/m$^3$) is the chemical concentration in the soil matrix, $C_i$ (kg/m$^3$) is the chemical concentration in the liquid-phase and $J_i$ (kg/m$^2\cdot$s) ($i = g, l$) is the diffusive-dispersive mass flux of chemical.
Like for water transport (Eq. 12), a dynamic boundary condition at the surface was set to accommodate the volatilization flux, which was calculated by considering a mass transfer limitation from the soil surface to the bulk atmosphere [Brutsaert, 1975; Grifoll and Cohen, 1994]. The boundary condition at the bottom was set as zero ethanol diffusive flux.

The governing equation for chemical transport (Eq.14) was solved with water content and liquid-phase velocities evaluated from equations (9) and (10), using a fully implicit scheme. The resulting discretized equations were a linear algebraic system with a tridiagonal-coefficient matrix, which was solved by the Thomas algorithm [Patankar, 1980; Press et al., 1986-1992].

### 3.2.2. Numerical simulation of water and chemical transport under severe dryness conditions

The performance of the present model has also been evaluated in a hypothetical numerical experiment of water and chemical transport and compared with the results obtained by using the MS-N retention function. In this experiment, a 1-meter-long Royal soil column (with retention data shown in Figures 1e and 2a) with a uniform water content of 0.25 m$^3$/m$^3$ was subject to an initial period of continuous evaporation for 4800 h, leading to very dry conditions, especially near the soil surface. After this initial period of 4800 h, the second stage of the experiment consisted of the simultaneous evaporation of water and the volatilization of an ethanol-contaminated layer situated at a depth of between 0.1 and 0.2 m, with an initial concentration in the soil-matrix equal to 1.0 kg/m$^3$, for 1200 h. The relative humidity of the atmosphere was set to 15% in both stages. This condition is well representative of some regions with hyper-arid climates [e.g. McKay et al., 2003].

The ethanol partition coefficient at the air-solid interface was calculated according to Goss [1994], whereas the ethanol partition coefficient at the water-solid interface was
estimated as suggested by Grifoll and Cohen [1996]. The molecular diffusion coefficients for water and ethanol vapor in air, and the molecular diffusion coefficient for ethanol in water at 20 °C were taken from Reid et al. [1987]. The dispersion coefficient was calculated following the model of Grifoll et al. [2001] with a dispersivity at saturation set to 0.5 cm. The atmosphere-side mass-transfer coefficients of water and ethanol vapors at the soil surface were estimated according to Brutsaert [1975]. The relative permeability was calculated using Campbell’s model [Campbell, 1974] with the parameters given by Morel-Seytoux and Nimmo [1999]. The Campbell conductivity model was chosen for two reasons. Firstly, in the dry range the hypotheses underlying such models as Burdine and Mualem do not hold. Secondly, Morel-Seytoux and Nimmo [1999] also used the Campbell expression to calculate the hydraulic conductivity. So, this conductivity model enables comparisons to be made that only depend on the SWR functions.

The evolution of water evaporation and ethanol volatilization fluxes determined by the MS-N retention function and the present model are compared in Figure 6. As shown in Figure 6a, both retention functions show the classical first stage of water evaporation at constant-rate. The falling-rate stage started at about $t = 350$ h with the MS-N retention function and at about $t = 600$ h with the present model. Because of this delay at the beginning of the falling-rate stage, there was a period in which the evaporation flux obtained with MS-N was lower than the flux obtained with the present retention function. However, from about $t = 1250$ h the tendency was for the evaporation flux obtained with the present model to be lower than the flux obtained with the MS-N function. This was because, as the top soil dries, lower water contents were obtained with the MS-N retention model in that region. This result is consistent with the SWR fits because, for a given matric suction and within the transition and BET ranges, the water content predicted by the present approach is higher than the water content predicted by the MS-N function (see Figs. 1e and 2a). As a consequence, the lower water
contents increased the water vapor diffusion within the top soil, which significantly increased the evaporation flux in the simulation with the MS-N retention function. The evolution of water content at various depths is shown in Figure 7. In general, within the first 10 cm adjacent to the soil surface, the water content was lower with the MS-N function, although there were some periods during which this was not the case. By contrast, the present approach led to lower water contents at depths greater than 50 cm. The comparison between the soil surface and 5 cm-depth curves, and between a depth of 10 cm and 50 cm-depth curves shows that water content gradients were higher during the MS-N simulation. These higher gradients were responsible for increased water vapor diffusion and a greater evaporation rate (Figure 6a). Note that when the MS-N function was used, at the end of the first stage \( (t = 350 \text{ h}) \) the water content was lower than 0.02 \( \text{m}^3/\text{m}^3 \); i.e. \( S < 0.06 \), a range in which the present approach fits the experimental data better than the MS-N model (see Figure 2a). Also, at \( t = 4800 \text{ h} \) the whole soil reached the BET conditions with the present retention model. On the other hand, at depths greater than 0.5 m, the MS-N retention function led to water contents higher than 0.017 \( \text{m}^3/\text{m}^3 \), the upper limit of the BET adsorption range.

The use of one retention function or another also led to differences in the transport behavior of ethanol. The concentration of ethanol within the soil was lower and the ethanol volatilization fluxes were higher with the MS-N retention function (see figure 6b). This was because the lower relative humidity that developed in the top soil during the simulation with the present model increased the availability of adsorption sites, which led to a lower volatilization flux than when the MS-N model was used. Additionally, the lower water contents resulting from the MS-N simulation increased the transport of ethanol by gas-phase diffusion within the top soil, which also favored the volatilization flux. Note that in both, the simulations with the MS-N and the present model, the chemical equilibrium between the solid and fluid phases has been calculated with a BET adsorption isotherm (in fact, the BET part of
the present model), as is indicated in Eq. 13. However, Figures 2a and 6b show that the use of an extended retention function that differs from the adsorption experimental data could lead to significant differences of the calculated chemical volatilization fluxes.

4. Conclusions

A new full-range SWR function with physical consistence in the dry range has been proposed. The approach takes advantage of the physical consistency and robustness of the BET adsorption isotherm to describe the very dry end, while preserving the capillary behavior of the classical BC function in the wet range. The transition from capillary to adsorption mechanisms is accomplished by a generalization of the Bradley’s isotherm, through a relationship between the logarithmic of the matric suction and a cubic polynomial of the water content. Continuity of the function and its derivative is assured through the different regions.

The validity range of the BET adsorption isotherm was established for a relative humidity below 30%. The generalized Bradley's isotherm was used between this point and $P_1 = -1.5$ MPa, above which the classical BC function was chosen because classical models of water retention work well in the wet range of soil water.

The proposed water-retention curve is quite similar to other full-range SWR models in most of the saturation range. However, the limiting behavior of matric pressure as dryness is approached is different: while most extended functions predict a finite matric pressure at zero water content, the present proposal predicts an infinite matric pressure according the adsorption theories. Therefore, in simulations using one or the other approaches one could expect differences in situations of low water content. Also, these differences affect the calculations of organic chemicals transport, since adsorption is highly dependent on relative humidity.
Acknowledgments

We gratefully acknowledge the financial assistance received from the DGICYT of Spain, under project FIS2005-07194 and from the Generalitat de Catalunya (2005SGR-00735). We also acknowledge the support received from the DURSI and the European Social Fund.
References


Yoon, H., A. J. Valocchi, and C. W. Werth (2003), Modeling the influence of water content on soil vapor extraction. *Vadose Zone J.* 2, 368–381.
Table captions

Table 1. BET adsorption isotherm parameters from literature.

Table 2. Summary of soil fitting parameters.

Table 3. Goodness of the present SWR function fit.
Table 1. BET adsorption isotherm parameters from literature.

<table>
<thead>
<tr>
<th>Source</th>
<th>Soil type</th>
<th>B</th>
<th>( W_m ) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Puri et al.</em> [1925]</td>
<td>5 different soils</td>
<td>15</td>
<td>6</td>
</tr>
<tr>
<td>id.</td>
<td>5 different soils</td>
<td>30</td>
<td>19</td>
</tr>
<tr>
<td><em>Orchiston</em> [1952]</td>
<td>podzol from Otago</td>
<td>14.4</td>
<td>39.8</td>
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<td>id.</td>
<td>red brown loam from North Auckland</td>
<td>15.2</td>
<td>33.3</td>
</tr>
<tr>
<td>id.</td>
<td>meadow soil from Great Barrier Island</td>
<td>13.0</td>
<td>37.3</td>
</tr>
<tr>
<td>id.</td>
<td>brown granular clay form North Auckland</td>
<td>15.2</td>
<td>29.8</td>
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<tr>
<td>id.</td>
<td>yellow-gray loam from Malborough</td>
<td>13.7</td>
<td>5.9</td>
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<tr>
<td>id.</td>
<td>alluvial from Canterbury</td>
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<td>id.</td>
<td>peat soil from Canterbury</td>
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<td><em>Chiou and Shoup</em> [1985]</td>
<td>woodburn dry soil (silt soil, 21% kaolinite)</td>
<td>37.6</td>
<td>11.7</td>
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<td><em>Valsaraj and Thibodeaux</em> [1988]</td>
<td>montmorillonite (natural unheated)</td>
<td>21</td>
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</tr>
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<td>id.</td>
<td>montmorillonite (preheated, 105 °C)</td>
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<td>11.67</td>
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<td>id.</td>
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<td>id.</td>
<td>montmorillonite (H-saturated, unheated)</td>
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<td>11.86</td>
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<tr>
<td>id.</td>
<td>montmorillonite (Na-saturated, unheated)</td>
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<td>9.31</td>
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<td>id.</td>
<td>montmorillonite (natural unheated at 35 °C)</td>
<td>19.6</td>
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<td>id.</td>
<td>illite (natural unheated)</td>
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<td>2.37</td>
</tr>
<tr>
<td>id.</td>
<td>illite (Ca-saturated, unheated)</td>
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<td>kaolinite (natural unheated)</td>
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<td>sand (green sand, unheated)</td>
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<td><em>Rhue et al.</em> [1989]</td>
<td>Li-kaolin</td>
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<td>id.</td>
<td>silica gel</td>
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<td>33.8</td>
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<tr>
<td><em>Amali et al.</em> [1994]</td>
<td>Riverbed sand</td>
<td>25.7</td>
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<tr>
<td>id.</td>
<td>Yolo silt loam</td>
<td>17.6</td>
<td>8.5</td>
</tr>
<tr>
<td><em>Ruiz et al.</em> [1998]</td>
<td>sand</td>
<td>7.11</td>
<td>0.524</td>
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<tr>
<td>id.</td>
<td>limestone</td>
<td>36.29</td>
<td>0.0412</td>
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<tr>
<td>id.</td>
<td>clay</td>
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<td>5.28</td>
</tr>
<tr>
<td><em>Chen et al.</em> [2000]</td>
<td>Yolo silt loam</td>
<td>128.07</td>
<td>15</td>
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<tr>
<td><em>de Seze et al.</em> [2000]</td>
<td>natural montmorillonite</td>
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<td>13</td>
</tr>
<tr>
<td>id.</td>
<td>lake sediment</td>
<td>53</td>
<td>12.4</td>
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Table 2. Summary of soil fitting parameters.

<table>
<thead>
<tr>
<th>Soil</th>
<th>$B$</th>
<th>$W_m$, mg/g</th>
<th>$P_b$, Pa</th>
<th>$\lambda$</th>
<th>$\theta_r$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palouse</td>
<td>39.49</td>
<td>11.26</td>
<td>-4507</td>
<td>0.32</td>
<td>0.034</td>
<td>0.44</td>
</tr>
<tr>
<td>Palouse B</td>
<td>11.39</td>
<td>32.52</td>
<td>-2866</td>
<td>0.19</td>
<td>0</td>
<td>0.55</td>
</tr>
<tr>
<td>Walla Walla</td>
<td>23.49</td>
<td>9.26</td>
<td>-4190</td>
<td>0.35</td>
<td>0.030</td>
<td>0.39</td>
</tr>
<tr>
<td>Salkum</td>
<td>124.3</td>
<td>11.62</td>
<td>-9932</td>
<td>0.29</td>
<td>0</td>
<td>0.48</td>
</tr>
<tr>
<td>Royal</td>
<td>68.00</td>
<td>7.01</td>
<td>-3939</td>
<td>0.50</td>
<td>0.034</td>
<td>0.35</td>
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<td>L-Soil</td>
<td>42.98</td>
<td>2.99</td>
<td>-1229</td>
<td>0.40</td>
<td>0.015</td>
<td>0.18</td>
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<td>Rothamsted</td>
<td>1071</td>
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<td>0.33</td>
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<td>0.51</td>
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<td>Yolo silt loam</td>
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<td>-4630</td>
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<td>0</td>
<td>0.52</td>
</tr>
</tbody>
</table>

$^a$Campbell and Shiozawa [1992]

$^b$Schofield [1935]

$^c$Chen et al. [2000a, 2000b]

$^d$Porosity was fixed in accordance with measured or estimated data.
Table 3. Goodness of the present SWR function fit.

<table>
<thead>
<tr>
<th>Soil</th>
<th>$R^2$ BET</th>
<th>RMSE</th>
<th>$(\Delta \theta_w)_{max}$ (v/v)</th>
<th>$\overline{\Delta \theta_w}$ (v/v)</th>
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<tr>
<td>$^a$Palouse</td>
<td>0.986</td>
<td>0.108</td>
<td>0.0096</td>
<td>0.0033</td>
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<tr>
<td>$^a$Palouse B</td>
<td>0.993</td>
<td>0.164</td>
<td>0.0134</td>
<td>0.0026</td>
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<tr>
<td>$^a$Walla Walla</td>
<td>0.990</td>
<td>0.088</td>
<td>0.0056</td>
<td>0.0015</td>
</tr>
<tr>
<td>$^a$Salkum</td>
<td>0.992</td>
<td>0.129</td>
<td>0.0077</td>
<td>0.0028</td>
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<tr>
<td>$^b$Royal</td>
<td>0.988</td>
<td>0.114</td>
<td>0.0028</td>
<td>0.0009</td>
</tr>
<tr>
<td>$^a$L-Soil</td>
<td>0.997</td>
<td>0.153</td>
<td>0.0015</td>
<td>0.0004</td>
</tr>
<tr>
<td>$^b$Rothamsted</td>
<td>0.999</td>
<td>0.129</td>
<td>0.0087</td>
<td>0.0043</td>
</tr>
<tr>
<td>$^c$Yolo silt loam</td>
<td>0.955</td>
<td>0.007</td>
<td>0.0049</td>
<td>0.0020</td>
</tr>
</tbody>
</table>

$^a$Campbell and Shiozawa [1992]
$^b$Schofield [1935]
$^c$Chen et al. [2000a, 2000b]
Figure captions

**Figure 1.** Data-model comparison for SWR functions: (a) Palouse, (b) Palouse B, (c) Walla, (d) Salkum, (e) Royal, (f) L-Soil, (g) Rothamsted. Dash-dotted line corresponds to the MS-N model [Morel-Seytoux and Nimmo, 1999], while solid line is for the present approach.

**Figure 2.** Comparison between experimental data, MS-N model [Morel-Seytoux and Nimmo, 1999] and the present approach represented at BET scale: (a) Royal soil, (b) L-Soil.

**Figure 3.** Present SWR model fitted to water adsorption data and Campbell model from Chen et al. [2000a, 2000b] (Yolo silt loam soil).

**Figure 4.** Comparison of water transport experimental data LW2 [Chen et al., 2000b] and numerical simulation including the present SWR function (a) percentage of initial water remaining in the soil, (b) water content profile at the end of the experiment (the dash-dotted line corresponds to the initial water content).

**Figure 5.** Evolution of measured and calculated volumetric water content at different depths during LW2 experiment [Chen et al., 2000b]. Nominal depths for experimental data: ● 1 cm, ○ 10 cm. Solid lines denotes the present simulation results at the indicated depth. Dash-dotted lines are for the simulation of Chen et al. [2000b].

**Figure 6.** Influence of water retention function on the evolution of (a) water evaporation, and (b) ethanol volatilization fluxes.
Figure 7. Evolution of the volumetric water content calculated with the MS-N model \cite{Morel-SeytouxNimmo1999} and the present model.
Figure 1(a)-(b)
Figure 1(c)-(d)
Figure 1(e)-(f)
Figure 1(g)
Figure 2

BET adsorption isotherm

Bradley generalized isotherm

Morel-Seytoux & Nimmo [1999] present model

Saturation

(a) Royal

(b) L-Soil

relative humidity, $x$
Figure 3
Figure 4

(a) Initial water content

(b) Experimental data

Simulation of Chen et al. [2000b]

Present simulation
Figure 5
Figure 6

(a) Evaporation flux (kg/m²-s) over time (hours).

(b) Volatilization flux (kg/m²-s) over time (hours).

Figure 7