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Water Vapor Adsorption and Soil Wetting

Abdelmonem Mohamed Ahmed Amer

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Abstract

Soil water management and irrigation practices largely depend on a timely and accurate characterization of temporal and spatial soil moisture dynamics in the root zone. Consequently, measurements and detailed information about soil water sorption, water content, behavior, and potential are required. In that concern, water vapor adsorption is an important phenomenon in arid and semi-arid regions, as well as in dry periods of tropical soils. Therefore, quantifying adsorption is important for agricultural water management, surface energy balance studies, ecological studies, and remote sensing investigations (changes in surface soil moisture content will affect land surface properties such as albedo, emissivity, and thermal inertia). The vapor pressure and isothermal adsorption of water vapor can be used to predict soil moisture adsorption capacity (W_a), specific surface area, and hydro-physical properties of arid soils such as in Egypt and in the tropical soils in Ecuador. Theory of adsorption of water vapor on soil particles is developed among the mono-molecular and poly-molecular adsorption with respect to Brunauer, Emmett, and Teller (BET) theory. Data of soil-water adsorption ($W\%$) at different relative vapor pressures (P/P_o) can be obtained for the soils, where the $W\%$ values are increased with increasing P/P_o in general. The highest values of water adsorption capacity (W_a), specific surface area (S), and other hygro-physical properties such as adsorbed layers and maximum hygroscopic water are observed in the clay depths of soil profiles, while the lowest values can be found in coarse textured soils (sandy and sandy loam soils profiles). Two equations were assumed: (1) to predict P/P_o at water adsorption capacity (W_a) and (2) to apply W_a in prediction of soil moisture retention, i.e., $\psi(W)$ function at $pF < 4.5$.

Keywords: Water adsorption capacity, vapor pressure isotherm, soil hydro-physical properties, specific surface area, poly-molecular adsorption, soil wetting

1. Introduction

The depletion in irrigation water in arid and semi-arid regions, as well as in some tropical zones, may be due to the discharge scarcity of water resources in dry periods at which the high temperature and dry weather supports to more evapotranspiration. In that concern, water vapor is adsorbed from the atmosphere by a thin layer of top soil where the amounts of adsorbed water can be considerable, up to 70% of daily evaporation depending on water vapor amount, pressure, and temperature [20, 17, 1].

Adsorbed water on soil surface layer can be caused not only by vapor adsorption but also by dew deposition. Dew deposition is a phenomenon recorded for most soil and climate types [16]. It occurs with decreasing the temperature, particularly during the night, when dew point is reached and it results in a discernible wetting of the surface.

The vapor pressure and isothermal adsorption of water vapor is used to predict soil moisture adsorption capacity (W_a) and the specific surface area (S). The specific surface area is closely related to the physic-chemical soil properties, which refer to the absence or presence of internal pores. It can be used to evaluate quality, fertility, chemical reactions, and mineralogical composition of soils and subsequently, its nutrition elements status for crop production.

2. Water vapor pressure

According to the kinetic theory, molecules in a liquid are in continuous motion reflecting their thermal energy. Occasionally, one or another of the molecules absorbs sufficient momentum to leap out of the liquid into the atmosphere above it. The relative movement rates of molecules depend upon the concentration of vapor in the atmosphere relative to its concentration at a state of equilibrium (i.e., when the movement in both directions of water and air is equal). An atmosphere that is at equilibrium with a body of pure water that is at atmospheric pressure is considered to be saturated with water vapor; the partial pressure of the vapor in such an atmosphere is called the saturation (or equilibrium) vapor pressure. The vapor pressure at equilibrium with any body of water depends upon the physical condition of the water (pressure and temperature) and its chemical condition (solutes), but does not depend on the absolute or relative quantity of liquid or gas in the system [11]. The saturation vapor pressure increases with increasing temperature. If the temperature range is not too wide, the dependence of saturation vapor pressure on temperature is expressible by the equation:

$$\ln P_o = a - b / T \quad (1)$$

where $\ln P_o$ is the logarithm to the base “e” of the saturation vapor pressure P_o , T is the absolute temperature, and a and b are constants.

3. Atmospheric humidity

Air humidity is expressed by either absolute humidity, which is known by estimation of the amount of water vapor already existing in unit volumes of air, or relative humidity, which is estimated as a percentage of the amount water vapor already existing in unit volumes of air and the amount of water required for the steam to satisfy this volume of air at the same temperature. Generally, the water vapor percentage change from one place to another is less significant in desert areas due to the lack of water, as well as in the polar regions where it is much colder and there is less evaporation and less possibility of the air to bear the water vapor; while water vapor is higher in the air in warm, rainy, and tropical regions [7]. On the other hand, the water vapor density decreases with height greater than the density of the main constituent gases of the air, i.e., when rising from 1.5 to 2 km above sea level, water vapor density is less twice than that of atmospheric layer in contact with the surface of the earth, and vanish at altitudes of more than 10–15 km [8]. In general, at all times and at different temperatures a part of water vapor remains in a gaseous phase even with predominance of condensation in the air. Therefore, water vapor is considered as one of the air gases component, and has a significant pressure like the rest of the gases in the atmosphere. This pressure (P) is linked to the quantity water vapor (Q) by the relationship [6]:

$$Q = \frac{1.06P}{(1 + \alpha T)} \quad (2)$$

where α represents volumetric expansion coefficient of air ($\alpha = 0.004$), and T is air temperature. From the relationship, it is clear that $Q = P$ when the temperature rises to 15°C, and thus relative humidity can be expressed in terms water vapor pressure rather than mass (quantity), i.e., relative humidity = actual pressure (P)/pressure saturated (P_0). The difference between saturated vapor pressure and actual vapor pressure is represented in the lack of air humidity, which is known as lack of saturation (or saturation deficit). The lack of saturation is equal to zero at the dew point, which means that the air could not carry other amounts of water vapor. The dew point can be obtained when the temperature is reduced to the degree at which the condensation of water vapor begins, and then the saturation pressure is reached. Thus, relative humidity can be expressed as a percentage of the saturated water vapor pressure at the dew point (i.e., at the temperature of condensation) to the saturated water vapor pressure at normal temperature. Thus, it is clear that the saturation of the air with water vapor is directly influenced by air temperature degree.

4. Water vapor and soil humidity

Water vapor either reaches the soil from the atmosphere or is formed in the soil by the evaporation of water. The migration of water vapor in soil depends not only on the difference

of vapor pressure in different sites, but also on the capacity of soil particle surfaces to attract and absorb the molecules of vapor.

On the other hand, the relative humidity values in soil can be transformed to water potential values ψ (Pa) according to Equation (3) [7, 14]:

$$\Psi = \frac{RT}{M} \ln \frac{P}{P_0} \quad (3)$$

where R is the gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature of the air (K), M is the molecular weight of water ($0.018015 \text{ kg mol}^{-1}$), and P and P_0 are the actual and saturated vapor pressures (Pa), respectively. The term $(P/P_0) \times 100$ is equal to relative humidity (H).

However, soil water contains solutes—mainly electrolytic salts—in highly variable concentrations. Since the vapor pressure of electrolytic solutions is lower than that of pure water, accordingly, soil water also has a lower vapor pressure even when the soil is saturated. In an unsaturated soil, the capillary and adsorptive effects further lower the potential and the vapor pressure.

Adsorption is an interfacial phenomenon resulting from the differential forces of attraction or repulsion occurring among molecules or ions of different phases at their exposed contact surfaces. Consequently, various types of adsorption can occur according to the different phases, such as the adsorption of gasses upon solids, gasses upon liquid surfaces, or liquids upon solids.

A distinction should be made between **adsorption**, being a surface attachment or repulsion, and its complementary term **absorption**, which refers to cases in which one phase penetrates or permeates another. For instance, some of the molecules in the gaseous phase (water vapor) may strike the surface of the liquid (soil moisture) and be absorbed in it. Actually, it is often difficult to separate the phenomenon of adsorption from that of absorption, particularly in the case of highly porous systems, and hence the non-committal term sorption is frequently employed.

On contact of soil particles with water vapor, electro-molecular force of interactions are formed that strongly attract dipoles of water to the surface of mineral particles; and the greater the unit surface area of the particles, the larger the number of water molecules in a bonded state.

5. Soil moisture films and adsorption capacity

The electro-molecular force is very strong, as much as several hundreds of mega-Pascal (MPa) for the first layer of bonded (adsorbed) molecules of water at the surface of particles. In the layers of water, the 1–3 rows of molecules that are closest to the mineral particle surface are firmly immobile adsorbed water or the so-called **adsorbed films**. Beyond these layers, the interaction forces attenuate rapidly and reach zero at a distance of approximately 0.5 mm from

the surface of the mineral particles; and hence, more moisture layers will envelope the particles and form the loosely bonded water or **wetting films**.

Amer [8] studied the molecules layers of the adsorbed films and proved that the three layers of adsorbed water can be expressed in term of soil moisture adsorption capacity (W_a) in the following form:

$$W_a = W_m + 2W_{me} \quad (4)$$

where W_m is the moisture content of the soil when water vapor is adsorbed in the monolayer, and W_{me} is the external mono-adsorbed layer of soil moisture content.

The W_m and W_{me} are used also to determine total, external, and internal specific surface areas (S , S_e , and S_i) by applying the BET method (Brunauer et al. [10]) as modified and described by Farrar [12] and Globus [13].

The property of moisture adsorption capacity (W_a) can be introduced as the critical limit between adsorbed and absorbed wetting films (pellicles) of soil moisture content, as well as correspond to capillary condensation [7]. However, the W_a values can be also derived from the soil moisture tension curve by applying the corresponding values of $\log(\psi_c)$ where ψ_c is the capillary condensation attitude [9].

The moisture adsorption capacity (W_a), maximum hygroscopic water (MH), specific surface area (S), and particle size composition are the most important indices characterizing the hygro-physical, physicochemical, and heat properties of soil. Moreover, these parameters are inter-related to each other; therefore, the value of a parameter of them can be obtained from the data of the other parameters.

6. Adsorption isotherms and BET theory

The relationship between vapor pressure and moisture content is difficult to be deduced by means of thermodynamics but can be obtained experimentally or from theories of soil moisture involving the molecular structure of the water films, whereas, soil sample is maintained in equilibrium with an atmosphere of water vapor, a thin film of moisture is adsorbed on the external surface of the soil particles. So the water vapor adsorption isotherms (at 25°C) on dried soil particles can be determined gravimetrically using different saturated salt solutions that have specific relative water vapour pressure (P/P_o) value for each solution. Table 1 shows the values of P/P_o for some saturated solutions of salts and also the corresponded chemical potential or its equivalent pressure at 25°C [7].

The vapor adsorption isotherms, specific surface area, moisture adsorption capacity, and hygroscopic parameters of soil have been found to be correlated with soil physical properties such as texture, cohesion, clay percentage, clay minerals, cation exchange capacity, water retention, and permeability. Figure 1 shows the water vapor adsorption isotherms for sandy soils, located at Mláky II near Sekule Bratislava (southwest Slovakia).

| Salt | P/Po | ψ | | | |
|--|------|--------|------|--------|----------|
| | | Atm. | pF | KPa | Joule/gm |
| K ₂ Cr ₂ O ₇ | 0.98 | 27 | 4.44 | 2780 | 2.78 |
| K ₂ SO ₄ | 0.97 | 43 | 4.62 | 4370 | 4.37 |
| KNO ₃ | 0.92 | 107 | 5.06 | 10830 | 10.83 |
| ZnSO ₄ ·7H ₂ O | 0.87 | 188 | 5.28 | 19010 | 19.01 |
| KCl | 0.84 | 233 | 5.38 | 23580 | 23.58 |
| KBr | 0.81 | 292 | 5.46 | 29550 | 29.55 |
| NH ₄ Cl | 0.77 | 348 | 5.56 | 35820 | 35.82 |
| NaCl | 0.75 | 386 | 5.60 | 39120 | 39.12 |
| NaNO ₃ | 0.74 | 413 | 5.62 | 41840 | 41.84 |
| NH ₄ NO ₃ | 0.62 | 653 | 5.82 | 66200 | 66.20 |
| Ca(NO ₃) ₂ ·4H ₂ O | 0.50 | 942 | 5.98 | 95530 | 95.53 |
| K ₂ CO ₃ ·2H ₂ O | 0.43 | 1155 | 6.07 | 117000 | 117.00 |
| KCH ₃ COO·1.5H ₂ O | 0.22 | 2031 | 6.32 | 205780 | 205.78 |
| LiCl·H ₂ O | 0.12 | 2781 | 6.47 | 292000 | 292.00 |

Table 1. Values of chemical potential (ψ) of some saturated solutions of salts and its equivalent pressures to relative vapor pressure at 20 °C.

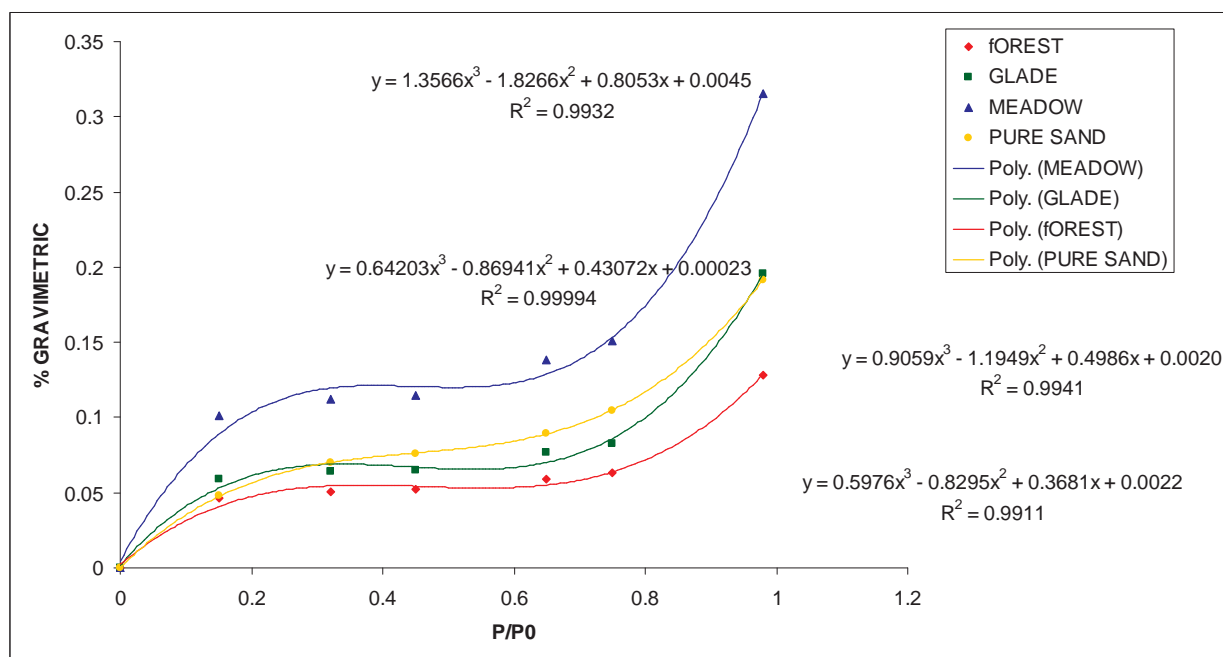


Figure 1. Unpublished data of the relationship between gravimetric adsorbed water (W%) and vapor pressure P/P_o in sandy soils (94% sand in average) with plant cover.

On the other hand, Figure 2 shows the adsorption isotherms for the clay minerals. However, a number of theories have been proposed to explain the observed relation between the vapor pressure and moisture content of a soil. The most widely used theory is from Brunauer, Emmett, and Teller [11], whereas they derived what has come to be known as the BET equation based on multilayer adsorption theory. In the BET theory, the explanation proposed for sigmoid type isotherm (Figure 1) is that the adsorption is in multi-molecular layers on the surface rather than a mono-molecular one. Farrar [12] and Amer [9, 8] used the water vapor adsorption isotherm method by applying BET theory based on the assumption that the isotherm is made up of monolayer physical adsorption combined with capillary condensation as follows:

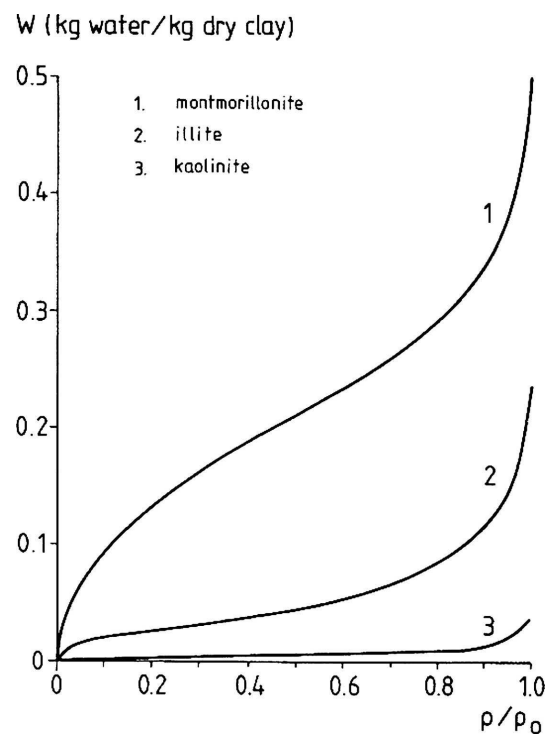


Figure 2. Adsorption isotherms for water on different clay minerals (reprinted from Verhoefe, et al., 2006 [20] upon Orchiston, 1954 [19]), P/P_o denote the soil relative humidity.

$$\frac{\frac{P}{P_o}}{V\left(1 - \frac{P}{P_o}\right)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P}{P_o} \quad (5)$$

where V is the volume of gas adsorbed at pressure P , V_m is the volume of a single layer of adsorbed molecules over the entire surface of the adsorbent (soil particles), P_o is the gas pressure required for monolayer saturation at the temperature of the experiment, and C is a constant for the particular gas, adsorbent, and temperature;

$$C = \exp \frac{E_1 - E_L}{RT} \quad (6)$$

whereas, E_1 is adsorption heat of the water adsorbed layer, E_L is condensation adsorption heat.

At values of P that are far from P_s and $C > 1$, adsorption leads to the formation of a monomolecular layer. As P approaches P_s , the number of free active centers that are always present on the adsorbent surface decreases and the multiplicity of complexes increases. At $P = P_s$, the condensation of vapor occurs.

7. Prediction of adsorbed layers (W_m & W_{me}) and adsorption capacity (W_a)

In order to estimate W_m and W_{me} , and then calculate the soil moisture adsorption capacity (W_a), the relation between relative vapor pressure (P/P_o) and moisture content ($W\%$) should be experimental, obtained by maintaining a soil sample in isothermal equilibrium with an atmosphere of water vapour.

The following linear form of the BET equation can be applied using the gravimetric of a single layer of adsorbed molecules over the entire surface of the soil particles:

$$\frac{P}{W(P_o - P)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} \cdot \frac{P}{P_o} \quad (7)$$

where W_m is the moisture content when the soil surface is completely covered by a monomolecular layer of water. C is a function of the state of the first adsorbed uni-molecular layer of water and soil particles surface. W is adsorbed soil moisture content (%) equilibrated with P/P_o , whereas P and P_o are the actual and saturated water vapor pressures. By plotting $P/W(P_o - P)$ as ordinate versus P/P_o at the segment 0–0.42 of the adsorption isotherm as abscissa, a straight line would be obtained. The intercept on the y-axis is then $1/W_m C$ and the slope is $C - 1/W_m C$. Hence W_m and C can be determined.

To determine W_{me} the BET Equation (7) can be developed with some assumptions to the next form:

$$W = \frac{W_{me}}{\left(1 - K_e \frac{P}{P_o}\right)} \cdot \frac{C_e}{\left(C_e + \frac{P_o}{P} - K_e\right)} + W_i \quad (8)$$

At high relative water vapor pressures, it can be assumed that the amount $\frac{C_e}{\left(C_e + \frac{P_o}{P} - K_e\right)}$ is equal unit, and then Equation (8) becomes:

$$W = \frac{W_{me}}{\left(1 - K_e \frac{P}{P_0}\right)} + W_i \quad (9)$$

where the suffixes (e) and (i) refer to the external and internal surfaces, respectively. The values of K_e in the indicated P/P_0 range were stated by Farrar [12] as 0.9 ± 0.01 ; but practically, it seems that K_e is an arbitrary coefficient ranged from 0.70 to 0.90 [4].

Equation (9) can be represented in the linear equation $y = mx + c$, where $y = W$, $m = W_{me}$, $x = 1 / (1 - K_e P/P_0)$, and $c = W_i$, so W_{me} can be obtained graphically as the intercept on the y - axis.

From W_m and W_{me} the soil water adsorption capacity (W_a) can be calculated (Equation 4).

8. Soil specific surface area

The specific surface of the adsorbent (soil) can be calculated by determining the number of molecules (volumetrically or gravimetrically) and multiplying this by the cross-sectional area of the molecules. Assuming that a single water molecule occupies some constant area on the sorbent surface (usually taken as 10.8°A^2), the total specific surface area (S) of the soil is then calculated as $S = 36.16 W_m \text{ m}^2/\text{g}$, and accordingly, the external specific surface is estimated as $S_e = 36.16 W_{me} \text{ m}^2/\text{g}$.

However, the internal specific surface area (S_i) may be calculated by the difference between S and S_e .

In general, high clay content in soil means increasing the specific surface areas, hygroscopic water, soil moisture content and retention, and water adsorption capacity (W_a) (Figure 3).



Figure 3. Clay soil samples were taken at depth >90 cm from the INIAP research station, Pichilingue, Ecuador ~containing ferrous and ferric minerals with the high values of specific surface area and water adsorption capacity (Final Report by Amer, 2014 [2] - SENESCYT, Prometeo Project, Ecuador).

Hygroscopic water exists as a very thin film at the solid-liquid interfaces of the soil particles. At the maximum hygroscopic water (MH), the surface of soil particles is almost completely covered with individual molecules of water. However, it is known that the maximum hygroscopic water (MH) is determined practically at $P/P_o = 0.98$.

9. Absorption water in relation to P/P_o and pF scale

Equation (7) can be developed to predict the vapor pressure (P/P_o) at water adsorption capacity (W_a) as follows:

$$\frac{\frac{P}{P_o}}{w \left(1 - \frac{P}{P_o} \right)} = A + B \frac{P}{P_o} \quad (10)$$

where, $A = 1/W_m C$, and $B = C - 1/W_m C$

From Equations 7 and 10;

$$W \left(\frac{P_o - P}{P_o} \right) = \frac{\frac{P}{P_o}}{A + B \frac{P}{P_o}} \quad (11)$$

Then at W_a :

$$\left(\frac{P}{P_o} \right)_{W_a} = \frac{P}{W_a (P_o - P) B} - \frac{A}{B} \text{ and } P = W_a (P_o - P) (A P_o + B P) \quad (12)$$

Relative vapor pressure $[P/P_o]_{W_a}$ at W_a is ranged between 0.42 to 0.51, indicating that at this range the soil moisture reach water *adsorption* capacity. Above this range ($P/P_o > 0.51$) the *absorption* process is prevailing. Hence, to predict the soil absorbed water, Equation (7) can be rearranged to be available for application along the range of high relative vapor pressure ($0.50 < P/P_o < 1.0$):

$$w = \frac{\frac{P}{P_o}}{\left[1 - \frac{P}{P_o} \right] \left[\frac{1}{W_m C} + \frac{C - 1}{W_m C} \cdot \frac{P}{P_o} \right]} \quad (13)$$

By applying the intercept ($1/W_m$) and the slope ($C-1/W_m$), we can obtain $W\%$ at P/P_o values.

On the other hand, soil water potential (ψ) values corresponded to the total range ($0.0 < P/P_o < 1.0$) can be calculated using Equation 3 in the following form (pF equation):

$$pF = 6.502 + \log [2 - \log H]$$

where pF = soil moisture potential, expressed as the common logarithm of the suction (ψ) in cm of water; H is the relative humidity ($H = P/P_o \times 100$); and P/P_o is the relative water vapor pressure [P being the actual water vapor pressure on the soil particles and P_o being the saturation vapor pressure of water at 20°C]. These parameters can be obtained by applying different appropriate salt solutions, whereas, the soil moisture potential (ψ) values which resulting from equilibrating soil samples with salt solutions that have different relative humidity (H). The ψ values expressed in pF at adsorption and absorption processes are in the range pF = 4.5–7.0.

10. Application of W_a for prediction of soil wetting

The increase in soil water suction is associated with a decreasing thickness of the hydration envelopes covering the soil particle surfaces and vice versa. The following equation was advanced by Nerpin & Chudnovski [17] to describe soil wetness (h) within limited suction ranges:

$$\psi = B / W^n \quad (14)$$

where ψ is matric or capillary-sorption potential, B and n are constants.

Taking moisture adsorption capacity (W_a) in consideration, the concept of the last relation (14) can be developed to predict the soil wetting expressed in moisture potential or matric suction (ψ) at pF < 4.5 as follows:

$$\psi = \frac{\psi_a}{\left(W_i - \frac{W_c}{W_{me}} \right)^n} \quad (15)$$

or in log form;

$$\log \psi = \log \psi_a - n \log \left(W_i - \frac{W_c}{W_{me}} \right) \quad (16)$$

where ψ_i and ψ_a are capillary-sorption potentials at soil water content (W_i) and moisture adsorption capacity (W_a), respectively. The W_c is called boundary moisture films.

By plotting $\log \psi_i$ against $\log (W_i - W_c/W_{me})$, we obtain $\log \psi_a$ as intercept and n as the slope.

Substituting the coefficients parameters $\log \psi_a$ and n in the equation 16, the $\log \psi_i$ then could be obtained at arbitrary soil water content (W_i). From the relationship between $\log \psi_i$ and W_i we obtain the integrated soil moisture (retention) curve (Figure 4) or $\psi(W)$ function.

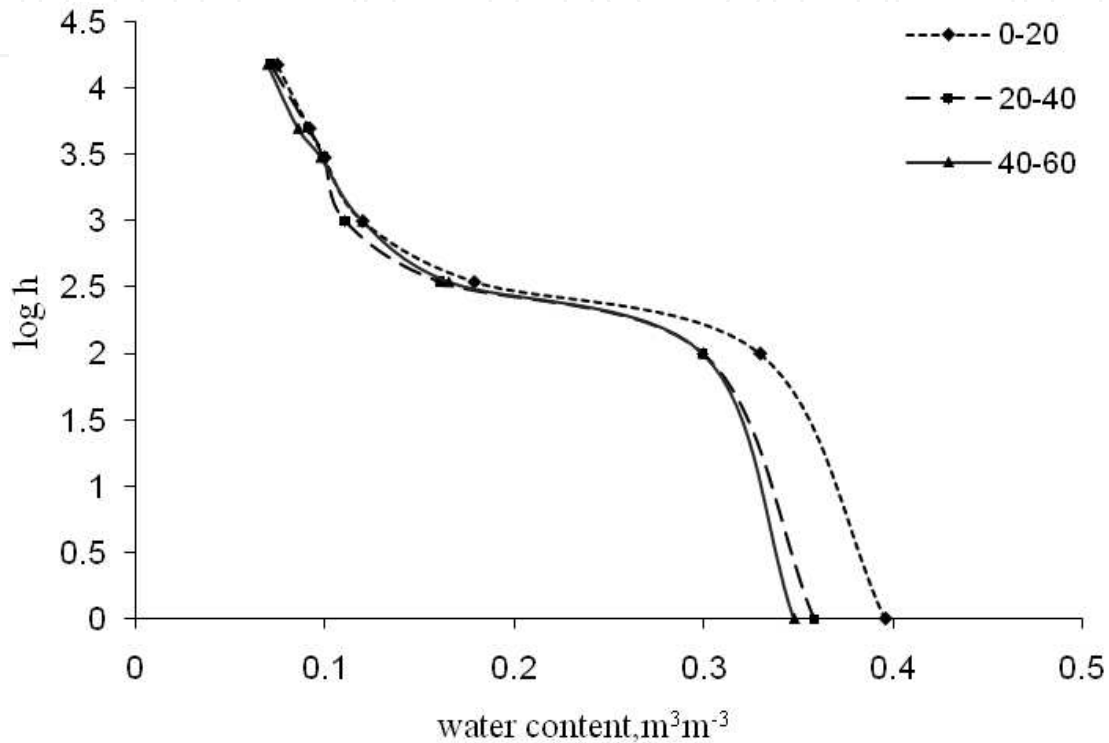


Figure 4. Moisture retention curves for three depths (cm) in Nubaria calcareous sandy loam soil (west Nile Delta, Egypt).

The moisture potential (ψ_i) can be expressed in $\log h$ (= pF), and called soil matric suction or pressure head (h), which is expressed as potential per weight (m) in SI units. In this case, the pF term is useful to apply as $pF = \log h$, when h is expressed in cm (Figure 4).

Author details

Abdelmonem Mohamed Ahmed Amer

Address all correspondence to: amer_abdel@hotmail.com

Soil Science Department, Faculty of Agriculture, Menoufia University, Shebin El-Kom, Egypt

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