CHAPTER III
MATERIALS AND METHODS

III.1. Soil samples

Three surface soil samples (0-40 cm depth) were collected to perform the present study. The soil samples were taken from different locations as follows:

1. Calcareous soil: The calcareous soil sample was collected from El-Hammam region, Matrouh Governorate (30° 48.814' N latitude, 29° 24.094' E longitude and 18 m above sea level).

2. The sandy soil: The soil was taken from Idko region, Behaira Governorate (31° 16.827' N latitude, 30° 15.484' E longitude and -2 m above sea level).

3. The sandy clay loamy soil: The soil was taken from Hammad village, Rashid region, Behaira Governorate (31° 19.694' N latitude, 30° 26.373' E longitude and 10 m above sea level).

Some of physical and chemical properties of the soil samples are reported in Table (1).

III.2. Soil Properties

Soil physical and chemical properties of the collected soil samples were determined according to the recommended procedures as follows:

III.2.1. Physical properties of soils

Bulk density of each soil sample was measured according to the weight of soil and the volume of packed column (**Klute, 1986**).

Particle-size distribution was determined by the hydrometer method (**Carter and Gregorich, 2008**).

Saturated hydraulic conductivity, K_s

The saturated hydraulic conductivity (Ks) was determined according to the constant head method (**Klute and Dirksen, 1986**).

III.2.2. Chemical properties of soils

The soil samples were air dried, passed through a 2 mm sieve and analyzed according to the following procedures.

Total carbonates content

Was estimated volumetrically using calcimeter and calculated as calcium carbonate percentage according to **Richards (1972).**

Organic matter content

Organic carbon (OC) was determined using modified Walkley-Blacks titration method (**Carter and Gregorich, 2008**). The organic matter content (OM) was calculated using the suitable constant ($OM = 1.724 \times OC$).

Total soluble salts

Electrical conductivity (EC) of soil: water extract, 1:2 (w/v) was measured using conductivity meter according to **Jackson (1973).**

Soluble Calcium and Magnesium

Soluble calcium and magnesium in soil: water extract were determined volumetrically by the versenate method (EDTA) using ammonium purpurate as an indicator for calcium and Erichrome black T for calcium plus magnesium (**Jackson, 1973**).

Table (1). Some physical and chemical characteristics of experimental soil

Parameters	Sandy loam soil	Sandy soil	Sandy clay loam soil
Particle size distribution, %			
Sand	68.65	91.87	56.99
Silt	13.75	5.00	9.63
Clay	17.6	3.13	33.38
Textural class	**Sandy loam**	**Sandy**	**Sandy clay loam**
Soil bulk density, Mg/m^3	1.417	1.617	1.227
Soil particle density, Mg/m^3	2.62	2.65	2.60
Hygroscopic water content , m^3/m^3	0.035	0.018	0.119
Saturation percentage, m^3/m^3	0.423	0.367	0.647
$CaCO_3$, %	29.82	3.27	0.20
Soil organic matter content, %	0.86	0.16	3.44
pH (1:2, soil : water suspension)	8.08	8.00	8.30
EC, dS/m (1:2, soil: water extract)	1.00	0.30	0.96
Soluble cations, meq/l			
Ca^{2+}	3.41	0.95	2.30
Mg^{2+}	0.80	0.90	3.10
Na^+	5.00	0.98	2.95
K+	0.90	0.11	1.18
Soluble Anions, meq/l			
$CO_3^= + HCO_3^-$	2.45	1.38	0.53
CL^-	4.95	1.05	2.00
$SO_4^=$	2.40	0.55	2.10
Available K, mg/kg	95.0	85.6	169.8

Soluble Sodium and Potassium

Soluble sodium and potassium was determined photometrically using flame photometer according to **Jackson (1973).**

Soluble Carbonates and Bicarbonates

Soluble carbonates and bicarbonates were determined volumetrically by titration against 0.1N hydraulic acid using phenolphthalein and methyl orange as indicators **(Jackson, 1973).**

Soluble Chlorides

Soluble chlorides were determined by titration against 0.05 N Silver nitrate solution and potassium chromate as an indicator **(Jackson, 1973).**

Soluble sulfates

Soluble sulfates were determined by turbidity method as an indicator **(Jackson, 1973).**

Exchangeable Potassium

The available K was extracted using NH_4OAc 1N (1:10. soil: water ratio) at pH =7 according to **Carter and Gregorich (2008),** then the K ion was measured using Flame Photometer method. The exchangeable fraction was calculated by subtracting the soluble from available fraction.

III.3. Soil hydraulic parameters

Soil water retention, $\theta(h)$ and soil hydraulic conductivity, $K(h)$ functions are specified. The soil water retention curve was determined using the pressure plate extractor according to the method described in **Klute (1986).** The water retention data was described using the van Genuchten model **(van Genuchten, 1980):**

$$S_e = \frac{\theta(h)-\theta_r}{\theta_s-\theta_r} = \frac{1}{(1+|\alpha h|^n)^m} \tag{30}$$

$$\theta(h) = \theta_r + \frac{\theta(h)-\theta_r}{\theta_s-\theta_r} \qquad h < h_e$$
$$= \theta_s \qquad h >= h_e$$
$$K(h) = K_s K_r(h) \qquad h < 0$$
$$= K_s \qquad h >= 0 \tag{31}$$

$$K_r(h) = \frac{\left\{1-(\alpha h)^{n-1}\left[1+(\alpha h)^n\right]^m\right\}^2}{\left[1+(\alpha h)^n\right]^{m/2}}$$

Where:

S_e is effective saturation (-);

$\theta(h)$ is the soil water content at matric potential, h $(L^3 L^{-3})$;

h   is the soil matric potential (L);

θ_r is the residual volumetric water content $(L^3 L^{-3})$;

θ_s is the saturated volumetric water content $(L^3 L^{-3})$;

n and **m(m=1-1/n)** are empirical coefficients; and

α is a fitting parameter (L^{-1})

The hydraulic conductivity function was described using the capillary model (Mualem, 1976) as applied to the van Genuchten model (**van Genuchten, 1980**):

$$K(h) = K_s S_e^{\tau} \left[1 - \left(1 - S_e^{1/m} \right)^m \right]^2 \tag{32}$$

Where:

K(h) is the unsaturated hydraulic conductivity(LT^{-1});

K_s is the saturated hydraulic conductivity (LT^{-1}); and

ι is the pore connectivity coefficient (assumed as 0.5 according to **Mualem, 1976**)

The saturated hydraulic conductivity (K_s) was determined using constant head permeameter method as described in **Klute (1986).**

The soil hydraulic parameters were fitted using the **RETC** model (**van Genuchten et al., 1991**).The soil water retention curve of soil samples were fitted.

Durner (1994) divided the porous medium into two (or more) overlapping regions and suggested to use for each of these regions a van Genuchten-Mualem type function (**van Genuchten, 1980)** of the soil hydraulic properties. Linear superposition of the functions for each particular region gives then the functions for the composite multimodal pore system (**Durner et al., 1999):**

$$S_e = w_1 \left[1 + (\alpha_1 h)^{n_1} \right]^{-m_1} + w_2 \left[1 + (\alpha_2 h)^{n_2} \right]^{-m_2} \tag{33}$$

Combining this retention model with Mualem's pore-size distribution model (**Mualem, 1976)** leads now to:

$$K(Se) = Ks \frac{(w_1 S_{e_1} + w_2 S_{e_2})^1 \left(w_1 \alpha_1 \left[1 - (1 - S_{e_1}^{1/m_1})^{m_1} \right] + w_2 \alpha_2 \left[1 - (1 - S_{e_2}^{1/m_2})^{m_2} \right] \right)^2}{(w_1 \alpha_1 + w_2 \alpha_2)^2} \tag{34}$$

Where: w_i are the weighting factors for the two overlapping regions, and α_i, n_i, m_i (=1-$1/n_i$), and i are empirical parameters of the separate hydraulic functions (i=1, 2), (**Šimůnek et al., 2013)**

III.4. Potassium Kinetic Isotherm

Triplicate 5 g soil samples were equilibrated in a 50 ml centrifuge tube with 50 ml of 0.01 M $CaCl_2$ solution containing 100 mg K/l. The soil samples were then agitated on a rotary shaker to achieve equilibrium for 0, 1, 5, 10, 20, 30, 60, 90, 120, 180, 240, 360 and 420 min and K ion concentration was measured by Flame photometer and expressed as mg/l.

III.5. Potassium Sorption Isotherm

Triplicate 5 g soil sample were equilibrated in a 50 ml centrifuge tube with 50 ml of 0.01 M $CaCl_2$ solution containing 0, 5, 10, 20, 30, 50, 100, 150, 200, 300 and 400 mg K/l as KCl. The soil samples were then agitated on a rotary shaker to achieve equilibrium for 30 min. and K ion concentration was measured by Flame photometer and expressed as mg/l.

Solute sorption is assumed to be given by linear isotherm equation as follows (**Matott, 2006; Mattot and Rabideau, 2008**):

$$S = K_d C_e \tag{35}$$

Where: S is the sorbed K (mg/g), C_e is the equilibrium concentration (mg/l) and K_d is the partition (sorption) coefficient (L/kg^1) as:

$$\frac{\partial S}{\partial t} = K_d \frac{\partial C}{\partial t} \tag{36}$$

The sorbed potassium was calculated according to the following formula:

$$S\,(\text{mg/g}) = \frac{(C_0 - C_e) \times V}{W} \tag{37}$$

Where: C_0 is the initial concentration (mg/l)
V is the volume of solution (ml)
W is the weight of soil (g)

III.6. Column experiments
III.6.1. Soil columns

Polyvinyl chloride columns, 65 cm long and 19 cm diameter (283.5 cm^2 surface area) with closed bottoms, were used in the study. The base of the columns was tightly sealed with silicon adhesive. The bottom 1 cm layer, in the columns, was coarse gravel as (drainage layer). A plastic tube of 1.0 cm diameter fitted into the drainage layer at 60 cm soil depth to collect the drainage water. The columns were hand-packed with air dried soil samples for height of 60 cm at constant bulk density by gently tapping for each soil (Fig. 5).

1 – Bottle

2 – KCl solution

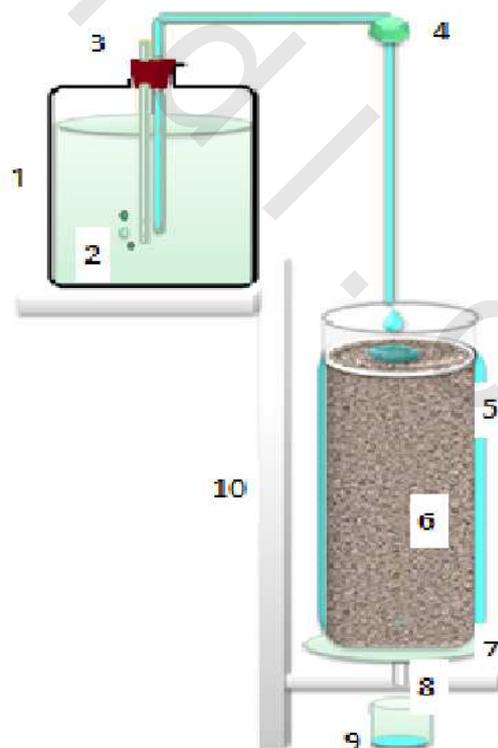3 – Rubber stopper

4 – Adaptor

5 – PVC Column

6 – Soil

7 – Plastic Plate

8 – Plastic tube

9 – Glass bottle

10 – Stand

Fig. (5). Layout of column experiment

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III.6.2. Mariotte's bottle

A Mariotte's bottle is a device that allows constant flow of a fluid from a reservoir, even when the fluid level in the reservoir changes **(Holden, 2005; Moore, 2004)**. **Glasses were** used to collect solute drained from soil column (Fig.6).
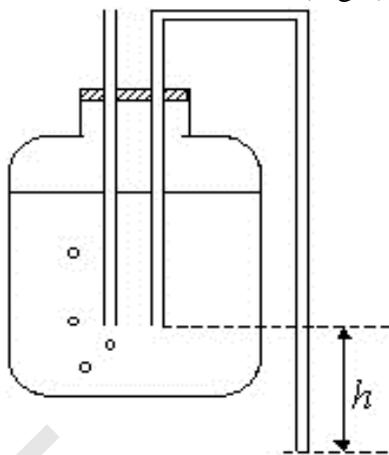

Fig. (6). Mariotte's bottle

III.6.3. Experimental setup and protocol

All soil columns were brought back to the laboratory and placed on a support base. The bottom of each column rested on a Hardback plastic plate perforated with 1cm diameter holes for the Drainage of solution, columns were filled with soil and compacted homogeneously until reached the required soil bulk density. The arrangement of the experiment allows supplying a potassium solution at constant rate. The soil columns were subjected to water flux until steady state out flow at the bottom of soil column with solutions of 12.5 (tape water as control), 100 and 200 mg K/l as KCL. The KCL solution was added at constant rate and the leachate collected at the bottom end of each column was recorded. The leachate was monitored for volume and concentration values at corresponding time till the salt front has passed the lowest end of soil column, and then stopped recording data. The solute drained from the bottom of column was collected in glass bottle then volume and K concentration were measured.

Table (2). Soil column experimental data (Sandy loam soil)

Parameters	K application rate (mg/l)		
	Control	100	200
Calcareous soil (Sandy loam soil)			
Diameter (cm)	19.0	19.0	19.0
Soil bulk density (Mg/m^3)	1.417	1.417	1.417
Water flux density (cm/min)	0.0233	0.0454	0.0233
Water content (cm^3/cm^3)	0.273	0.294	0.278
Pore water velocity (cm/min)	0.0853	0.154	0.0838
Run Time (min)	1095	1095	1095

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Table (3). Soil column experimental data (Sandy soil)

Parameters	K application rate (mg/l)		
	Control	100	200
(Sandy soil)			
Diameter (cm)	19.0	19.0	19.0
Soil bulk density (Mg/m^3)	1.617	1.617	1.617
Water flux density (cm/min)	0.088	0.095	0.102
Water content (cm^3/cm^3)	0.204	0.210	0.215
Pore water velocity (cm/min)	0.431	0.452	0.474
Run Time (min)	360	360	360

Table (4). Soil column experimental data (Sandy clay loam soil)

Parameters	K application rate (mg/l)		
	Control	100	200
(Sandy clay loam soil)			
Diameter (cm)	19.0	19.0	19.0
Soil bulk density (Mg/m^3)	1.24	1.24	1.24
Water flux density (cm/min)	0.0067	0.00252	0.0035
Water content (cm^3/cm^3)	0.546	0.547	0.593
Pore water velocity (cm/min)	0.0123	0.0046	0.0059
Run Time (min)	5940	5940	5940

III.7. Water Flow and Solute Transport Models (Theory)

III.7.1. Water Flow

The one dimensional water flow can be described by the Richareds equation (1931):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h) \right] \tag{38}$$

Where θ is the volumetric water content (L^3 L^{-3}), h is the metric head (L), K(h) is the unsaturated hydraulic conductivity (LT^{-1}), t is the time (T) and Z is the vertical coordination (L) taken positively upward.

The water retention characteristics θ (h) and the unsaturated hydraulic conductivity function, K (h) are given by the Mualem-van Genuchten model (**van Genuchten, 1980**), Eq. (3-4 and 3-5).

The initial and boundary conditions of water flow are given as:

$$q(z,t) = q \qquad z = 0 \tag{39}$$
$$h(z,t) = h_0(z) \qquad t = 0$$

The lower boundary conditions are:

$$q(z,t) = -K(h) \qquad z = -L \tag{40}$$

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$$h(z,t) = 0 \qquad z = -L$$

The main objective of the present experiment is calculating the percolation of water at the bottom of the soil column periodically as influenced by the application of heterogeneity for different type from three soils.

III.7.2. Solute Transport

The partial differential equation governing one-dimensional advective-dispersive solute transport (ADE) under transient water flow conditions in partially saturated porous medium is taken as:

$$\frac{\partial \theta C}{\partial t} + \frac{\rho \partial S}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) - \frac{\partial q C}{\partial z} \tag{41}$$

Where: C is the total solute concentration in solution (ML^{-3}), S is the sorbed solute concentration (MM^{-1}), ρ is the soil bulk density (ML^{-3}), D is the effective dispersion coefficient ($L^2 T^{-1}$), q_w is the volumetric water flux (LT^{-1}). The second term on the left side, Eq. (41) is equal to zero for non-reactive solute.

The volumetric flux q_w is calculated with Darcy's Law:

$$q_w = -K\left(\frac{\partial h}{\partial z} + 1\right) \tag{42}$$

Where: K is the hydraulic conductivity (LT^{-1}) and h is the metric head (L) and z is the spatial distance (L).

The dispersion coefficient (D) is calculated according to **Bear (1972):**

$$\theta D = |\lambda L| q_w + \theta \tau D_w \tag{43}$$

Where: λ_L is the longitudinal dispersivity (L), D_w is the aqueous ionic or molecular diffusion coefficient of solute in water (L^2T^{-1}) θ is the volumetric water content and τ is the tortuosity factor given by (**Millington and Quirk, 1959**):

$$\tau = \frac{\theta^{7/3}}{\theta_s^2} \tag{44}$$

Where: θ_s is the saturated water content.

III.8. Parameters Estimation

III.8.1. Estimating of convection-Dispersion model parameter (Breakthrough curves):

When a solution of different chemical concentration from the residual soil solution is passed through the soil, the chemical concentration in the composition of drainage water (effluent) will gradually change. The process of replacing the resident soil solution with a different solution is termed miscible displacement and is demonstrated by the leaching of salts, the distribution of fertilizer, pesticides, waste products and other chemicals, and the use of tracers for following water movement through porous materials. By measuring the concentration change of the effluent of a soil column, information about the transport properties of the porous soil medium and the behavior of the solution moving through the soil can be obtained.

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h)\right] \tag{45}$$

The connective-dispersion (model) equation (CDE) is often used to describe solute transport through soils. A common form of the CDE is:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} \tag{46}$$

Where C is the solute concentration, t is time, D is the dispersion coefficient ($D = \lambda_L v$), v is pore water velocity ($v = q/\theta$), R is the retardation factor ($R = 1$ for non-reactive solution), λ_L is the longitudinal dispersivity and z represent a vertical coordination (distance).

Analytical solution to Eq. (46) have been developed for a number of specific initial and boundary conditions and many important soil physics problems involved estimating solute transport parameters based on fitting analytical solutions of CDE, or alternative models to measure breakthrough curves from miscible displacement experiments using CXTFIT model **(Parker and van Genuchten, 1984). Butters and Bandaranayake (1993)** have provided and excellent discussion of this approach.

The solute concentration distribution in a soil column with uniform initial (resident) concentration, C under steady state flow replaced at $t = 0$ with a solution of constant concentration, C0 is amenable to an analytical solution. The initial and boundary conditions are given and boundary conditions are given by:

$$C(z,0) = C_i$$

$$C(0,t) = C_0 \tag{47}$$

$$\frac{\partial C}{\partial t}(\infty, t) = 0$$

The solution to Eq. (3-13) subject to these initial and boundary conditions (**Nielsen and Biggar, 1963 and van Genuchten and Wierenga, 1986**):

$$\frac{C(z,t) - C_i}{C_0 - C_i} = \frac{1}{2} erfc \frac{Rz - vt}{\sqrt{4DRt}} + \frac{1}{2} \exp(\frac{vz}{D}) erfc \frac{Rz + vt}{\sqrt{4DRt}} \tag{48}$$

$$\frac{C(z,t)}{C_0} = \frac{1}{2} erfc \left\{ \frac{z - v^* t}{\sqrt{4D^* Rt}} \right\} + \frac{1}{2} \exp\left(\frac{v^* z}{D^*} \right) erfc \left\{ \frac{z + v^* t}{\sqrt{4D^* Rt}} \right\} \tag{49}$$

Where: erfc(u) is the complementary error function and the remaining components were defined previously.

A simple solution commonly used displacement experiment is obtained by retaining only the first term on the right-hand side of Eq. (3-22).

$$\frac{C}{C_0} = \frac{C(z,t) - C_i}{C_0 - C_i} = erfc \frac{Rx - vt}{\sqrt{4DRt}} \tag{50}$$

Where: C_i is the minimum concentration value recorded at time $t = 0$ for the leachate at the bottom of soil column and C_0 is the maximum concentration values recorded at maximum time (t) for the leachate at the bottom of soil column at steady state.

III.8.2. Initial and Boundary conditions

The solution of Eq. (46) requires knowledge of the initial distribution of the pressure head or water content within the flow domain:

$$h(x,t) = h_i(x) \qquad\qquad t = t_0 \tag{51}$$

$$\theta(x,t) = \theta_i(x) \qquad\qquad t = t_0$$

Where: hi [L] is a prescribed function of x, and to is the time when the simulation begins. Initial condition can also be set (in the graphical user interface) to be equal to water content at field capacity, which is calculated as follows (**Twarakavi et al., 2009**):

$$S_{fc} = \frac{\theta_{fc} - \theta_r}{\theta_s - \theta_r} = n^{-0.60(2 + \log_{10}(K_s))}$$ (52)

Where θ_{fc} and S_{fc} are the water content and saturation at field capacity, and θ_r, θ_s, n, and K_s are the soil hydraulic parameters for the **van Genuchten (1980)** model. Note that the water content at field capacity corresponds to the hydraulic conductivity of about 0.01 cm/d (**Twarakavi et al., 2009**). The initial pressure head at field capacity is calculated from the water content at field capacity using the **van Genuchten (1980)** retention curve model (**Šimůnek et al., 2013**).

III.8.3. Water Mass Transfer

The mass transfer rate, Γ_w, in (53) for water between the fracture and matrix regions in several dual-porosity studies (**Phillip, 1968; Šimůnek et al. 2003**) has been assumed to be proportional to the difference in effective saturations of the two regions using the first-order rate equation:

$$\Gamma_w = \frac{\partial \theta_{im}}{\partial t} = \omega \left[S_e^m - S_e^{im} \right]$$ (53)

where θ_{im} is the matrix water content, ω is a first-order rate coefficient (T^{-1}), and S_e^m and S_e^{im} are effective fluid saturations of the mobile (fracture) and immobile (matrix) regions, respectively (**Šimůnek et al., 2013**).

Coupling eq.(53) with a dual-porosity non-equilibrium flow model leads to the usual soil hydraulic parameters needed for the equilibrium model, two additional parameters characterizing the matrix region (i.e. its residual, θ_{rim}, and saturated, θ_{sim}, water contents), and the first-order mass transfer coefficient ω. By additionally assuming that the residual water content of the fracture region is equal to zero (and hence that residual water is present only in the immobile region), one could further decrease the number of model parameters. When the rate of exchange of water between the fracture and matrix regions is assumed to be proportional to the difference in pressure heads between the two pore regions (**Gerke and van Genuchten, 1993a**), the coupling term, Γw, becomes:

$$\Gamma_w = \alpha_w \left(h_f - h_m \right)$$ (54)

Which: α_w is a first-order mass transfer coefficient [$L^{-1}T^{-1}$]. (**Šimůnek et al., 2013**)

III.9. Numerical Simulation

The water flow and solute transport equations with initial and boundary conditions were solved numerically with the HYDRUS-1D code (**Simunek et al., 1999**). The HYDRUS-1D code is based on finite element according to the Galerkin method, and time derivatives in solute transport equation were approximated by a Crank-Nicholson finite differences scheme. The governing equations are implemented in computer simulation tools, which can then be tested, modified, and/or (in) validated against new experimental data (**Köhne et al., 2008**).

There are three different versions of the HYDRUS software packages currently in use; HYDRUS-1D, HYDRUS-2D, and HYDRUS (2D/3D). While each model considers

similar basic processes, their main difference lies in the dimensionality of the problems they can address. While HYDRUS-1D considers one-dimensional problems associated with, for example, soil columns, lysimeters, soil profiles and plots, HYDRUS- 2D solves two-dimensional or axisymmetrical three-dimensional problems as encountered on the lab or field scale, and HYDRUS (2D/3D) calculates both two- and three-dimensional problems. HYDRUS (2D/3D) is an upgrade and extension of HYDRUS-2D **(Šimůnek *et al*., 2008)**. The program may be used to analyze water and solute movement in unsaturated, partially saturated, or fully saturated porous media. The flow region may be composed of nonuniform soils. Flow and transport can occur in the vertical, horizontal, or a generally inclined direction. The governing flow and transport equations are solved numerically using Galerkin-type linear finite element schemes. HYDRUS also includes a Marquardt-Levenberg type parameter optimization algorithm for inverse estimation of soil hydraulic and/or solute transport and reaction parameters from measured transient or steady-state flow and/or transport data **(Šimůnek *et al*., 2013).**