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Estimation of Apparent Activation Energy in Soils Affected by Incubation Time and Organic Matter Application.

Shaaban, S.M and A.M. Zaghloul

Water Relations and Field irrigation Dept. and Soils and Water use Dept. National Research Centre, Dokki, Cairo, Egypt.

Abstract: Soil columns experiment was conducted to study the effect of temperature on steady state saturated vertical flow of water by applying the concept of activation energy (AE). Two soils were used, sandy soil (*Typic Psamments*), and alluvial clay soil (*Typic tourrerts*) either with or without addition of 2% composted ligno -cellulosic materials (OM). Soil columns were incubated at 5, 23 and 50^0C for three periods (2, 4 and 6 months). The parameters of the flow equations were related to temperature and apparent activation energies. The ranges of apparent activation energies were 2.7 to 3.8 kJ mol^{-1} for sandy soil and 44.1 to 61.5 for alluvial soil, increased in OM application to be 11.2 to 24.6 and 60.5 to 392.3 for both soils, respectively. The sensitivities of temperature effects on the steady-state saturated for vertical flow were linearly related to the AE and inversely proportional to the absolute temperature (T). In general, temperature effects on the water flow processes were larger in the fine-textured soils and/or mixed soil with composted ligno -cellulosic materials. The predicted results were highly correlated with the measured data with coefficients of determination (r^2) larger than 0.98 and the relative errors of the predicted processes were within 10%. Therefore, the procedure may be a reliable method to estimate various soil water processes changing with the temperature.

Key words: Soil, Organic matter, Temperature, Infiltration, Activation energy.

INTRODUCTION

Most of the newly reclaimed area in the deserts of Egypt are sandy soils. These coarse textural soils have a high infiltration rate together with the problems of wind erosion and degradation. Under irrigation, severe losses of precious water and applied nutrients occur and desired yield levels are difficult to attain. On the other hand heavy clay soils have a low rate of infiltration together with the problems of high water retention capacities, inadequate aeration and poor drainage.

The infiltration rate (IR) of a natural porous body depends on its sorptivity and saturated hydraulic conductivity, which in turn is a function of the intrinsic permeability of the medium and the fluidity of the penetrating liquid(Hillel., 1980). At the initial stages of infiltration, soil sorptivity is the primary factor affecting IR; but at prolonged infiltration times, the hydraulic conductivity becomes the controlling factor. Several parameters are known to affect the IR . These include: vegetation, soil characteristics (compaction, pore volume, particle size distribution, water content), water quality (EC, adj.SAR) and temperature (Hillel, 1980).

Previous studies addressed a number of causes leading to decreases in IR of soils including physical clogging (Siegrist, 1987), biological clogging (Vandevivere and Baveye, 1992), entrapped air (Seymour, 2000) surface sealing (Moore, 1981) and dispersion and swelling of clay soil (Ikeren and Singer, 1998). Other research focused on the possible effect of temperature (T) on hydraulic conductivity of porous bodies (Constantz, 1982; Constantz, *et al*., 2001).

Theoretically, everything else being equal, IR into a given soil will decrease as the temperature (T) of the system decreases since viscosity of the percolating water will increase. Water viscosity changes by 2% per degree Celsius in the relevant environmental T range of 15 to 35°C, leading to an estimated 40% change of IR between summer and winter in arid zones (Chunye, *et al*., 2003). However, laboratory studies have given conflicting results. While some studies showed a greater T dependence of unsaturated hydraulic conductivity than predicted from changes in the water viscosity (Constantz, *et al*., 2001). Others concluded that the T effects on the hydraulic conductivity were close to the predictions from viscosity changes (Hopmans and Dane, 1986).

The majority of the previous studies on T effects were conducted under controlled conditions in the laboratory using small soil columns (Chunye, *et al*., 2003).

Soil temperature and its seasonal variations are important for understanding surface energy transfer processes and regional ecosystem functions of the terrestrial environment (Portmann, *et al*., 2009). Soil temperature affects plant growth, soil respiration, microbial decomposition, organic matter storage and mineralization, and a variety of chemical reactions and pedogenic processes in the soils (Brooks, *et al*., 2004). Changes in soil temperature can have profound impacts on soil functions and carbon balances in ecosystems (Schimel, *et al*., 2004).

Corresponding Author: Shaaban, S.M and A. M. Zaghloul Water Relations and Field irrigation Dept. and Soils and Water use Dept. National Research Centre, Dokki, Cairo, Egypt.
E-mail: Shaabansm@yahoo.com

Soil organic matter (SOM) plays an important role in soil structure and soil nutrients (Blanco-Canqui and Lai, 2007). It provides inorganic nutrients through decomposition, which is vital for soil fertility and productivity. It also affects soil water infiltration and soil structure that have major impacts on soil erosion and water management (Franzluebbers, 2002). Lopez-Bermudez, *et al.,* 1996 showed that a progressive recovery of vegetation cover helped improve SOM content and soil physical properties by reducing soil bulk density and increasing soil aggregate stability and saturated hydraulic conductivity (Li and Shao, 2006).

The present study aims to investigate the temperature effects on soil water vertical flow at constant head of water by applying the concept of activation energy.

MATERIALS AND METHODS

Water Flow Equations and Apparent Activation Energies:

The steady-state flow in soils can be described by the Darcy equation:

$$Q = KA.\Delta H \quad (1)$$

where Q is the discharge ($cm^3\ s^{-1}$), K is the hydraulic conductivity ($cm\ s^{-1}$), *A* is the cross-section area (cm^2), and ΔH is the hydraulic gradient ($cm\ cm^{-1}$). Eq. (1) can be expressed by

$$Q = [(K_0\ pg)/\eta)][A\ \Delta H] \quad (2)$$

in which K_0 is the intrinsic hydraulic conductivity (cm^2), reflecting the effect of soil matrix or any modification applied in soil system on water flow, p is the fluid density ($g\ cm^{-3}$), *g* is the gravitational acceleration ($cm\ s^{-2}$), and η is the water viscosity ($g\ cm^{-1}\ s^{-1}$). The water viscosity changes with temperature, which may be quantified with the Arrhenius form of (Zhang, *et al*., 2003).

$$1/\eta = b\ \exp(-E_V/RT) \quad (3)$$

Here b is a constant, E_V is the apparent activation energy ($Jmol^{-1}$) for viscosity change of pure water, R is the gas constant (8.31451 $J\ mol^{-1}\ K^{-1}$), and T is the absolute temperature in Kelvin. Assuming that the fluid density is independent of temperature, from Eq. (3) we have (Zhang, *et al*., 2003)

$$Q = BA\ \Delta H\ \exp(-E_d/RT) \quad (4)$$

where B is a constant and E_d is the apparent activation energy ($J\ mol^{-1}$) of steady-state flow, which is a lumped parameter to account for factors having temperature effects on water flow, such as fluid viscosity, soil water content, and soil properties. Using Eq. (4) and plotting ln Q vs. 1/T, we can evaluate E_d from the plot slope. In turn, Eq. (4) can be used to calculate state flow under different temperatures.

Experiments:

Soil columns experiment (15-cm long with a diameter of 5.0 cm), was conducted to study the temperature effects on steady state saturated for vertical flow of water at constant head by applying the concept of activation energy (AE). Two soils were chosen in this study the 1^{st} was sandy soil (*Typic Psamments*), and the 2^{nd} was alluvial clay soil (*Typic tourrerts*). Part of these soils were modified with 2% composted ligno -cellulosic materials (sawdust, plant residues and organic manure at the ratio of 1:1:1, respectively) as a source of organic matter (OM). Some physical and chemical properties of the soils and compost are presented in table 1 and 2 (Klute, 1986; Page *et al*., 1982). The columns were packed to ensure uniform bulk density for each soil. After packing, the soil columns were saturated by fresh water.

Soil columns were incubated at three different temperatures (5, 23 and 50^0C) for three periods (2, 4 and 6 months). Through the experiment, soil moisture was maintained at 60% of water holding capacity. After each incubation time, soils were evaluated by determination of their hydraulic conductivity (Klute, 1986) as influenced by OM and temperature regime. Worth to mention that the water used for compensating loss by evaporation or which used for determination of hydraulic conductivity have the same temperature that of incubation.

RESULTS AND DISCUSSION

Barrier to discuss the obtained results it should be mention that water flow in the studied soil samples were the mean value for three replicates at each temperature and per each incubation time. The calculated standard errors (SE) were within 0.06 cm^3/h, means the highly significance of observed results. Also, with the consistent repeated measurements, According to the equation (Zhang,*et al*., 2003).

Table 1: Physical and chemical properties of soils used.

a)Mechanical analysis					
soil No.	Coarse sand %	Fine sand %	Silt %	Clay %	Texture
Soil 1	45.32	51.84	2.51	0.33	sand
Soil 2	5.05	7.45	30.86	56.64	clay

b)Hydrophysical analysis						
Soil No.	Bulk density Mg m^{-3}	Total porosity %	Total water holding capacity* %	Field Capacity* %	Wilting Percentage* %	available moisture* %
Soil 1	1.598	39.70	19.08	5.76	1.94	3.82
Soil 2	1.416	46.57	34.23	29.18	20.04	9.14

c) Chemical analysis								
Soil No.	pH	Total $CaCO^3$	Active $CaCO^3$	Organic matter	Surface area	Amorphous materials mg/kg		
	1:2.5	%	%	%	m^2/g	Fe_2O_3	Al_2O_3	SiO_4
soil 1	8.00	3.00	0.20	0.22	4	Nd	0.5	6.00
soil 2	7.68	3.43	3.06	0.73	210	0.39	32.6	4.63
* on weight basis								

Table 2: Some chemical properties of applied compost.

PH (H_2O)	Salinity	Moisture %	Mineral content	CEC c mole kg^{-1}
7.15	EC dSm^{-1} 1.12 Na^+ % 0.01	4.27	(Ash) % 29.46	146
Organic component	Macro elements	Secondary elements	Micro elements	Heavy metals
OM % 60.27 OC % 35.04 ON % 1.78 C:N 19.68	$NH^+_4 + NO_3$ % 1.81 P_2O_5 % 0.32 K_2O % 0.45	Ca^{+2} % 1.10 Mg^{+2} % 0.33	Fe μgg^{-1} 112.0 Mn μgg^{-1} 45.0 Zn μgg^{-1} 36.0 Cu μgg^{-1} 11.1	Cd μgg^{-1} 0.36 Co μgg^{-1} 0.43 Ni μgg^{-1} 2.01

$$\text{Ln } Q = \alpha - (E_d / RT) \quad (5)$$

where α is the intercept and E_d /R is the slope, E_d /R =329.5^{o}k, thus E_d = 2740 J mol^{-1} =2.74 kJ mol^{-1} and the measuring of discharge data at different temperature, activation energy AE was calculated for used soils as affected by time of soil incubation via the plotting of E_d vs.1/T. The linear form of data in figure (1) represents the good fitting of the data to this model with R^2 ranged between 0.92** to 0.99**. As shown in table (3) the effect of applied OM to both soils indicate the increase in AE. After two months of incubation AE increased from 2.74 to 11.25 kJ mol^{-1} in sandy soil, versus 44.07 to 60.48 kJ mol^{-1} in alluvial clay soil. Moreover, increasing the incubation time for both soils either treated or not with OM led to increase the AE to be after 6 months of incubation 219 and 138% that of AE after two months for sandy soil with and without addition of OM, in sequence. Relevant values of alluvial clay soil were 638 and 139%, respectively.

Prediction of Temperature Dependent:

Theoretically, everything else being equal, IR into a given soil will decrease as the temperature (T) of the system decreases since viscosity of the percolating water will increase (Chunye- Lin, *et al*., 2003). As there is no significant difference between the discharge values of the incubation periods of two and four months, discussion will be concentrated on the data of two and six months incubation time. The discharge of steady state saturated vertical flow of water changing with the temperature is related to the apparent activation energy with Eq. (4) or the linear form of the model (Eq.5), therefore, the discharge could be predicted at any temperature based on measured data at two temperatures.

Table 3: Apparent activation energies (kJ mol^{-1}) of water flow processes in used soils as affected by times of soil incubation.

Time of soil incubation	AE	R^2	AE	R^2
Sandy soil				
	-OM		**+OM**	
2 Month	2.74	0.99**	11.25	0.93**
4 Month	3.75	0.99**	18.66	0.92**
6 Month	3.79	0.99**	24.62	0.99**
Clay soil				
	-OM		**+OM**	
2 Month	44.07	0.99**	60.48	0.98**
4 Month	50.27	0.99**	386.52	0.92**
6 Month	61.49	0.95**	392.28	0.98**

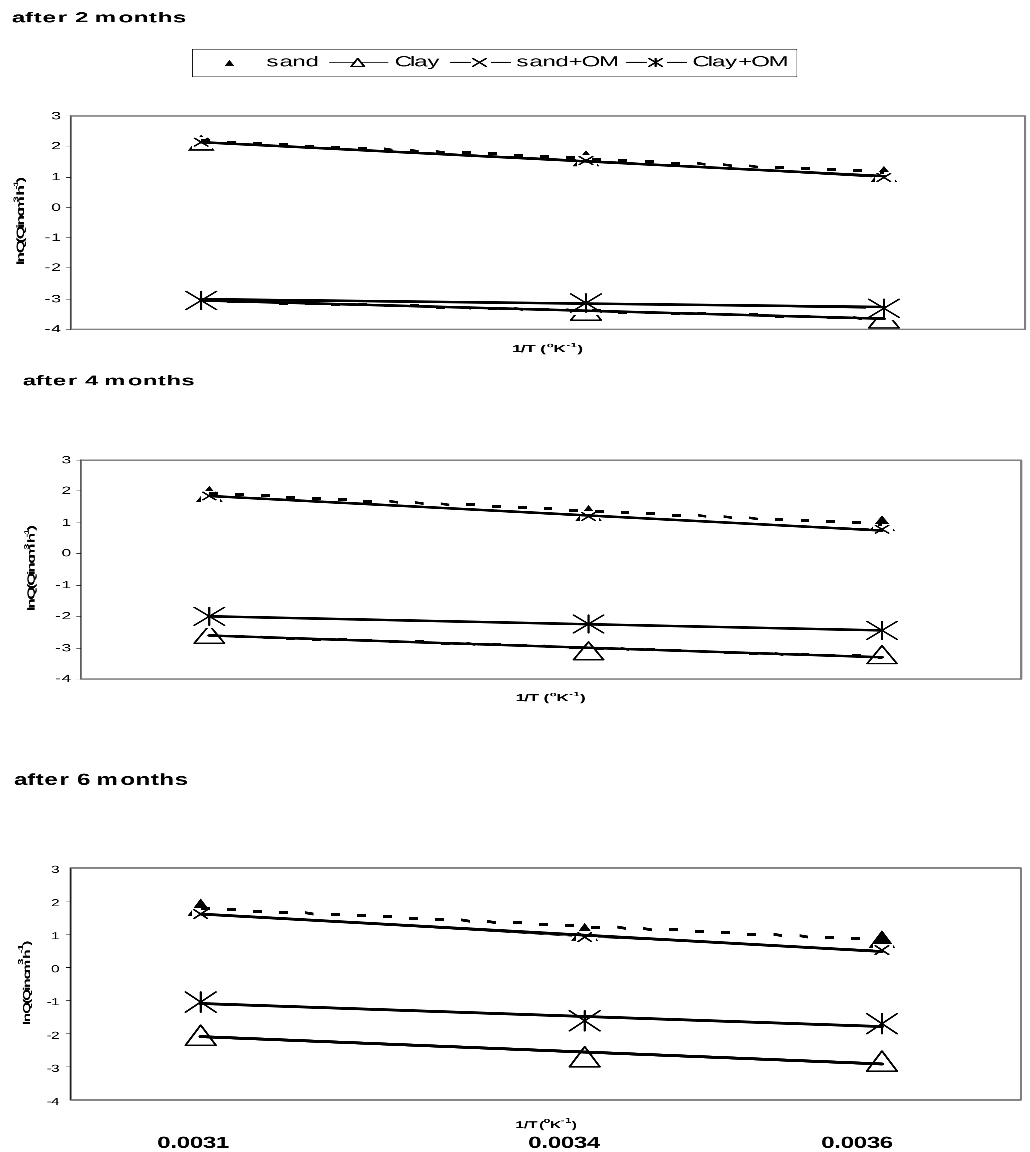

Fig. 1: Relationship between natural log of discharge Q and the absolute temperature.

The predicted values were compared with the measured ones in table 4. Generally, after 2 months incubation time, the absolute relative error of the prediction ranged between 4 and 7% in sandy soil, increased to be between 9 and 10% after application of OM. The respective values were between 0.5 and 4% in alluvial soil increased to be between 2 and 6% after application of OM. Increasing the incubation time, generally, led to decrease the relative error. In the literature, temperature dependence of the flow transport was frequently related to the temperature change of the liquid viscosity (Constantz, 1982; Hopmans and Dane, 1986). However, besides the liquid viscosity, other soil and water parameters, such as soil water content, soil texture, soil organic matter, and others, may have impaction the temperature dependence of the flow processes in soils (Franzluebbers, 2002).

As shown in the same table, after 2 months incubated soils, increasing the temperatures regime led to decrease the discharge values in both sandy and sandy amended with OM soils. In contrast, application of OM led to increase the discharge values in alluvial soil i.e improvement of the discharge in these soils with significant variation between alluvial and sandy soils in this important parameter. The same trend was observed in the same soils undergo to different incubation times.

The predicted and measured results are highly correlated for all the cases with coefficients of determination (r^2) larger than 0.98**. The predicted values for sandy soil after six months have an excellent agreement with the measured data. Nevertheless, the prediction precision for most cases is within 10% of absolute relative estimated errors. However, as mentioned above that the apparent activation energies account for various factors related to temperature effects on water flow, application of organic matter including, fluid viscosity, soil water content, and soil physical and chemical properties. To further improve predictions of temperature dependent flow processes in soils, it may be essential to account for the temperature dependence of apparent activation energies.

Table 4: Predicted and measured discharge values (cm h^{-1}) of steady state saturated vertical flow of water at different temperature for chosen soils.

Temperature	Measured values	Predicted values	Relative error
2 Month			
Sandy soil			
5	8.60	9.16	6.51
23	8.43	8.86	5.10
50	8.24	8.64	4.85
Sandy soil + OM			
5	8.57	9.43	10.04
23	7.62	8.38	9.97
50	7.40	8.14	10.00
Alluvial soil			
5	0.32	0.33	3.13
23	0.62	0.64	3.23
50	1.21	1.22	0.83
Alluvial soil +OM			
5	0.61	0.64	4.92
23	1.22	1.25	2.46
50	1.70	1.80	5.88
6 Month			
Sandy soil			
5	8.48	8.51	0.35
23	8.21	8.25	0.49
50	8.13	8.19	0.74
Sandy soil + OM			
5	8.28	8.39	1.33
23	6.90	7.02	1.74
50	6.02	6.14	1.99
Alluvial soil			
5	0.53	0.54	1.89
23	1.03	1.06	2.91
50	2.01	2.03	0.99
Alluvial soil +OM			
5	1.02	1.06	3.92
23	2.04	2.07	1.47
50	2.83	2.93	3.53

Summary and Conclusions:

The concept of apparent activation energy was applied to quantify temperature effects on water flow processes, in saturated soils. The discharge of steady-state saturated flow was related to temperature and apparent activation energies. The relationships were derived mainly based on the temperature dependent relationship of water viscosity. Then other factors related to temperature effects on water flow, such as soil water content and soil properties, were accounted for implicitly with lumped apparent activation energies. Apparent activation energies were estimated with measured data of the processes at temperatures 5 to 50^{0}C for four soils. The ranges of apparent activation energies were 2.7 to 3.8 kJ mol^{-1} for the steady-state saturated flow for sandy soil, increased in OM application in this type of soils and significantly increased again in alluvial and OM modified alluvial soils. Data showed that temperature effects on the steady-state saturated flow were linearly related to the activation energy and inversely proportional to the absolute temperature. In general temperature effects on the water flow processes increase with soil clay content as well as application of OM in soil system. Based on the temperature dependent relationships, the parameters of steady-state saturated flow can be calculated using measured processes at different temperatures. Then the processes at other temperatures can be predicted. Comparing with measured data of the processes for different soils at different temperatures. The prediction procedure was examined and obtained excellent predicted results. For all the cases, the predicted results were highly correlated with the measured data with coefficients of determination (r^2) reached to 0.98** and the relative errors of the predicted results were within 10% in most cases. Therefore, the procedure may be a reliable method to estimate various soil water processes changing with the temperature.

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