

**INDIAN JOURNAL
OF
METEOROLOGY AND GEOPHYSICS**

VOL. 13

OCTOBER 1962

NO. 4

551·579·5

**Theoretical Investigation of Vapour Pressure above the
Capillary Head in Soils***

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(Received 29 June 1961)

ABSTRACT. It is found that vapour pressure decreases with height above the capillary head depending on the vapour pressure at the capillary head and the surface of the soil column. Important causes of the decrease are due to adsorptive force of the soil particles on vapour molecules and the resistive force offered by the soil particles to the passage of vapour. Combining these two forces, a differential equation was formed and solved to give correct values of vapour pressure at all levels within the soil column.

1. Introduction

Determination of vapour pressure in a porous media is very important in soil physics and chemical engineering. There are many equations to express pressure drop of vapour and gases flowing through a porous medium, but equations to express pressure drop due to molecular diffusions are rare.

Parker (1922) stated that there must be great forces holding water to soil. According to him, below the water holding capacity (maximum value) of soil, water is held by an attractive force called adhesion. These forces cause an increase in freezing point depression of soil water, a decrease in vapour pressure of soil water and a decrease in the rate of evaporation as the soil moisture content is lowered. Dorsey (1940) quoting the works of McHaffie and Lenher stated that the amounts of water adsorbed on glass has lower equilibrium vapour pressure than

vapour pressure of water at the same temperature, unless the adsorbed layer is several hundred molecules thick. Shereshefsky and Russell (1953) found that the radius of curvature of a liquid surface can be many times than that predicted by Kelvin's equation for a definite lowering of vapour pressure. In one case he obtained a vapour pressure corresponding to a radius of curvature which was 200 times that obtained by Kelvin's equation. Carman (1956) stated that when an adsorbable gas is caused to flow through a porous septum under a constant pressure gradient, it will give rise to a corresponding gradient of surface concentration, parallel to the direction of flow. A surface concentration gradient must accompany flow of an adsorbable gas. Carman also stated that so far as calculations are concerned, the multi-layer region (of adsorbed vapour) can be approached equally well as surface diffusion and as flow of capillary condensate.

*Partly (experimental part) from the Ph. D thesis submitted at the University of Washington, Seattle, U.S.A. (1958)

It is clear from the above review that adsorptive force will reduce the vapour pressure and that the molecules adsorbed on certain surfaces can be several hundred molecules thick before vapour pressure becomes equal to that of water at the same temperature. It is also clear that vapour pressure at a curved surface can be much less than that calculated by means of Kelvin's equation.

2. Theory

Above the capillary head up to the top of the soil column, the surface of the soil particles adsorb water vapour. The thickness of vapour adsorbed in equilibrium with the vapour decreases with height since the vapour concentration in the pores also decreases with height. The distribution of vapour pressure in a soil column must have some similarity with that of the distribution of vapour pressure in the atmosphere. The variation of vapour pressure with height in an isothermal case is easier to study. It is well known that pressure change of atmosphere with height is exponential. In view of Dalton's law of partial pressure, vapour pressure change with height also should be exponential. It is given by the equation (Penman 1955)

$$\begin{aligned} h_0 - h_s &= (RT/Mg) \ln (P_s/P_0) \\ &= -(RT/Mg) \ln (P_0/P_s) \end{aligned} \quad (1)$$

where P_0 and P_s are the vapour pressures at heights h_0 and h_s respectively, M is molecular weight of water vapour. Writing a similar equation for the height h_y in between h_0 and h_s , one gets

$$h_y - h_s = (RT/Mg) \ln (P_s/P_y) \quad (2)$$

Dividing eqn. (2) by eqn. (1), it is seen that

$$(h_y - h_s)/(h_0 - h_s) = \ln (P_s/P_y) / -\ln (P_0/P_s)$$

Putting $(h_y - h_s) = h_1$, $(h_0 - h_s) = H$ and $-\ln (P_0/P_s) = K$, the above equation is

$$\ln (P_s/P_y) = K(h_1/H) = Ky_1$$

where $y_1 = h_1/H$

$$\text{or } P_y = P_s \exp (-Ky_1) \quad (3)$$

Note that since $H - h_1 = h$ and $h/H = y$, $y + y_1 = 1$.

Consider an isothermal soil column in between capillary head (defined below) and surface of the soil column. Capillary head is the level in soil column whose height above water table is equal to the height of water column that can be supported by the capillary pull of the soil and is found by the method described by Puri (1939). At the capillary head the moisture content is "field capacity." As the moisture content is lowered from field capacity adsorptive force comes into play reducing the vapour pressure from saturation value. The vapour pressure at the capillary head is saturation vapour pressure and suppose the surface of the soil column is exposed to a lower vapour pressure. There are two main causes which reduce the vapour pressure above the capillary head. The first is the resistive force offered by the soil particles for the passage of vapour and the second is the adsorptive force. The distribution of vapour pressure P by the above two causes could be expressed by the equation

$$P = F(x, f)$$

$$\text{i.e., } dP = (\partial P/\partial x) dx + (\partial P/\partial f) df \quad (4)$$

where x is the distance through which the vapour moves and f is the adsorptive force. If there is no adsorptive force in soil then equation similar to (3) will give the distribution of vapour pressure in an isothermal soil column. Then h_1 is the height above the capillary head, where the vapour pressure is P_y , H is the length of soil column from the capillary head to the surface of the soil column and P_s and P_0 are the vapour pressures at the capillary head and at the surface of the soil column respectively. Thus equation (3) will give the distribution of vapour pressure when resistive force is the only force that reduces the vapour pressure in a soil column.

In adsorbing media, the adsorptive forces reach out from the surface of the soil particles adsorbing many layers of vapour molecules on the surface. This force is maximum in very dry soil and zero when moisture is equal to or more than field capacity. The

structure of adsorbed phase is similar to that of atmosphere surrounding the earth. It is assumed that adsorption potential is similar to gravitational potential. According to this view, potential E_z at any point on the outer surface of the adsorbed molecules, whose equilibrium pressure due to the adsorbed molecules is P_z is given by the equation (Brunaur 1943)

$$E_z = RT \ln (P_s/P_z) \quad (5)$$

As vapour pressure increases, potential decreases and becomes zero when vapour pressure becomes saturated vapour pressure P_s . When vapour pressure is P_s , the moisture content becomes field capacity (at the capillary head). Above the capillary head moisture content decreases with height and hence vapour pressure also decreases with the height. Hence one could write an equation of the following type.

$$E_z = RT \ln (P_s/P_z) = G (W_c - W_z)$$

$$\text{and } E_0 = -RT \ln (P_0/P_s) = G (W_c - W_0)$$

where E_0 is the potential at the surface of the adsorbed molecular layer when adsorbed moisture is W_0 gm/100 gm of soil at vapour pressure P_0 . Similarly W_c and W_z are the moisture content at vapour pressure P_s (at the capillary head) and P_z respectively. G is a constant. Dividing the former equation by the latter, one gets

$$\ln (P_s/P_z) = -\ln (P_0/P_s) (W_c - W_z) / (W_c - W_0)$$

Now putting $-\ln (P_0/P_s) = K$, $(W_c - W_z) = w_1$ and $(W_c - W_0) = W$ the above equation becomes

$$\ln (P_s/P_z) = K (w_1/W) = Kz_1$$

$$\text{where } z_1 = w_1/W$$

$$\text{or, } P_z = P_s \exp (-Kz_1) \quad (6)$$

Note that $(W_c - W_0) - (W_c - W_z) = (W_z - W_0) = w$ and $w/W = z$, $z + z_1 = 1$.

Equation (6) gives the distribution of vapour pressure in a column of soil due to adsorptive force.

Thus there are two different values of vapour pressure obtained by considering two different forces. Both the values are on the same exponential curve. Hence the resultant vapour pressure P_m of P_y and P_z will be given by the geometric mean of P_y and P_z .

Hence

$$P_m = (P_y P_z)^{\frac{1}{2}}$$

$$= [P_s \exp (-Ky_1) P_s \exp (-Kz_1)]^{\frac{1}{2}}$$

$$= P_s \exp [-K (y_1 + z_1)]^{\frac{1}{2}}$$

$$\text{or } P_m = P_s \exp (-Km_1/2) \quad (7)$$

$$\text{where } m_1 = y_1 + z_1 = h_1/H + (W_c - W_z) / (W_c - W_0) \quad (8a)$$

Equation (7) will give the vapour pressure at any point in the soil column, provided height above the capillary head and moisture content at each level are known.

$$\begin{aligned} \text{Note that } y + z &= h/H + (W_c - W_0) / (W_c - W_0) \\ &= m \end{aligned} \quad (8b)$$

With the above ideas in mind one could get the same solution (equation 7) from the solution of a differential equation based on the adsorptive and resistive forces offered by the soil particles. It was found from experiments that diffusion of vapour into soil depends on concentration of vapour in addition to the vapour pressure gradient. It is also found that vapour diffusion depends on porosity as was shown by Rengmark and Freden (1957). In soil there exists a lower limit of concentration below which the wet front (the common boundary between dry region and moist region of the soil) or the diffusing front does not advance at all, because the diffusing vapour is all used up in the soil above the front. This fact was very clearly shown by John (1958). Hence it is reasonable to write the differential equation as follows

$$D (d^2P/dn^2) = (\partial P/\partial t) + cvP \quad (9)$$

where D is the diffusion constant of the vapour through the soil and according to

de Vries (1950) $D = D_0 v b$. Here D_0 is the diffusion constant of the vapour in air, v is the porosity of the soil and b is a constant whose value according to de Vries is 0.66. From what has been discussed above one has to conclude that n is a function equal to the value shown by equation (8a), i.e.,

$$n = h_1/H + w_1/W = m_1$$

and c is a constant. All the symbols have the same meaning as given in the last few pages. Hence the equation (9) can be written as (at steady state)

$$D_0 v b (d^2P/dn^2) - c v P = 0 \quad (9a)$$

It is interesting to note that Stern and Shniad (1958) obtained exactly similar equation for diffusion of one solution into another solution kept in the interspaces of small glass beads. He also found a diffusion front which did not advance when concentration fell below a certain value. Since v is in both the terms of the equation, it can be cancelled and the equation can be written as

$$D_0 b (d^2P/dn^2) - c P = 0$$

$$\text{i.e.,} \quad (d^2P/dn^2) - (c/D_0 b) P = 0$$

$$\text{or,} \quad (d^2P/dn^2) - (K^2/4) P = 0 \quad (10)$$

where $(K^2/4) = c/D_0 b$. The equation is a second order linear homogeneous one whose solution is

$$P_n = A \exp(-Kn/2) \quad (11)$$

This is exactly the solution given by Stern and Shniad (1958). Now putting the boundary condition and remembering that n varies from 0 at the capillary head to 2 at the surface of the soil column (ref. equation 8a)

$$P_s = A \exp(-K \cdot 0/2)$$

$$= A \quad \text{at the capillary head}$$

$$\text{and } P_0 = A \exp(-K \cdot 2/2)$$

$$= P_s \exp(-K) \quad \text{at the surface of the soil column.}$$

$$\text{Hence,} \quad P_s = P_0 \exp K$$

$$\text{Therefore,} \quad P_n = P_0 \exp K \exp(-Kn/2)$$

$$= P_0 \exp K(2-n)/2$$

$$= P_0 \exp Km/2 \quad (12)$$

$$\text{where } m = h/H + w/W \quad (\text{i.e., equation 8b})$$

It is noticed that equations (7) and (11) are identical. Equation (12) can be used to find the vapour pressure at any point in the soil column. If the adsorption is not very strong as in case of sand, the contribution due to the term w/W in equation (12) will be very small.

Vapour pressure in a soil column might change depending on packing, water table, temperature and humidity of the air at the surface of the soil column. If the humidity change of the outside air is small, then one could assume that there is no appreciable change in moisture content of the soil. Similarly if the temperature change is also small, then also moisture content will not change to any appreciable extent. Mallik (1940) has shown that diurnal change of moisture is very small. Hence the only factor that changed the moisture content of a particular soil column of uniform packing is the change in the water table. This implies that, only in those cases, the relation between vapour pressure and moisture content given by equation (12) could be verified, in which the water table was at the same place as it was just before moisture analysis was done. Moisture content of the soil with height could be determined only once without disturbing the packing. But those cases are not enough to establish the validity of equation (12). This difficulty could be circumvented as described below and equation (12) could be used for other cases whose moisture content was not determined experimentally.

If the packing is kept constant, then it is reasonable to assume that moisture content at the capillary head, wet front and

at the surface of the soil column must remain constant, no matter where the capillary head and wet front are situated. Graphs showing the relation between the moisture content and height above the capillary head, when plotted on semilogarithmic paper (moisture on semilog axis) consisted of two straight lines joining at the wet front. Hence moisture content of any column of the soil having the same packing could be found by the above idea. The above idea could be mathematically expressed by the following equations:

$$\ln W_l = \ln W_0 + l \ln (W_F/W_0) \quad (13a)$$

for dry region

$$\ln W_L = \ln W_F + L \ln (W_c/W_F) \quad (13b)$$

for moist region

$$\text{and } \ln W_l = \ln W_0 + l \ln (W_c/W_0) \quad (13c)$$

for soils like sand
which has only
dry soil above the
capillary head

where W_l , W_F , W_L , W_0 and W_c are the moisture content in the dry region, at the wet front, in the moist region, at the surface of the soil column and at the capillary head respectively. l is the relative distance of the point in the dry region (where the moisture content is W) from the surface of the soil column. L is the relative distance from the wet front, of the point in the moist region where the moisture content is W_L . Equations at 13 (a, b, c) are valid only for soils whose moisture content has reached quasi-steady or steady state. Thus equation (12) could be verified by using equation (13) for any column of soil provided the packing remains constant and the moisture content at the capillary head, wet front and at the surface of the soil column are known, even though moisture content in each level was not determined experimentally.

3. Experiment

A simple modified form of Regnault's dew point hygrometer was designed and

constructed to measure vapour pressure in soil. The modified form consists of a clean polished metal surface which would be cooled by means of an ice bath until dew starts to form. The temperature of the dew point was taken by means of an embedded thermocouple very close to the surface of the hygrometer. In order to measure vapour pressure in soil, a perforated tube (perforation facing downward) was placed horizontally at a prescribed depth. The ends emerged from the soil and were connected to a sealed pump and to a sealed hygrometer. The sketch of the apparatus is given in Fig. 1. The method is simple, accurate and requires no calibration.

Vapour pressure was measured at four different levels in soils kept in large plastic tubes of length 91.5 cm, cross-section 323.2 sq. cm and wall thickness 0.6 cm. Two separate experiments were done, one using sand and the other using sandy soil. The vapour pressure at the capillary head was taken as saturation vapour pressure and that at the surface of the soil column was taken as the vapour pressure of the room. The room temperature and humidity were kept constant. Humidity was kept constant by exposing 36 sq. ft of saturated solution of magnesium nitrate. A typical chart of the daily thermohygrograph record is shown in Fig. 2. The observed and calculated values of vapour pressure are given in Table 1.

4. Discussion

It is important to note that direct determination of moisture content with height was done only when the capillary head was 25.5 cm below the surface of the soil column, in the case of sand and 49.5 cm below the surface of the soil column in the case of sandy soil. The capillary head was fixed at those levels not by a single criterion. It was fixed at that level by knowing the moisture content at the capillary head, the capillary rise above the water table and sometimes by knowing the visible colour

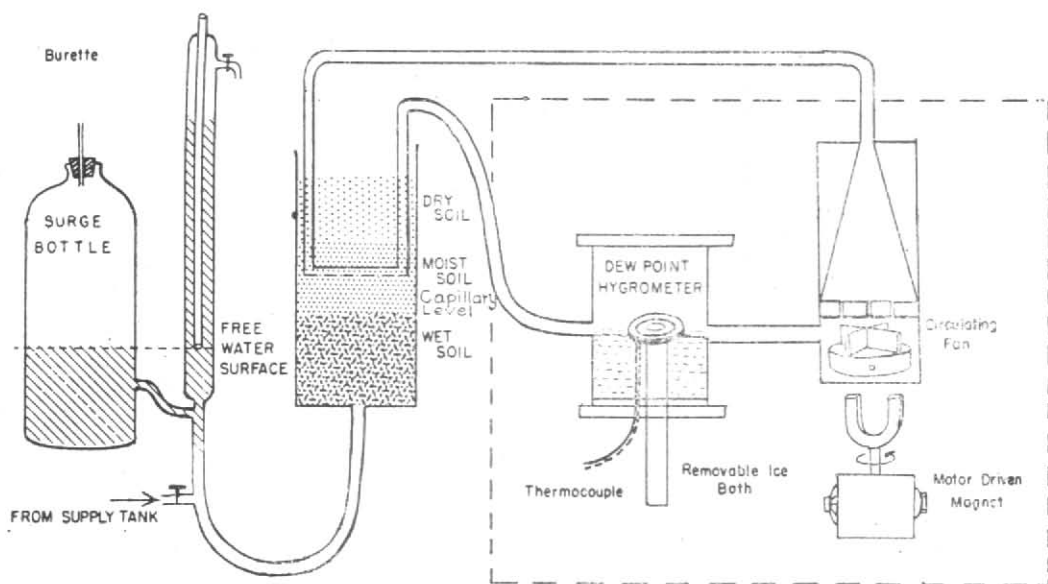


Fig. 1. Apparatus to determine vapour pressure and evaporation

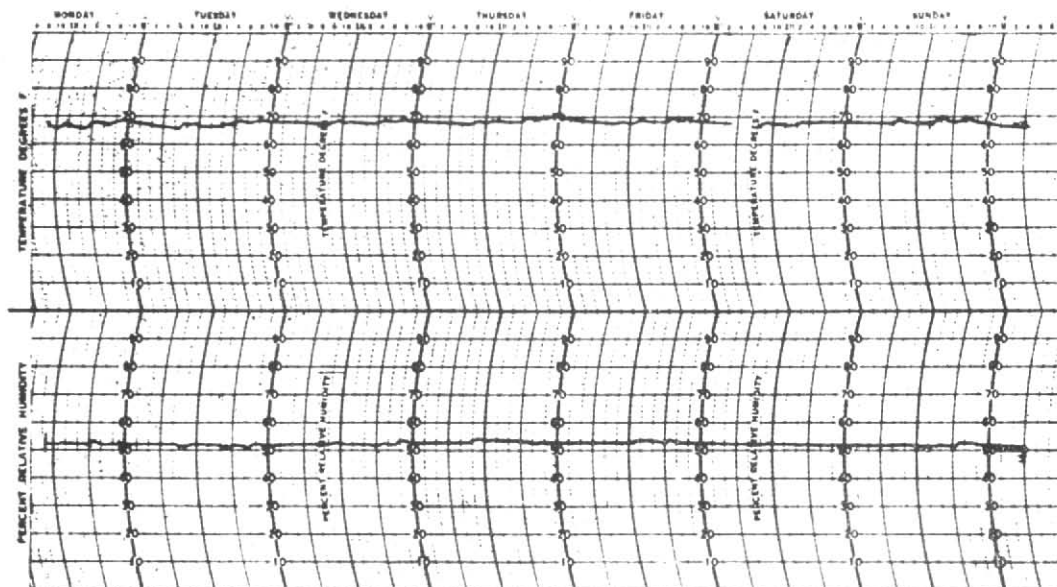


Fig. 2. Record of daily thermo-hygrograph at University of Washington for the period 7-14 April 1957

TABLE 1

Calculated and observed vapour pressure in a sandy soil and sand column

Depth below the surface of soil column (cm)	Moisture content (gm/100 gm)	Vapour pressure in cm of Hg		Remarks
		Observed	Calculated	
Sandy soil				
0	0.93	0.996	1.020	Expt. 1 Temp. 21°C; Sandy soil, Moisture content found by equation: Quasi-steady
10.0	1.40	1.118	1.074	
20.0	2.12	1.153	1.137	
30.0	3.20	1.233	1.213	
40.0	4.82	1.316	1.306	
75.0	16.8	1.880	1.922	
0	0.93	1.301	1.305	Expt. 5 Temp. 26°C; Sandy soil; Moisture content found by expt.: Steady state
7.5	6.00	1.516	1.522	
17.5	7.78	1.758	1.702	
27.5	10.20	1.880	1.893	
37.5	13.00	1.966	2.123	
49.5	16.8	2.455	2.509	
0	0.93	1.147	1.147	Expt. 8 Temp. 23.5°C; Sandy soil; Moisture content found by equation: Steady state
10.0	5.96	1.349	1.353	
20.0	7.58	1.539	1.488	
30.0	9.63	1.617	1.651	
40.0	12.33	1.767	1.862	
52.0	16.8	2.154	2.195	
0	0.93	1.301	1.320	Expt. 3 Temp. 26°C; Sandy soil; Soil: moisture found by equation Quasi-steady
10.0	1.62	1.471	1.398	
20.0	2.86	1.626	1.498	
30.0	5.0	1.734	1.635	
40.0	6.76	1.796	1.772	
75.0	16.8	2.455	2.539	
Sand				
0	0.010	0.996	1.02	Expt. 5 Temp. 21°C; Sand; Moisture content found by expt.: Steady state
5.0	0.014	1.140	1.087	
10.0	0.021	1.153	1.158	
14.0	0.028	1.267	1.219	
19.0	0.052	1.316	1.304	
25.5	1.5	1.854	1.921	
0	0.010	1.237	1.330	Expt. 6 Temp. 26°C; Sand; Moisture content found by expt.: Quasi-steady
5.0	0.014	1.448	1.426	
10.0	0.021	1.554	1.516	
14.0	0.028	1.641	1.597	
19.0	0.052	1.692	1.712	
25.5	1.5	2.564	2.558	

Experiment number refers to that in thesis

Quasi-steady state in sandy soil is the state when the wet front in the sandy soil column moved very slowly

Note that the wet front in experiment 1 is at 42.5 cm below the surface of the soil column and that in the case of experiment 3 it is 32.5 cm below the surface of the soil column. Moisture content of the wet front is nearly 5.4 per cent, i.e., 5.4 gm/100 gm of soil.

TABLE 1 (contd)

Depth below the surface of soil column (cm)	Moisture content (gm/100gm)	Vapour pressure in cm of Hg		Remarks
		Observed	Calculated	
Sand				
0	0.010	1.146	1.200	Expt. 1 Temp. 23.5°C; Sand: Moisture content found by equation: Steady state
7.0	0.017	1.375	1.306	
12.0	0.025	1.494	1.388	
16.0	0.033	1.539	1.456	
21.0	0.10	1.641	1.568	
27.5	1.5	2.164	2.297	
0	0.010	1.342	1.400	Expt. 2 Temp. 26°C; Sand: Moisture content found by equation: Steady state
7.0	0.017	1.666	1.524	
12.0	0.025	1.742	1.619	
16.0	0.033	1.796	1.702	
21.0	0.10	1.854	1.815	
27.5	1.5	2.455	2.693	

Experiment number refers to the experiment number in the thesis. Quasi-steady in sand is the state just before the daily water intake by the sand column has become exactly constant, even then the intake was nearly constant

change due to change in moisture content. This implies that only in experiments (5) and (6) with sand and in experiment (5) with sandy soil (see Table 1) moisture content with height was determined experimentally. For all other experiments (see Table 1), moisture content was determined by means of equation (13) or by means of graphs in Fig. 3. Moisture content at the capillary head, wet front and that at the surface of the soil column are indicated in Fig. 3.

In general the observed and theoretical values are in good agreement. This proves that equations (12) and (13) are correct. It is also seen that equation (12) gives correct results, whether the soil column is long or short, whether the soil is sand or sandy soil, whether the soil is dry or moist and whether the soil moisture has reached quasi-steady or steady state. These are indicated in Table 1. One could notice that the percentage of error is very small except for a very few cases. This is not bad when one looks into the fact that the value of

vapour pressure at the surface of the soil column (given in Table 1 as calculated) is a value chosen such that when it is used, the equation (12) will give correct values for all other levels. Choosing a value for the vapour pressure of the surface of the soil column is reasonable, since the observed value is actually the room vapour pressure and not that of the surface. One must also realize that surface vapour pressure will change by about ± 4 per cent if the temperature of the room changes by $\pm 1^\circ\text{C}$. It is seen from Fig. 2 that this much change is possible. Moisture determination are also subject to some uncertainty. Despite all these errors, the observed and calculated values of vapour pressures are in good agreement.

Determination of moisture content with height is not very difficult at isothermal condition. Yet such a data is not available and hence it is difficult to test the validity of equation (13) for more cases. But equation (13) has been verified by the results of equation (12). Experiments in Table 1 give

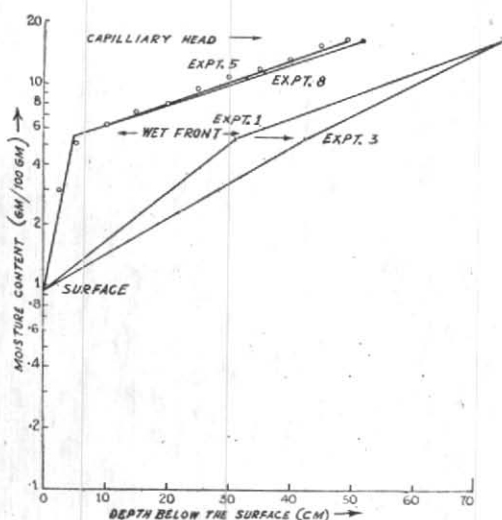


Fig. 3

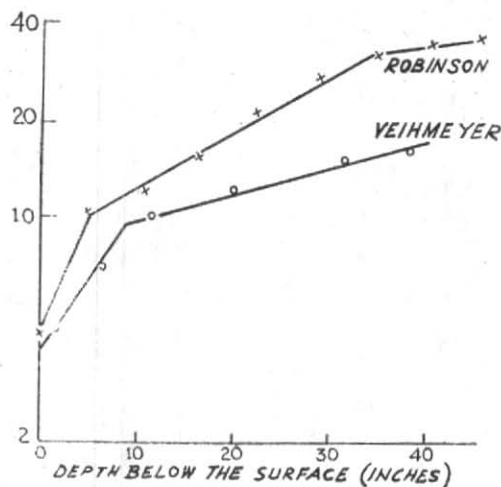


Fig. 4

validity to equation (13). Next best proof that can be given for equation (13) is from nonisothermal cases. Veihmeyer (1927) has given the distribution of moisture content with height in case of clay loam, covered from precipitation. He took 1000 pounds of the soil in a drum 4 ft in depth and kept the upper open end of the drum in flush with the ground. When experiment was started in 1921, he added 200 pounds of water. Then at intervals of months he found the moisture content with depth. The semilog curve (between the moisture content with height) obtained from his data for 1925 shows a kink at the point where the soil started to dry. Fig. 4 shows the kink at 8.5 inches below the surface of the soil column. According to Veihmeyer the soil dried up to 8 inches down. Hence it is reasonable to think that the kink was exactly at the wet front. Similar graph is also obtained from the data of Robinson (1951).

5. Conclusions

Solution of a differential equation, formed basing on the adsorptive and resistive forces offered by the soil particles, gave values of vapour pressure in agreement with the observed values. An equation was also found to determine the moisture content with height, provided the moisture content at the capillary head, wet front and that at the surface of the soil column are known.

6. Acknowledgements

The author is thankful to Dr. F. I. Badgley for his keen interest in the work and to U.S. Atomic Energy Commission for the support of the work through the Eddy Diffusivity Project at the University of Washington. He is also thankful to Prof. Devi Dayal and Mr. T. N. Davey for some helpful discussions.

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Appendix I

Symbols

- b* a constant in the diffusion equation; according to de Vries $b = 0.66$
- c* another constant in the diffusion equation
- D* diffusivity constant of water vapour in soil (unit area/unit time)
- D₀* diffusivity constant of water vapour in air " "
- E₀* potential at the surface of the adhering water layer on the soil particles at W_0 gm/100gm moisture content and at vapour pressure P_0 cm of Hg
- E_z* potential at the surface of the adhering water layer on the soil particles at W_z gm/100gm moisture content and at vapour pressure P_z cm of Hg
- E_c* potential at the surface of the adhering water layer on the soil particles at W_c gm/100gm moisture content and at vapour pressure P_s cm of Hg
- f* adhesive force (gm/sq. cm)
- g* acceleration due to gravity
- G* a constant
- h₀* height above the surface, where the vapour pressure in the atmosphere is P_0 cm of Hg
- h_y* height above the earth where the vapour pressure is P_y
- h_s* height above the earth where the vapour pressure is P_s
- h₁* height above the capillary head, where the vapour pressure is P_y
- h* depth below the surface of the soil column where the vapour pressure is P_y
- H* total length of the soil column $h_1 + h = H$
- K* $= -\ln(P_0/P_s)$
- l* relative length of the dry soil column from the surface of the soil column to the point where the moisture content is W_l
- L* relative length of the moist soil column from the wet front to the point where the moisture content is W_L
- M* molecular weight of water vapour
- m₁* $= h_1/H + (W_c - W_z)/(W_c - W_0) = y_1 + z_1$
- m* $= h/H + (W_z - W_0)/(W_c - W_0) = y + z$
- n* $=$ same as m_1
- P₀* vapour pressure at the height h_0 from the surface of the earth or vapour pressure at the surface of the soil column
- P_y* vapour pressure at the height h_y from the surface of the earth or vapour pressure at depth h cm below the surface of the soil column
- P_s* vapour pressure at the height h_s from the surface of the earth or vapour pressure in the soil column where the moisture content is W_s

P_z	vapour pressure in the soil column where the moisture content is equal to W_z
w	$=W_z - W_0$
w_1	$=W_c - W_z$
W	$=W_c - W_0$
W_F	moisture content at the wet front
W_c	moisture content at the capillary head
W_0	moisture content at the surface of the soil column
W_l	moisture content in the dry region at a relative distance l of the dry region from the surface of the soil column
W_L	moisture content in the moist region at a relative distance L of the moist region from the wet front
W_z	moisture content at the point where the vapour pressure is P_z cm of Hg
x	distance
y	$=h/H$
y_1	$=h_1/H$
z	$=w/W$
z_1	$=w_1/W$

Appendix II

Application of Clausius-Clapeyron equation for determining change of soil vapour pressure with temperature

The equation (12) expresses the distribution of vapour pressure when the temperature is constant. The equation is

$$P_n = P_0 \exp. K(w/W + h/H)/2 \quad (12)$$

The well-known equation of Clausius-Clapeyron is

$$\ln P_s = (A - B/T) \quad (14)$$

where A and B are constants and P_s is the saturation vapour pressure at T° A. Equation (14) could be rewritten as

$$P_s = e^{(A - B/T)} \quad (14a)$$

Now if r represents the relative humidity then one could write

$$rP_s = r e^{(A - B/T)} \quad (15)$$

$$\text{and } P_0 = r_0 P_s = r_0 e^{(A - B/T)} \quad (15a)$$

where P_0 and r_0 are the vapour pressure and relative humidity at the surface of the soil column. Substituting the above equation (15a) in equation (12) one gets

$$\begin{aligned} P_n &= r_0 e^{(A - B/T)} e^{K(w/W + h/H)/2} \\ &= (P_0/P_s) e^{(A - B/T)} e^{K(w/W + h/H)/2} \quad \text{since } r_0 = P_0/P_s \end{aligned}$$

It was shown in the steps between equations (11) and (12) that

$$P_s = P_0 \exp. K$$

Hence,

$$\begin{aligned} P_n &= (P_0/P_0 e^K) e^{(A - B/T)} e^{K(w/W + h/H)/2} \\ &= e^{-K + A - B/T + K(w/W + h/H)/2} \\ &= e^{A + K(w/W + h/H - 2)/2 - B/T} \\ &= e^{A^* - B/T} \end{aligned} \quad (16)$$

where $A^* = A + K(w/W + h/H - 2)/2$ is a constant for a level having constant moisture content. Equation (16) is the modified Clausius-Clapeyron equation for vapour pressure of soil moisture. P_n in equation (16) may be considered as a saturation vapour pressure of soil moisture.

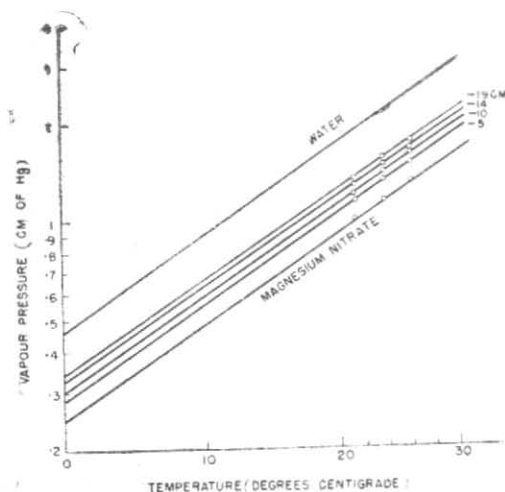


Fig 1. Vapour pressure versus temperature
(Linear graph)

Note that $A^* < A$. An equation formed on the basis of equation (16) for the level —19 cm in sand is

$$\ln P_n = 2.303 \left[8.915 - \frac{2290}{T} \right]$$

$$\text{or} \quad \log P_n = \left[8.915 - \frac{2290}{T} \right] \quad (16a)$$

and that for water for the same range of temperature is

$$\log P_s = \left[9.051 - \frac{2290}{T} \right]$$

The calculated (by means of equation 16a) and observed values are given in Table 1. A graph relating temperature and vapour pressure in sand at different measured levels are shown in Fig. 1. Pressure is taken along a co-ordinate which is in log scale and temperature is taken along the other co-ordinate which is reciprocal scale. The graphs are straight line graphs. From this it is clear that adsorbed moisture is different from free water; but in so far as its vapour pressure temperature relation is concerned, it also obeys Clausius-Clapeyron equation (16a), provided the vapour pressure at each level is taken as the saturation vapour pressure of the adsorbed moisture.

It may be concluded therefore that vapour pressure in a soil can be predicted when moisture content, length of the soil column and temperature are changed to new values.

TABLE 1
Vapour pressure at —19 cm in sand

Depth below the surface of the soil column (—cm)	Temperature (°C)	Vapour pressure in cm of Hg	
		Observed	Calculated by eqn. (16a)
19	21	1.316	1.304
19	23.5	1.600*	1.524*
19	26	1.692	1.712

*Interpolated value from values at —14 and —21 cm