WATER FLUX IN MOIST SOIL: THERMAL VERSUS SUCTION GRADIENTS

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That thermal gradients cause moisture transport in soil has been well known for at least 50 years. It is, however, surprising that so little attention has been paid to this phenomenon, since soil in its natural environment is continuously subject to changing temperatures. In 1957 Philip and de Vries (14) published a theoretical article in which they attempted to reconcile the few existing experimental data. Since then, alternative approaches have been suggested by Derjaguin and Melnikova (5), Matthes and Bowen (12), and Taylor and Cary (16). The experimental observations available are, however, insufficient to make a fair test of any of the proposed theories. As a general statement, about all that can be said is: A thermal gradient in soil will cause water to move from a warm to a cooler area in both the liquid and vapor phases, and the rate of transfer is greater than can be predicted with Fick's law and the diffusion coefficient for water vapor into air.

The experiment reported in this article was designed to yield data defining the relative importance of thermal gradients in transporting soil moisture and to probe the mechanisms of transfer.

EXPERIMENT

A specially designed apparatus was built to measure the simultaneous fluxes of heat and moisture across an unsaturated soil sample. The construction and operation of this unit have previously been described in some detail (1).

A sample of Columbia loam soil, 3.4 cm. thick and 19.8 cm. in diameter, was placed between two porous ceramic plates in a lucite chamber. Each plate was in contact with a water reservoir, the upper one heated and the lower one cooled. These water chambers were connected externally through a glass tube containing an air bubble. By fixing the tube in a vertical position and varying the length of the air bubble, pressure differences were created between the water reservoirs. The air bubble also served as a flow meter.

The apparatus, except for the flow meter, was placed in a vacuum chamber for insulation. Then, from a heat-loss calibration and steady-state energy input measurement the heat flow across the soil was calculated. The net heat flux and the net water flux across the soil sample was thus measured as a function of the thermal gradient across the sample and the pressure difference between the water reservoirs. These steady-state observations were made at various average soil-moisture suctions and soil temperatures.

The soil-moisture conductivity associated with the water-pressure differences between the plates was measured at suctions of 5, 10, 18, 25, and 34 cm. of Hg with each at average temperatures of 8, 18, and 33°C. This was done by running a small pressure difference first with and then against a constant thermal gradient. This gave two net flux measurements, the difference between them being due to moisture transport under the pressure gradient. The calculation of this conductivity (K, length per unit time) was made after correcting the pressure difference between the water chambers for the head loss across the porous plates. The conductivity of each plate was measured as 0.32 mm./day at 18°C. at the end of the experiment, and was taken as inversely proportional to the viscosity of water. The average values at 18°C. of the observed soil moisture conductivities are listed in table 1. As might be expected (8), the average values of the conductivities indicated that their temperature dependence was inversely proportional to the viscosity of water. All measurements were made on the same sample over a period of 7 months. At suctions of 5, 10, and 18 cm. Hg the system was on a desaturation cycle, and at 25 and 34 cm.

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[1] Contribution of the Southwest Branch, Soil and Water Conservation Research Division, Agricultural Research Service, in cooperation with the Irrigation Department, University of California, Davis.

Hg suction it was on a wetting cycle. The sample was prepared by washing a slurry of the soil into the chamber as the excess water was drawn out through the plates. This gave some stratification in the direction parallel to moisture flow, but it produced excellent contact with the plates. The sample at a suction of 18 cm. Hg had a moisture content of 19.2 per cent, a bulk density of 1.2, and an air-filled void fraction of 50 per cent. It was noted that, under these conditions, isothermal measurements of conductivity agreed satisfactorily with those measured under a simultaneous thermal gradient; however, this value was an order of magnitude less than that reported by Davidson *et al.* (4), who used gypsum solutions and shorter-term experiments.

RESULTS

The net moisture flux was the sum of two components, that flowing due to the pressure difference and that due to the thermal difference. By calculating the pressure flow component as described in the preceding paragraph and subtracting it from the net flux, the thermal flow component was found. These data for the 5-, 10-, and 18-cm. Hg suctions are plotted in figure 1, together with the simultaneous net fluxes of heat.

The temperature dependence of the net heat flux was much larger than could be accounted for by the temperature dependence of the heat conductivity of the soil materials, thus most of the rise in heat flux at higher average temperatures was due to the transfer of latent heat of vaporization as the vapor flow increased. The temperature dependence of this net heat flux was used to calculate the rate of vapor transfer through the soil. For this particular system when there is no soil, only air at atmospheric pressure, that is a sample with 100 per cent porosity, the rate of

TABLE 1

Values of various quantities at 18° C. calculated during the analysis of data

Suction (*cm. Hg*)	β $f(J_q)$	β $f(J_w)$	β used	% vapor	*K* (*mm./day*)	cm. H_2O/cm. equivalent to 0.5° C./cm.	*Q* (*cal./g.*)
5	1.9	1.6	1.7	21	0.60	2	1.7×10^{-2}
10	2.5	2.2	2.3	38	0.18	6	3.4
18	2.6	2.0	2.4	46	0.095	10	4.9
25					0.014	50	
34					0.005	250	

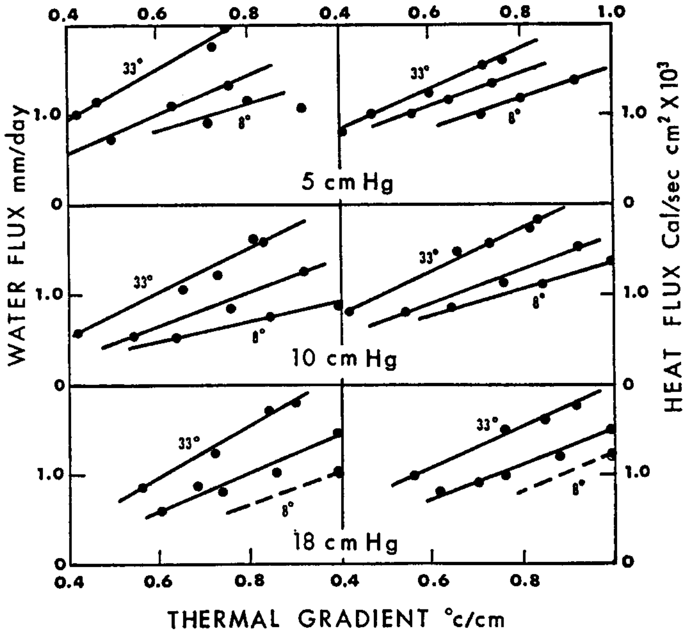

FIG. 1. Net heat flux and net thermal moisture flux shown as a function of temperature gradient. Data are for suctions of 5, 10, and 18 cm. Hg, at average temperatures of 8, 18, and 33°C.

vapor transfer may be described by the relation (2):

$$J_v = -\frac{\beta pDH}{R^2T^3}\nabla T \qquad (1)$$

where J_v is the vapor flux; p, D, H, and T the average vapor pressure, diffusion coefficient of water vapor into air, latent heat of vaporization, and absolute temperature, respectively; R the universal gas constant; β a unitless factor equal to one; and ∇T the thermal gradient between the porous plates. It is reasonable to assume that this equation should describe the flow of water vapor from one plate through the soil to the other plate by simply adjusting the constant factor (β) to account for an increased diffusion path, lower porosity, and any difference between the effective microscopic pore thermal gradients and the macroscopic measured gradient. Assuming β to be independent of temperature, it can be calculated from the increase in vapor flux between 8 and 33°C. (as reflected in the net heat flow curves) and equation (*1*)[2]. These results are shown in table 1.

It was also possible to calculate β from the temperature dependence of the net thermal moisture flux curves by assuming that the temperature dependence of thermally driven flow in the liquid phase is inversely proportional to the viscosity of water[3]. Then since

$$J_{tw} = -\beta\frac{pDH}{R^2T^3}\nabla T + J_{tl} \qquad (2a)$$

for a given thermal gradient

$$(\Delta J_{tw}) = \beta\Delta\left(\frac{pDH}{R^2T^3}\nabla T\right) + J_{tl}\left(1 - \frac{\eta_1}{\eta_2}\right) \qquad (2b)$$

where J_{tw} is the net thermally driven water flux; η the viscosity of water; J_{tl} the thermally driven liquid phase water flux [corresponding to η_1 in equation (*2b*]; and Δ the difference in water flux at two average temperatures. For this method the differences between both the 8° and 18° curves and the 18° and 33° curves are required for simultaneous solutions, since β and J_{tl} are unknowns. Calculations of β from equation (*2*) are given in table 1. Since the two methods of calculating β did not give exactly the same results, intermediate values were chosen and are listed in table 1. Using these values, the per cent of thermally driven vapor phase flow was calculated from equation (*1*) and the curves in figure 1. Presented with these results (table 1) is a comparison between the magnitude of the net thermally driven moisture transport and the flow resulting from a pressure gradient expressed as the head of water in cm./cm., which was equivalent to 0.5°C./cm. A more detailed analysis is presented in figure 2 and discussed in the following sections.

One other term, the heat of transport in the liquid phase, was calculated. This quantity is defined in the following manner. The general phenomenological equation for moisture transport in this particular system has been previously derived (2) as

$$J_w = -L_wR\left(\nabla \ln\frac{p}{p_0}\right) + L_{wq}\nabla\frac{1}{T} \qquad (3)$$

where J_w is the net water flux; L_w and L_{wq} phenomenological coefficients; ∇ the gradient between the porous plates; and p/p_0 is the per cent relative humidity divided by 100. Here the heat-capacity factor has been neglected, and the effects of any possible solute flow are also not considered[4]. The first term on the right represents flow due to the pressure difference, and the second term the flow due to the thermal gradient. From equation (*2a*) then

$$L_{wq}\nabla\frac{1}{T} = -\beta\frac{pDH}{R^2T^3}\nabla T + J_{tl} \qquad (4a)$$

where

$$J_{tl} = L_{lq}\nabla\frac{1}{T} = -L_{lq}\frac{1}{T^2}\nabla T \qquad (4b)$$

[2] For example, at 10 cm. Hg suction the increase in heat flux between 8° and 33° at $\nabla T = 0.8$°C./cm. is seen in figure 1 to be 0.63×10^{-3} cal./sec. cm². If the temperature dependence of the Fourier conductivity of the soil is the same as that of water, an increase of only 0.11×10^{-3} cal./sec. cm.² would have occurred. Therefore, 0.52×10^{-3} cal./sec. cm.² must have been latent heat which corresponds to the evaporation of 0.775 mm. H_2O/day. From equation (*1*) J_v at 33° − J_v at 8° = $\beta \times 0.305$ mm./day or $\beta = 0.775/0.305 = 2.5$.

[3] As already pointed out, this appears to be valid for liquid-phase flow induced by a suction gradient. When flow arises from other potentials, there is increasing evidence that the transport phenomena are closely related (3, 9, 10).

[4] Equation (4) is the same as that proposed by Taylor and Cary (16) except for a factor of T which arises in the arbitrary choice of driving forces taken from the entropy function.

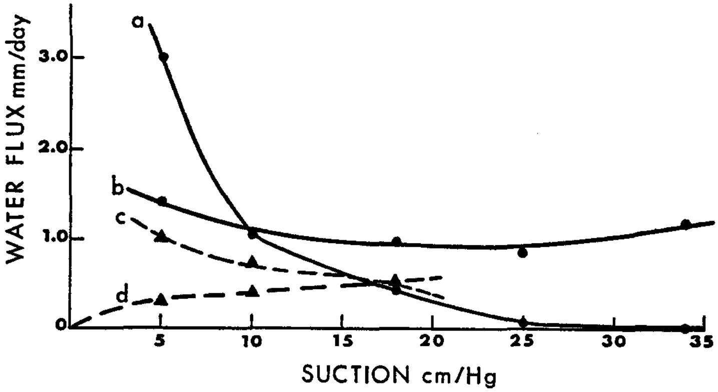

FIG. 2. A comparison at 18°C. of the various components of moisture transfer. Curve *a* is that which flows due to a pressure gradient of 5 cm. H_2O/cm., while *b* is the net thermal transfer of moisture from warm to cool under a temperature gradient of 0.8°C./cm. Curves *c* and *d* are the components of curve *b* in the liquid and vapor phases, respectively.

and L_{lq} is the phenomenological coefficient describing the flow of water in the liquid phase due to a thermal gradient. The net liquid phase flux may be written then as

$$J_l = -L_{wl} R \nabla \ln \frac{p}{p_0} - L_{lq} \frac{1}{T^2} \nabla T \qquad (5)$$

where L_{wl} describes isothermal liquid phase transport. The heat of transport in the liquid phase (Q) is then L_{lq}/L_{wl}, assuming the Onsager reciprocal relation in the liquid phase. The factor $R \nabla \ln p/p_0$ may be expressed as $\bar{V}/T \nabla P$ where $\bar{V}$ is the specific volume of water and ∇P represents a pressure gradient between the plates (15). Then since $(J_l)_T = K \nabla \phi$,

$$L_{wl} = \frac{KT}{a\bar{V}\rho} = \frac{KT}{a} \qquad (6)$$

where $\nabla \phi$ is the pressure gradient in cm. per cm. and a is the acceleration of gravity. Using values of K from table 1, values of L_{lq} calculated from equation (*4b*), and the data in figure 2, it was possible to evaluate the heat of transport Q. These results are shown in table 1 and their physical meaning is discussed in the following sections.

Mechanisms of transfer: Vapor phase

At the onset of this discussion it is helpful to note that equation (*1*) is essentially Fick's first law for the diffusion of water vapor into air[5]. The β used with this relationship is equal to one when the porosity is 100 per cent and the air is stable (2, 7). When soil is added to the system one might expect β to become less than unity as the porosity becomes less than 100 per cent and as the diffusion path length increases. However, β was greater than one in all cases. In fact, vapor transfer between the plates was from 2 to 5 times greater through the soil sample than through stable air. This may have been due to large microscopic thermal gradients across the air spaces in the soil, that is the thermal conductivity of the solid and liquid components is much greater than that of air. Woodside and Kuzmak (18) estimated that the thermal gradients across the air spaces may be from 2 to 20 times those measured across the bulk soil sample. Another possibility is convective transfer in the air-filled pores. This could conceivably arise from unsymmetric microscopic temperature distributions due to the different thermal conductivities of the soil materials.

Mechanisms of transfer: Liquid phase

An interpretation of the experimental liquid phase heat of transport values is a suitable way to begin the discussion of mechanisms of liquid flow.

The companion heat flux equation associated with equation (*5*), that is the flow of heat through solid-liquid phases of the soil, is

$$J_q = -L_{ql} \frac{\bar{V}}{T} \nabla P - L_q \frac{1}{T^2} \nabla T \qquad (7)$$

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[5] Use the Clausius-Clapeyron equation and the perfect gas law for this transition.

where

$$L_{ql} = L_{lq} \quad (8)$$

according to the Onsager relation. In the particular case where $\nabla T = 0$, one notes that equation (7) still predicts a heat flux. This is the heat (Q') carried by the water flowing due to a head difference. With $\nabla T = 0$

$$J_q = -L_{ql}\frac{\bar{V}}{T}\nabla P = Q'J_l = Q'L_{wl}\frac{\bar{V}}{T}\nabla P \quad (9)$$

where equation (5) is used to express J_l. Obviously then $Q' = L_{ql}/L_{wl}$, which is the heat of transport already calculated through the application of equation (8).

The physical meaning of this quantity is obvious in some cases. Consider, for example, water evaporating from a surface, diffusing through air, and recondensing on a second surface, all in an isothermal system where an osmotic difference is creating the vapor pressure gradient. Here the heat flux is the 580 cal./g. latent heat of vaporization (H). Therefore, $H = L_{wq}/L_{wl} = Q$, which has been previously shown (2). The physical significance of Q may be demonstrated in the liquid phase by considering the classic example of a diffusing molecule. In order for a specific molecule to make a random jump in the x direction from one point to another it must accidentally gain enough surplus energy to break any of its existing bonds and push other molecules aside as it moves to the next position where its average energy becomes again the same as its neighbors. In this case the surplus, or activation energy, was gathered from the neighborhood of its first position and then dissipated along the route and into the neighborhood of its next position. This represents a heat transfer in the x direction, that is in an open system with no simultaneous back diffusion the heat of transfer is some fraction of the activation energy. In the special case of evaporation of water this fraction is unity (2). In a liquid system the heat transported by the jump of a single molecule has been suggested to be in the neighborhood of half its activation energy (6).

Considering the activation energy of moisture film flow to be approximately represented by the temperature dependence of the viscosity of water (17), that is 225 cal./g., it is striking that the experimental heats of transport measured here are only a few thousandths of their maximum limit. Suggested then is the following model of molecular transfer in an unsaturated soil moisture film.

It is well known that in liquid water the molecules tend to be bound together by hydrogen bonds. A single water molecule might, at most, come under the influence of four hydrogen bonds for an instant, and some instant later be entirely free from any bonds. The water at any given temperature and pressure then could be expected to have a certain percentage of its molecules having no bonds, a certain percentage having one bond, and so on up to some percentage being influenced by four bonds. This average hydrogen bond distribution has in fact been calculated by Nemèthy and Sheraga (13) and published together with diagrams and a complete discussion. The soil moisture films may be expected to exist in a similar state, modified somewhat by surface adsorption to the solids, the air-water interface, and dissolved ions. A little thought suggests that the fraction of unbonded water molecules and the diameter of the bonded groups may largely determine the flow properties in such a film. In the event of a net force gradient, the unbonded molecules would be what "lubricates" the flow of bonded groups of water molecules, and for "diffusion-type" transfer they could largely determine the net number of random "jumps" in a given direction in accordance with their own concentration gradient. An unequal distribution of diffusion jumps could also cause microscopic pressure gradients on the bonded groups.

This concept provides a reasonable explanation for liquid phase water flux due to a thermal gradient. Since there are more free molecules as the temperature rises, there is more random movement. At any given cross-section there are a greater number of movements from the warm to the cool than from the cool to the warm, and so a net flux. This transport mechanism is not restricted to a thermal gradient; it could arise as well from an ion or osmotic gradient which changes the number of free-water molecules. A moisture content gradient would also change the free-water-molecule concentration, as it varies their mean molecular distance from the force field of the solid-liquid interface.

The very low heats of transport support the concept of movement regulated by the unbonded molecules. That is, in order to make a "diffusion jump" a water molecule does not have to gather a big bundle of activation energy, break bonds, move, and then release the energy by forming new bonds, but rather most of the movement is in the "no-bond" fraction of molecules and thus very little extra energy is required to "jump." The activation energy or temperature dependence in such a system reflects changes in the hydrogen bond distribution rather than specific mechanisms of flow.

Particularly related to the case at hand is the interpretation of the two liquid phase transfer curves (*a* and *c*) shown in figure 2. The vertical distances between them are arbitrary but their relative slopes are a property fixed by the soil. They suggest to this writer that the mechanism of transfer under the head difference between the plates was significantly different from that of the transfer due to the thermal gradient when the moisture suction was less than 8 cm. Hg. Likely, there was a significant pressure gradient through the film parallel to the direction of flow in the 0- to 10-cm. Hg suction range, and the free-water molecules were acting to "lubricate" the flow as well as to control the migration due to the temperature difference. Then as the suction approached 12 cm. Hg the pressure gradient became small[6] and the transport of moisture occurred by increasingly similar mechanisms under both the temperature and the pressure differences, that is as the gradients in the temperature and the depth of the moisture film induced changes in the fraction of unbonded water molecules and the size of the bonded groups.

The air-water interface surface tension gradient has not been given here as an explanation for the thermal driving force (14). This writer presently feels that this is a secondary effect, as it is now known that thermal osmosis occurs in saturated systems where there is no air-water interface.

The phenomenological flow equations

The phenomenological flow equations, in their simplest form, give the simultaneous flux of heat and moisture through soil as

$$J_w = -L_w R \nabla \ln \frac{p}{p_0} - L_{wq} \frac{1}{T^2} \nabla T \qquad (10)$$

and

$$J_q = -L_{qw} R \nabla \ln \frac{p}{p_0} - L_q \frac{1}{T^2} \nabla T \qquad (11)$$

where $L_{wq} = L_{qw}$. Moreover, if the flow is entirely in the vapor phase, $L_{qw} = HL_w$; or if it is entirely in the liquid phase, $L_{qw} = QL_w$. One may replace the phenomenological coefficients in equations (*10*) and (*11*) with combinations of other terms which are generally more familiar, that is

$$J_w = -\left(\frac{KTR}{a} + \frac{\beta pD}{\rho RT}\right) \nabla \ln \frac{p}{p_0} - \left(\frac{KQ}{aT} + \frac{\beta pDH}{R^2T^3\rho}\right) \nabla T \qquad (12)$$

and

$$J_q = -\left(\frac{\rho QKTR}{a} + \frac{\beta pDH}{RT}\right) \nabla \ln \frac{p}{p_0} - \left(\frac{\beta pDH^2}{R^2T^3} + K_f\right) \nabla T \qquad (13)$$

where K_f is the Fourier thermal conductivity coefficient for the soil. The form of equations (*12*) and (*13*) comes about from the combination of details developed in the preceding sections and in previous articles (2, 16). Equation (*12*) was used to predict fluxes for some of the more extreme conditions of this experiment, using values of K, β, and Q from table 1. These predicted values may be compared to the experimentally observed moisture flow rates in table 2. Since the parameters used to calculate the net moisture flow came from the mean values of observed data, it is not surprising that there is good agreement. However, the division of flow components again emphasizes the significance of the thermal gradient[7] and shows that any equation based only on the pressure differences between the plates would have

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[6] A simple analogy to the pressure gradient approaching zero may be taken from a cylinder filled with fluid and contained by a piston on either end. A force applied to the piston on one end will be transmitted to the piston on the other end. However, the force will not be transmitted if the fluid freezes tightly to the cylinder walls so that the pressure gradient through the fluid inside the cylinder becomes small. The analogy follows then from the structured concept of adsorbed water as discussed by Low (11).

[7] The phase separations of the thermally induced flow at 25 and 34 cm. of suction are not presented since the analysis may be significantly affected by experimental errors as the vapor transfer reaches the neighborhood of 100 per cent. The observed net thermally driven flow is, however, expressed in figure 2.

TABLE 2

Predicted and observed values of moisture flow at various soil moisture suctions where J_v is the vapor transfer, J_θ is transfer due to the pressure gradient, and J_{tl} is liquid-phase transfer due only to the thermal gradient

Suction	K	T	∇T	h	J_v	J_θ	J_{tl}	J_w	
								Net	Observed
cm. Hg	$\frac{cal.}{°C.\ cm.\ sec.}$	°C.	°C./cm.	cm. H₂O/cm.	mm. day				
5	1.30×10^{-3}	7.0	0.71	−0.2	0.13	−0.09	0.85	0.89	0.86
5	1.63	18.7	0.63	−1.8	0.22	−1.08	0.93	0.07	0
5	1.29	32.4	0.42	−2.1	0.32	−1.76	0.78	−0.66	−0.81
10	1.19	6.3	0.64	2.4	0.15	0.31	0.45	0.91	0.92
10	1.20	17.8	0.54	−2.6	0.25	−0.47	0.48	0.26	0.14
10	1.43	34.6	0.82	0.9	0.92	0.23	0.92	2.07	2.08
18	0.93	8.6	1.12	−6.4	0.31	−0.45	0.60	0.47	0.63
18	1.14	20.0	0.99	0.3	0.49	0.03	0.66	1.17	1.41
18	1.04	33.2	0.56	−4.5	0.62	−0.65	0.48	0.45	0.32

been unsatisfactory. Individual values of K_f were calculated from equation (*13*) and the heat flux data in figure 1. These are also shown in table 2.

SUMMARY

Simultaneous flows of heat and moisture were measured across a loam soil sample under various thermal and pressure gradients. The data were collected in a manner such that the liquid and vapor flow components could be separated and such that the liquid component could further be divided into that flowing due to pressure differences and that due to thermal differences. It was found that a temperature gradient of 0.5°C./cm. at a soil moisture suction of 5 cm. of Hg would move as much water through the soil as a pressure gradient of 2 cm. of water per cm. At a suction of 34 cm. of Hg this temperature gradient was equivalent to 250 cm. of water per cm. Vapor transport through the soil was several times greater than could be predicted with Fick's law and the diffusion of water vapor in air, even though at soil moisture suctions of less than 18 cm. Hg this vapor transfer accounted for less than half of the net thermally driven water flux. A linear thermodynamic moisture flux equation was developed in terms of commonly used flow coefficients and variables. This equation predicted fluxes in agreement with experimental observations. A mechanism for unsaturated flow in the liquid phase through soil is proposed. This proposal is based on current theories of the hydrogen bond distributions in water and the observed flow rates under simultaneous pressure and thermal gradients.

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