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The Dynamics of Soil Water

Part II—Temperature and Solute Effects

JOHN W. CARY

Agricultural Research Service, USDA
Kimberly, Idaho

S. A. TAYLOR

Utah State University
Logan, Utah

I. INTRODUCTION

Changes in the soil temperature and solute concentration occur continually under natural field conditions. Examples of the variations in solute concentration are given in chapter 14, particularly Fig. 14–13 and 14–14. In addition to this type of change induced by moisture flow, the concentration of the soil's solution oscillates between saturation under dry conditions to very dilute values after a rain or irrigation. Soil temperature, like solution concentration, continually changes. Its variation is conveniently classified as diurnal (Fig. 13II–1) and seasonal (Fig. 13II–2). The diurnal thermal changes are generally significant to a depth of 20 or 30 cm; the soil zone which contains the greatest proportion of plant roots. The seasonal temperature wave extends well below the zone of most crop roots.

These dynamic thermal and osmotic changes create gradients of physical properties in the soil that may influence the movement of soil water. Thus the questions arise: in what manner may these changes affect the flow of soil water, and under what conditions are these affects significant? As in the description of other physical systems, the primary driving force for water is pictured as a water potential gradient. Its effectiveness is defined as the hydraulic conductivity. Changes in the soil's solutes and temperature may affect both the water potential gradient and the hydraulic conductivity. In addition, the flow of heat along a temperature gradient and the flow of solutes along a concentration gradient may affect the net water flow.

II. CHANGES IN CONDUCTIVITY

Osmotic and thermal changes have been shown to alter the conductivity of moisture in soil. Gardner et al. (1959) have reported the effects of exchangeable sodium percentage and soil solution concentration on the weighted-mean diffusivity for two soils. For normal soils with low sodium, the diffusivity doubled as the concentration was increased from 2 meq/liter to 100 meq/liter. However, when the exchangeable sodium was high, diffusivities dropped by orders of magnitude as the salt concentration was reduced. Quirk and Schofield (1955) have studied

the permeability of several soils as affected by the concentration of salt in the water entering the soil. Over a period of 5 hours, the permeability of a calcium soil decreased by 25% when pure water was entering the surface, but by only 5 percent over the same time period when 1×10^{-3} M $CaCl_2$ solution was allowed to enter the soil. Again the effect on sodium soils was many times greater. Changes in water conductivities caused by the dissolved salt result principally from the effect of concentration on the expansion of the electric double layer around the soil's colloidal particles. The expansion of the double layer increases as the concentration of salts decreases; thus there is a tendency for the particles to swell or to disperse and clog pores. The viscosity of liquid film in the neighborhood of the double layer is higher than that of water (Low, 1960); thus, a dispersion of soil colloids may have the additional secondary effect of directly reducing the mobility of the soil water.

Jackson (1963) has measured the effect of temperature on the weighted-mean diffusivity for three soils. As the temperature rose from 5 to 45C, the diffusivities doubled in an approximately linear fashion. This temperature dependence was described by the temperature dependence of the ratio of surface tension to the viscosity of water and seems to be adequate to describe thermally induced changes in the diffusivity at the low matric suctions associated with infiltration. At greater suctions, however, soil water conductivity appears to be more temperature dependent than is free water viscosity. Meeuwig (1964) found that the temperature dependence of the soil water viscosity was two or three times that of free water viscosity in the three soils studied. Although the effect was most in the dry soils, a difference in temperature dependence of the viscosity was clearly evident at soil water suctions as low as 100 mbars.

III. CHANGES IN POTENTIAL

The energy status of the soil water is influenced by temperature and salt concentration. The question is: Do gradients of such quantities as kinetic energy, osmotic pressure, vapor pressure, and surface tension give rise to a significant transfer of soil water? Experiments have shown that under certain conditions they do.

The effects of thermal and osmotic gradients on water vapor diffusion through the soil's gas phase are easily recognized since the transfer of such water is directly proportional to the vapor concentration (vapor pressure) gradient. This relation (Fick's first and second laws) may be written as

$$q = - D(dc/dx) = - (D/RT)(dp/dx) \qquad [13\mathrm{II}\text{--}1]$$

and

$$\partial c/\partial t = D(\partial^2 c/\partial x^2) \qquad [13\mathrm{II}\text{--}2]$$

where q is the vapor flux, D a constant diffusion coefficient for the vapor, c the concentration of vapor, x the direction of flow, R the universal gas constant, T the absolute temperature, p the vapor pressure of the moisture, and t the time. Jackson (1964) has rewritten equation [13II–1] in a form similar to that of the diffusion equation for soil water as discussed in part I of chapter 13. For two soils the diffusion coefficient varied between 10^{-5} and 10^{-4} cm²/sec. in the dry range with
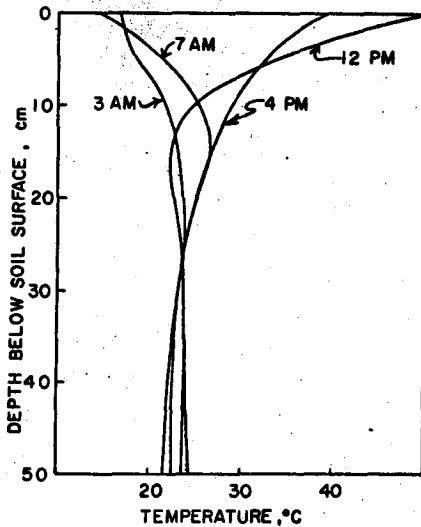
Fig. 13II–1. Daily summer temperature changes in a fallow field soil. Data from Onchukov (1957) or see Carson and Moses (1963).
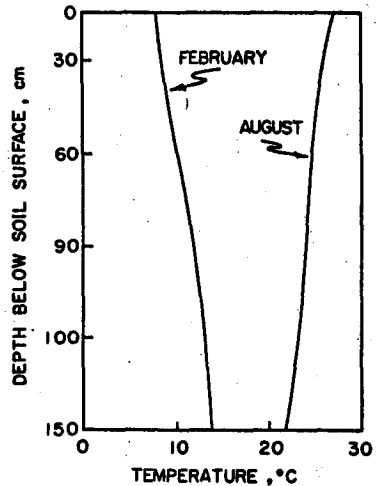
Fig. 13II–2. Average soil temperatures under a fallow soil in the winter and summer. Data from Qashu and Zinke (1964) or see Carson and Moses (1963).

volumetric water contents from 0.01 to 0.08. Roughly, this means that if the soil water content changed from 1 to 6% over a 10-cm distance, the induced water flux would be 0.2 mm/day. Such flow would be primarily in the form of vapor diffusion under nearly isothermal conditions. The vapor pressure gradient causing the transport would be caused partly by the difference in matric suction on the soil water and partly by the concentration changes in the soil solution. Under field conditions, temperature gradients would have further influenced the vapor pressure differences, since a continuous thermal wave passes through the soil. Matthes and Bowen (1963) have written equation [13II–2] with D as a variable and p as a function of temperature. In this form they were qualitatively able to predict changes in soil water contents responding to both changes in T and changes in D as it varied with soil density.

The vapor pressure of water is very sensitive to changes in temperature. The change in vapor pressure as the temperature drops from 26C to 25C would be approximately equivalent to that which occurs between pure water and a solution with an osmotic pressure of 80 bars. Moreover, the apparent diffusion coefficients for water vapor under a thermal gradient are surprisingly large. Experimentally, dT/dx is generally measured, and dp/dx is inferred from the known relation between vapor pressure of pure water and temperature. Using this approach, values of D calculated from equations [13II–1] and [13II–2] are always greater than one would expect from known values of the diffusion coefficient of water vapor into air, corrected for porosity and diffusion path length. Philip and De Vries (1957) in summarizing the literature prior to 1957 pointed out that the thermally induced transfer of water through soil was from 4 to 18 times greater than that pedicted by this simple theory. Part of the trouble seems to arise from the fact that the macroscopic thermal gradient is less than the microscopic thermal

gradients across the internal air spaces due to the heterogeneity of thermal conductivities of the soil's constituents. Thus, the over-all thermal gradient does not correctly describe the internal vapor pressures. This has been discussed by Woodside and Kuzmak (1958). Also, a part of the discrepancy is caused by a thermally driven liquid phase component of transfer from the warm to cool which accompanies the vapor diffusion. Philip and De Vries (1957) developed equations to account for this liquid phase flow based on liquid-air surface tension differences induced by the thermal gradient. This was a notable advance in the theory, though it is now recognized to have one serious shortcoming; thermally induced water flow does not become zero in the absence of internal liquid-air interfaces at saturation (Corey and Kemper, 1961; Taylor and Cary, 1960). This problem has been explored by Deryaguin and Melnikova (1958) and more recently by Cary (1965) using current theories of hydrogen bond distributions in water.

From time to time, some thought has been given to describing thermal water transport, coupled with osmotic and suction-induced flow, with a free energy expression analogous to Darcy's law; for instance,

$$q_w = - K'(\mathrm{d}\mu/\mathrm{d}x) \qquad [13\text{II}-3]$$

where q_w is the flux of water, K' is a conductivity for water, μ is the chemical potential of the soil water, and x is distance. However, one soon finds this equation must be limited to isothermal conditions, both for theoretical reasons and intuitively because the free energy of pure water decreases as the temperature rises. Moreover, μ is a function of both soil matric potential (suction) as indicated by a tensiometer and the solute potential (or osmotic suction). This has led to further difficulties because in some cases the solute potential is effective in causing water flow through soil and in some cases it is not. Still other problems arise from the opposite temperature dependences of the soil's matrix suction and its relative humidity (Kijne and Taylor, 1964).

Under normal field conditions, the net water flow is the sum of liquid and vapor transfer as affected by simultaneous changes in matric potential, temperature, and solute potential. The failure of simple expressions to completely describe the flow has caused recourse to a more basic consideration for analytical treatment of the problem. In particular, a system which is not in equilibrium, will, under natural conditions, spontaneously readjust such that entropy becomes a maximum. Any natural spontaneous change is an irreversible process which creates entropy. Since the creation of entropy is a time and rate dependent quantity, it seems reasonable to suppose that the natural transport of mass and energy in the soil system will occur simultaneously in a way such that the entropy proceeds toward a maximum. Based on this philosophy and certain assumptions (Taylor and Cary, 1964), it can be argued that the flux of water in the soil may be described by

$$q_w = \sum_{j=1}^{n} L_{wj}\left[\psi_g - \frac{\mathrm{d}(\mu_j)_T}{\mathrm{d}z}\right] - L_{wh}\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}z} \qquad [13\text{II}-4]$$

where q_w is the net water flux, j represents any one of the n various mass species in the soil which can move, ψ_g the gravitational potential, $\mathrm{d}(\mu_j)_T/\mathrm{d}z$ the gradient of chemical potential of the "j" mass species at temperature T, L phenomenological coefficients, the subscripts w and h signify water and heat, and $\mathrm{d}T/\mathrm{d}z$ is the

thermal gradient. For the particular case of $dT/dz = 0$ in a solute-free soil, equation [13II–4] reduces to any of the well known forms of Darcy's law or the water diffusion equation which have received much study.

In the special case where $dT/dz = 0$, the solute potential of the soil solution is created by a single solute and gravity effects are negligible, equation [13II–4] becomes

$$q_w = - L_{ww} RT \frac{\mathrm{d}\ln p}{\mathrm{d}x} - L_{wk} \frac{\mathrm{d}\mu_k}{\mathrm{d}x} \qquad [13\text{II}-5]$$

using the identity $(\mathrm{d}\mu_w)_T/dx \equiv RT \ (\mathrm{d}\ln p)/dx$ where p is the aqueous vapor pressure. The flux of solute is described by an analogous equation

$$q_k = - L_{kw} RT \frac{\mathrm{d}\ln p}{\mathrm{d}x} - L_{kk} \frac{\mathrm{d}\mu_k}{\mathrm{d}x} \qquad [13\text{II}-6]$$

and the tendency for water to move with solute and solute to move with water is expressed by the interaction coefficients such that

$$L_{wk} = L_{kw}. \qquad [13\text{II}-7]$$

The water and solute transmission coefficients are expressed by L_{ww} and L_{kk}. To illustrate the meaning of the two terms in equation [13II–5], consider the following situations. First, in a soil where no osmotic gradient exists, $\mathrm{d}\mu_k/dx = 0$ and so the moisture flow would be described by the first term. In this case, it might be convenient to rewrite equation [13II–5] as

$$q_w = - L_{ww} \overline{V} \frac{\mathrm{d}P}{\mathrm{d}x} = - K \frac{\mathrm{d}P}{\mathrm{d}x} \qquad [13\text{II}-8]$$

where the vapor pressure gradient has been replaced by its equivalent in a pressure gradient as given by tensiometers, e.g. Taylor and Kijne (1964). If there were a solute concentration gradient in the solution, but the water-filled pores were so large that no osmotic water movement occurred, then the flow would still be described by equation [13II–8] with dP/dx taken to reflect only the matric suction. In this case $\mathrm{d}\mu_k/dx \neq 0$ and $\mathrm{d}\ln p/dx$ would reflect the sum of both matric suction and osmotic components of the energy gradients. For equation [13II–5] to describe the flow, L_{wk} would have a value such that the sum of the two terms in [13II–5] would equal the single term in equation [13II–8]; e.g., the solute force would be substracted out. On the other hand, if the water-filled pores in the soil were so small that they behaved as a perfectly semipermeable membrane then $L_{wk} = L_{kw} = 0$, and the flow of water would be described by the first term of equation [13II–5] or by equation [13II–8] with P representing the sum of both matric and solute potentials (e.g. the total suction). In intermediate cases where some solute can "leak" through the soil water films, the solute potential gradient becomes only partly effective in causing moisture flow and is characterized by the value of L_{wk}. It is these intermediate cases in which equation [13II–8] fails. This type of analysis is receiving increased attention in plant-water relations (Dainty, 1963), as well as in soil water and solute relations (Abdel Aziz and Taylor, 1965).

The effect of osmotic potential gradients on liquid phase soil water flow is related to the salt sieving phenomenon. Equation [13II–6] describes the isothermal transfer of salt in soil when both solute and matric potential gradients

exist. The first term describes the amount of solute which would be carried along with the flow of water in the absence of any solute potential gradient. The second term accounts for the diffusion of solute along its own potential (concentration) gradient. Under conditions where the solute is, to some degree, excluded from the water flow path (e.g. salt sieving), the value of L_{kw} decreases accordingly. This is the condition which can give rise to osmotically induced flow of water. That is, the more the solute is excluded from some portion of the water flow path, the more effective a solute concentration gradient will be in developing a liquid phase water flow. In fact, where the Onsager reciprocity relation holds, a functional relation (equation [13II–7]) is fixed between solute sieving and osmotically induced water flow. Detailed studies of the mechanics and conditions which lead to this type of transfer have been made by Kemper and Maasland (1964), Kemper and Evans (1963), and Kemper (1961). Their data indicate that solute sieving and osmotic water flow in clays may be significant in water films up to at least 100A thick. Taylor and Cary (1960) have experimentally demonstrated small solute-induced flow of water flows through a tightly packed sample of saturated loam soil. The simultaneous movement of water and KCl has also been demonstrated in a silt loam soil and in kaolinite at an average water potential of –31.2 joules/kg (312 millibars suction) in response to a salt concentration difference between 0.2 M and 0.3 M across a soil plug 2.86 cm long (Abdel Aziz and Taylor, 1965). Concurrently, a hydraulic head difference of 10 cm of water induced a flow of both salt and water and the results were in accordance with equations [13II–5], [13II–6], and [13II–7]. Burns and Dean (1964) have demonstrated osmotically induced water flow in soil. Their experiment showed a flux of water into $NaNO_3$ bands and a subsequent redistribution of nitrate. However, Kemper (1961) has pointed out that for normal soils, osmotic gradients are probably not very effective in moving water until the matric suction rises above 1 bar. Exceptions could occur near the surface when fertilizer granules are present or where salt is accumulated by the evaporative process (Cary, 1964; Doering et al., 1964).

When thermal and suction gradients are creating water flow in the absence of significant solute effects, equation [13II–4] may be written as

$$q_w = L_{ww}\left[\phi - \frac{\mathrm{d}(\mu_w)_T}{\mathrm{d}x}\right] - L_{wh}\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}x} \qquad [13\mathrm{II}\text{–}9]$$

where the first term describes the flow of moisture due to gravitational and water potential (matric suction) gradients and the second term accounts for the flow induced by a thermal gradient. Though equation [13II–9] is a natural consequence of the time rate of entropy change in the soil system, it may be derived independently on the basis of flow mechanisms as shown by Philip and De Vries (1957). There is also a simultaneous heat flow equation which goes with [13II–9] and a reciprocal relation between heat and water flow coefficients similar to that shown in equation [13II–7]. In this case, the reciprocal relation provides a theoretical tool for exploring molecular energy transport (Cary, 1965; Taylor and Cary, 1964). Methods for handling the heat transfer equation in soil have been treated in a monograph edited by Van Wijk (1963). Laboratory methods are now available for separating the vapor phase flow and the liquid phase flow components from the net water transfer (Jackson, 1965; and Cary, 1965), thus the liquid and vapor phase components of each of the two terms in equation [13II–9] may be studied separately. This allows the transfer coefficients L_{wr} and

$L_{w\lambda}$ to be evaluated in terms of more commonly used numbers such as the soil's water conductivity, vapor diffusion coefficients, heat of vaporization, etc. (Cary, 1965). However, these coefficients depend on soil properties, and there is no *apriori* way of writing down their exact values. Some experimental measurements are required for each soil.

A thermal gradient in soil may cause large net quantities of water transfer. Even at saturation a small water flux may be observed (Taylor and Cary, 1960). Cary (1965) has shown that in one loam soil with a soil water suction of only −6.6 joules/kg (66 mbars suction), a thermal gradient of 0.5C per cm would cause as much water transfer as a hydraulic head gradient of 2 cm of H_2O/cm. At this water content, 80% of the thermally induced water transfer was in the liquid phase. When this soil's water potential was lowered to −45 joules/kg (450 mbars suction), a thermal gradient of 0.5C/cm moved as much water as a hydraulic head gradient of 250 cm of water per cm. At a water potential of −220 joules/kg (2.2 bars suction), Taylor (1962) reported a temperature difference of 1°/cm would cause as much water flow as a water potential difference of 140 joules/kg/cm (1.4 bars/cm); and if the soil was at a potential $< -12.6 \times 10^3$ joules/kg (126 bars), a temperature difference of one degree caused about the same water flow as a water potential difference of 8×10^3 joules/kg (80 bars). Presumably the flow at the lower potentials was largely in the vapor phase. As may be noted in Fig. 13II–1, gradients of 0.5C/cm or more may be expected under field conditions.

Perhaps the most striking example of thermal water transfer in the field is that which results from a frost zone at the soil surface. For example, Willis et al. (1964) have presented field data showing a water table drop of more than 120 cm as the moisture moved upward under the thermal gradient into a frost zone. Other striking examples of this type of flow have been reported by Ferguson et al. (1964) and by Meyer (1960). Evidently the freezing zone sharply reduces the downward gravitational and matric suction flow which leaves the net result determined by the thermal gradient which operates in the same direction over a period of several months. The fact that diurnal thermal waves passing through the soil surface layers in the summer do not cause such an obvious transfer of water does not mean they are less important, but only that steep water potential gradients must develop to account for any net water flow against the thermal gradients. When soil water moves up through the profile and into the atmosphere, an energy requirement of 570 to 800 cal/g of water must be eventually supplied for the phase change. Such large energy requirements produce temperature gradients in the soil, and thus, soil water flow must ultimately be closely related to heat transfer (Wiegand and Taylor, 1962; Anderson and Linville, 1962).

IV. SUMMARY

From the experimental evidence available in the literature, it is possible to make some statements about water flow in response to solute and temperature gradients under field conditions.

1) Changes in temperature and solute concentration of the soil solution may affect water flow in any, or all, of three ways—by changing the conductivity of the soil (Gardner et al., 1959); by changing the water potential (Kijne and Taylor,

1964); or by inducing water to flow along solute or thermal gradients (Taylor and Cary, 1964).

2) Normal variations in either the temperature or the solute concentration of field soils may change the hydraulic conductivity by a factor of at least two. In the event of a high sodium adsorption ratio, changes in the concentration of salts may cause changes in the conductivity to exceed two or three orders of magnitude.

3) Thermal gradients directly cause water to flow from warm areas to cool areas in both the liquid and vapor phase. This transfer will occur at any water content, but it becomes progressively more important as the soil becomes drier. In general one may expect normal thermal gradients in the root zone to be about as effective as the gravitational potential in moving water when the soil is near saturation. At field capacity these thermal gradients will be about 10 times more important than gravity and will become 1,000 times more effective than gravity before the permanent wilting percentage is reached. Although the largest thermal gradients occur in daily cycles through the principle rooting area of a crop, thermally induced flow is quite striking during winter as water moves up into the frozen zone.

4) Salt concentration gradients may cause water to flow through soil in both the liquid and vapor phase. Transport in the vapor phase results from gradients in the solution's vapor pressure. While liquid phase, solute induced flow has been experimentally demonstrated in saturated and unsaturated loam soils, normal solute gradients in productive field soils probably do not move significant amounts of water until the water potential is reduced to the neighborhood of −100 joules/kg (1 bar suction) except when salts are accumulated at the surface due to evaporation or when fertilizer granules are present.

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