PART IV: APPLICATION OF THERMOCOUPLE PSYCHROMETERS TO DETERMINATIONS OF WATER POTENTIAL IN SOIL AND OTHER MEDIA

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THE USEFULNESS OF WATER POTENTIAL MEASUREMENTS IN SOIL AND RELATED MEDIA

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As psychrometers for measuring soil water potential become readily available, scientists are increasingly interested in utilizing the technique. Our purpose in the following pages is to suggest some useful applications of this method for studying the properties of soil and related systems. We will also point out some of the present limitations so that persons beginning work in this area may make the best possible use of their initial efforts.

There are three general areas in which psychrometer measurements of soil water potential may be useful: (1) the analysis of water flow, (2) characterizing the state of the soil-water system through thermodynamics, and (3) water potential correlation with observations of biological responses. Because of the information already available, it is particularly important that careful planning precede experimental work on soil water flow and soil thermodynamics. Considerably less is known about the correlation of soil water potential and biological activities in soil. Experiments in this area cannot be planned as objectively, but should still be based upon all the principles and related responses that are presently recognized.

WATER POTENTIAL AND SOME GENERAL EFFECTS OF SOIL VARIABLES

Soil water chemical potential, by definition, is the change in total free energy of a system resulting from a change in water content as all other quantities and variables remain constant:

$$\mu_w = \frac{\partial G}{\partial n_w} \qquad [1]$$

where μ_w is the chemical potential of soil water, G is the free energy of the soil, and n_w is the water content in moles. It is not possible to assign a unique numerical value to μ_w, but differences in chemical potential may be evaluated by using the psychrometer and the approximate relation,

$$d\mu_w = RT\ d(\ell n\ e) \qquad [2a]$$

$$\Delta\mu_w = \mu_w - \mu_w^o = RT\ \ell n\ \frac{e}{e_o} \qquad [2b]$$

where R is the gas constant, T the temperature in °K, and e the vapor pressure. Because of the rather loose nomenclature of soil water energy or soil water potential, the quantity $\Delta\mu_w$ is sometimes erroneously thought of as the difference in free energy between water molecules in the soil and molecules in pure water. From the definition (equation [1]), this physical interpretation is obviously incorrect since the free energy of the system includes not only the change in the energy of the water molecules added to the system, but also changes in the energy of surface interfaces, dissolved molecules and ions, and all other entities in the soil whose energy state are affected by changes in the water content (Cary et al. 1964).

The soil water energy or potential may or may not include a gravitational potential component, depending on the convenience of the investigator. However, it always includes osmotic contributions from dissolved material, interfacial energy contributions from the air-water and solid-water interfaces, and the contribution of ambient pressure. The temperature of μ_w and $\mu_w{}^\circ$ is necessarily taken as constant (equation [2]). The potential changes from interface phenomena are called matric potential, and can be measured with tensiometers or pressure plates. Changes from dissolved components are called osmotic potential, and can be estimated from electrical conductivity measurements and chemical analysis (Rose 1966).

The effects of common variables on soil water potential are generally similar, but not exactly the same as their effects on pure water. For example, increasing the ambient pressure in soil increases the soil water potential. Adding soluble salt to the soil decreases the soil water potential. However, the amount of decrease may be different from that of a pure water system because of the possibilities of precipitation effects from other salts already in the soil, and of soil particle dispersion or flocculation which can change the matric component. Adding water to soil increases the water potential, but the relationship between soil water content and soil water potential is not unique, showing significant hysteresis over the whole range of soil water contents. Increasing the temperature of pure water decreases its chemical potential. No such simple relationship exists for changing the temperature of the soil water system because temperature also affects the surface tension of the soil solution, the volume of any entrapped air, and the solubility of salts (Childs 1969, Hagan et al 1967, Hillel 1971, Rose 1966). The time required to reach complete equilibrium in soil may be a deceptive factor when attempting to make exacting measurements of the effects of changes in these variables. The large surface area of soil, the activity of microorganisms, and the slow rate of some chemical reactions, particularly with silica, may create conditions which require weeks for true equilibrium to develop.

WATER FLOW IN POROUS MEDIA

Water flows through soil in both liquid and vapor phases. Flow in the vapor phase is by diffusion along vapor pressure gradients, or by viscous flow of soil-air along ambient pressure gradients. Liquid phase flow may arise in varying degrees from gradients of matric potential, gravitational force, temperature differences, and osmotic gradients. Since the psychrometer measures the water vapor pressure in the soil, which may be interpreted as the sum of matric and osmotic potentials (equation [2b]), it is apparent that psychrometer measurements alone will not indicate the amount of water flow or even the direction of net movement. Additional information on matric or osmotic potentials is always needed (Hagan et al. 1967).

Liquid water flow under constant temperature conditions generally obeys Darcy's law in one dimension (Childs 1969, Hillel 1971, Rose 1966).

$$Q_w = -K \left(\frac{\partial \psi_\tau}{\partial z} + \frac{\partial \psi_g}{\partial z}\right) \qquad [3]$$

where Q_w is the flux of water, K the hydraulic or capillary conductivity, ψ_τ the matric potential (in cm water), ψ_g is the gravitational potential (cm water), and z the depth. Two thermocouple psychrometers spaced vertically in the profile will allow estimation of $\partial\psi_\tau/\partial z$ only if the salt content of the soil solution causes a negligible osmotic potential, i.e. less than 5% of the total water potential. In this case if the temperature is uniform, the direction of liquid flow can be determined. The flow rate cannot be calculated unless the hydraulic conductivity is known.

When flow rates are relatively large, the soil water contents are near saturation and the matric potential near zero. Most instances of important flow during infiltration are in response to small values of $\partial\psi_\tau/\partial z$. To measure this gradient accurately, with a spacing of 10 cm between measurement points, requires a matric potential accuracy of -50 cm of water (0.05 bars), which is beyond the capability of present thermocouple psychrometers.

When the values of the matric potential gradients are relatively large, such as during soil drainage and drying, the flow rates are quite small. The water contents are lower and the hydraulic conductivities are very small and difficult to measure. Thus the calculated flow rates may be quite inaccurate even though the value of $\partial\psi_\tau/\partial z$ is accurately measured. The psychrometer may be useful in measuring $\partial\psi_\tau/\partial z$ under some of these conditions when the matric potential is less than -1 bar and tensiometers cannot be used. Psychrometer data must, of course, be supplemented by simultaneous measurements of the osmotic potential in order to arrive at values for $\partial\psi_\tau/\partial z$. Ingvalson et al. (1970) have developed an instrument where the thermocouple psychrometer is combined with a salinity sensor. This allows for estimation of the water potential and osmotic potential at the same location, which may prove helpful in this type of situation.

In general, it appears doubtful that thermocouple psychrometers will be as useful as tensiometers in measuring liquid water flow under isothermal conditions unless some significant breakthrough develops which improves their accuracy by an order of magnitude. Psychrometers may be used to indicate the direction of liquid water flow beyond the range of tensiometers provided the salt content of the soil solution is known from independent measurements, and the temperature is uniform.

An equation often used to characterize water vapor flow in one dimension is:

$$q_v = -D \left(\frac{\partial \rho_v}{\partial z} \right) + \rho_v v_a' \qquad [4]$$

where q_v is the vapor flux, D the effective water vapor diffusion coefficient in soil, ρ_v the water vapor density, and v_a is the average velocity of the soil air. Thermocouple psychrometers, in theory, may provide measurements of $\partial \rho_v / \partial z$ and ρ_v. However, over the range of soil water potentials where psychrometers function well, the change in water vapor pressure is relatively small. Significant water vapor flow occurs in soils through the soil surface where water potentials may be as low as -1000 bars, well beyond the range of present thermocouple psychrometers. Since the water vapor density of soil air is exponentially dependent on temperature, the vapor flow in response to temperature gradients that normally occur in soils is generally much larger than flow under isothermal conditions in the psychrometer range. For example, a temperature difference of 0.2°C will cause a vapor density gradient equivalent to a water potential difference of 15 bars. It is obvious that psychrometers that are accurate in the very dry soil range need to be developed and used in conjunction with temperature measurements to arrive at the values of p_v needed for equation [4]. Hygrometers, which do not function well in the thermocouple psychrometer range, may prove useful in the dry soil range (Campbell et al. 1971, Richards and Decker 1963).

To bring the preceding discussion into perspective, one should be aware of the relative magnitude of soil water flow under various conditions. Four divisions may be conveniently considered: infiltration of surface water, flow to plant roots, flow in drier soil, and flow in frozen soil.

Infiltration rates of water into soils may vary from as much as 100 cm hr^{-1} to as low as 0.01 cm hr^{-1} with the most common soils grouped around 1 cm hr^{-1}. Water flow above the wetting front is predominantly in the liquid phase, responding to the sum of the matric and gravitational potentials. During infiltration the soil water content near the surface is usually near saturation, with relatively large hydraulic conductivities and hydraulic head gradients approaching 1.0 cm of water per cm of depth.

Water uptake rates by plant roots are normally much less than infiltration rates. The combined water uptake by the root system of a complete plant cover will normally be less than 1 cm day^{-1}. If a water table exists near the plant roots, or the soil water contents are high, liquid water flow to the plant roots in response to matric potential gradients will be the principal transfer mechanism. If no water table or restricting soil layer exists, water will redistribute within two or three days after irrigation to the so-called "field capacity" condition. The liquid water flow thereafter may be quite low, in the neighborhood of a millimeter or less per day. Water flow to plant roots will then occur over only short distances of a few centimeters, but for several weeks plants may transpire water at rates near that of free water evaporation from the surface, provided the roots are well distributed throughout the profile. Even if roots are not well distributed, root growth into moist soil may be sufficiently great to keep up with the evaporative demands of the atmosphere.

Water flow through the soil becomes less than 0.1 mm day^{-1} in the drier range at soil water potentials below those needed to maintain transpiration at a rate near the demand of climatic conditions. This breaking point depends on the soil physical properties, and may occur at -0.5 bar matric potential in sands to as low as -5 bars matric potential in clays. However, even when the soil is dry, water flow in the top 15 cm near the surface may be quite active under some microclimatic conditions. Water will move out of this region as a vapor in response to large water vapor density gradients and ambient pressure fluctuations arising from air turbulence across the soil surface. This may occur along high water potential gradients of the order of 100 bars cm^{-1}. The total water flow by this mechanism can be relatively large over a year, depending on the frequency of wetting and drying cycles. With one wetting and drying cycle, total water flow from the soil to the atmosphere may be around 2 cm in many situations (Hagan et al 1967, Hillel 1971, Rose 1996).

Water flow in frozen soil may be significant, varying from less than a 0.1 mm per day to as much as 1.0 cm per night under some special short term conditions. The flow occurs primarily in the liquid phase, moving in unfrozen films along temperature gradients into the coldest areas. Ice freezes out of the soil solution in a pure state, and since its vapor pressure is lower than that of supercooled water, the ice determines the water vapor pressure in the soil. As ice crystals form in the soil pore spaces, the soluble salts are concentrated in the unfrozen films which soon fall to the same vapor pressure as pure ice. While the water potential in frozen soil is important in determining flow, it is easier to obtain from accurate temperature measurements and handbook values of ice vapor pressure than from psychrometers (Hoeckstra 1966, Cary and Mayland 1971).

DETERMINING THE STATE OF THE SOIL WATER SYSTEM FROM THERMODYNAMIC FUNCTIONS

The potential use of psychrometers to determine soil thermodynamic functions appears to be extensive, particularly as refinements are made that increase the range and accuracy of vapor pressure measurements. One area of interest rises from the Gibbs-Duhem relation:

$$-n_w \, d\mu_w = n_1 \, d\mu_1 \; . \; . \; . \; n_i \, d\mu_i \qquad [5]$$

Since the psychrometer is capable of measuring the chemical potential of soil water, equation [5] suggests a number of possibilities for arriving at the chemical potential and activities of ionic species dissolved in the soil water system. Such information is needed in studies of solubility and equilibrium constants, as well as for reaction rates and kinetics. Of course the psychrometer is already used to measure osmotic potentials of solutions and to infer the concentrations of these solutions.

Because the change in chemical potential with temperature gives the negative of the partial molar entropy,

$$\left(\frac{\partial \mu_w}{\partial T}\right)_{Pn_i} = -S_w \qquad [6]$$

where S is the partial molar entropy of the soil water, a number of thermodynamic functions can be evaluated. Once the differential entropy is calculated, changes in enthalpy follow from

$$\Delta\mu_w = \Delta H_w - T\Delta S_w \qquad [7]$$

where H_w is the partial molar enthalpy of the soil water. While the psychrometer may be used directly in calculating these quantities, it might also be used indirectly through equation [5] to assist in the calculation of differential entropies and enthalpies of other chemical species in the system (Guggenheim 1957).

Partial molar values of entropies and enthalpies calculated from equations [6] and [7] are difficult to interpret in terms of a physical model. They are, by definition, slopes of a line at a particular point and do not give any information about the average magnitude of the entropy or enthalpy of the system. The best use of these quantities may eventually come in testing partition functions developed from statistical mechanical models of soil water films (Eisenberg and Kauzmann 1969).

More useful quantities, in terms of physical interpretation, are integral entropies and enthalpies. Integral quantities may be calculated from the Gibbs' surface excess equation and vapor pressure measurements of the soil system at varying water contents:

$$\phi A = RT \int_0^e \frac{w}{e}\, de \qquad [8]$$

where ΦA is often called the surface potential, and w is water content by weight. This function may then be used in combination with either heat of wetting data as affected by water content, or vapor pressure data as affected by temperature, in simple equations to calculate integral values of entropy and enthalpy. These values give some idea of the average value of enthalpy and entropy and the structure of the surface film. While integral quantities are easier to interpret in terms of physical properties of the soil water solution, a number of assumptions are involved concerning the inertness of other components in the system, leaving ample room for future theoretical and experimental development (Cary et al. 1964, Kohl et al. 1964).

It has been known for many years that the concentrations of solutes at the air-water interface are not the same as their concentrations in the bulk solution. This concentration in the interface is generally called the surface excess and is a function of the chemical potential and the surface tension:

$$\Gamma = -\left(\frac{\partial \sigma}{\partial \mu_1}\right)_T \qquad [9]$$

where Γ is the surface excess, and σ is the surface tension. Because of the large air-water interface area in unsaturated soil, it is likely that both surface excess and surface tension affect, as least indirectly, most physical and biological processes in the soil. Since they are uniquely related to the chemical potential of water in the system, the psychrometer offers unexplored potential. The psychrometer may also prove useful in the study of some of the other rather special thermodynamic concepts in surface chemistry, such as changes in the energy, entropy, and enthalpy of the surface phase. Some theoretical development in this area is already available, and of course the chemical potential of the water is involved in these relations (Adamson 1960).

In general, the use of psychrometery in soil thermodynamics is largely unexplored at the present time. It is an area in which significant scientific advancement appears possible both in the development of theory and experimental techniques (Adamson 1960, Cary et al. 1964, Kohl et al. 1964, Marshall 1964).

CORRELATION OF WATER POTENTIAL WITH OTHER OBSERVED QUANTITIES

There are, of course, an infinite number of studies that one might do with psychrometers in soil and related media, in which various parameters are varied and the potential changes recorded. From the preceding discussion, it is obvious that this type of "shotgun" approach will probably not be very fruitful in yielding new knowledge concerning changes in the soil physical system. Experiments involving such variables as temperature, water content, density, pressure, and salt concentrations should be well planned in accord with the known principles and theoretical relations already available. On the other hand, much less is known about responses of biological systems such as plant root growth, seed germination, and soil organisms to changes in water potential. It may be necessary to carry out some preliminary experiments to gain some insight of how these entities respond to changes in soil water potential. Still it appears that no fundamental progress will be made with water potential as a single parameter approach in the obviously complex soil system. Before making water potential measurements, every effort should be made to develop a theoretical hypothesis which includes other related variables such as temperature, pressure, salt concentration, specific ion effects, etc. which might affect the system (Russell 1961, Slayter 1967, Toussoun et al. 1970).

FUTURE OF SOIL PSYCHROMETER MEASUREMENTS

Much remains to be done. Progress to the present time has been mainly in developing psychrometer hardware which is capable of making water potential measurements in soil. The most significant results from these first measurements have been in the area of separating osmotic and matric potential components. This has led to some preliminary information on the effect of these components on biological systems and on soil water movement. Increasing the range of vapor pressure measurements of the psychrometer will lead to better understanding of water flow, particularly in the vapor phase. It will also be used with matric potential or osmotic potential measurements in studies of unsaturated liquid phase flow. Many interesting things remain to be learned concerning the thermodynamic functions and physical state of the soil water system, and psychrometry may well play a major role. Psychrometers will also be important in developing meaningful models of the response of the biological systems to soil water potential. The use of psychrometry to indirectly aid in the determining of the activities of dissolved components may prove important. It is obvious, however, that the psychrometer cannot be used as a single tool nor the water potential as a single parameter to evaluate biological response, soil water movement, or other physical changes under the natural field conditions. Simultaneous measurements of other properties must be made and experimental work carefully planed to utilize our existing body of knowledge.

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