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Vapor Pressures of an Air-Water Interface During Evaporation[1]

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SYNOPSIS. Low evaporation rates from soil caused solutes in the soil solution to accumulate at the air-water interface and reduce the vapor pressure. Nearly tenfold increases in concentration at the interface were observed with $ZnSO_4$ in a cool moist soil. $CaCl_2$, $AlCl_3$, sucrose, and hexadecanol accumulated to lesser degrees, depending on the evaporation rate and the temperature. The small amount of water movement required to develop this increase suggests the phenomena may also occur next to semipermeable membranes, such as plant roots.

IT IS well known that salts accumulate near the soil surface as it dries. It is also generally recognized that the movement of salts toward the surface may affect the drying rate in two ways. First, this increase in concentration may change the rate at which moisture is conducted up toward the evaporation sites. Second, increasing concentrations of salt reduce the vapor pressure of water, i.e., decrease the tendency of the water molecules to escape from the liquid and move into the air. The effect of these two mechanisms on the drying of soil has been studied by Qayyum and Kemper (5). Boon–Long (2) has reported data showing similar phenomena affecting the evaporation of water from plants.

The purpose of the experiment reported in this article was to study the effect of salt on the vapor pressure of soil moisture. Equilibrium vapor pressures of many pure solutions are well known, as are vapor pressures for an increasing variety of soil solutions. However, equilibrium vapor pressures may be quite different from the vapor pressures of solutions during evaporation. This has been demonstrated by Cary (3) with KCL solutions drying from a porous plate. As water flows toward an air-water interface where evaporation is occurring, it carries dissolved salts. Since the salts do not evaporate they must remain behind at the interface. The increasing concentration at the air-water interface lowers the vapor pressure of the water and causes the salts to diffuse back toward the lower concentrations in the bulk solution. The net movement of salt in the moisture film at any given time will be the difference between the salt flux being carried along with the water flow and the salt flux which is diffusing back against the water flow. That is

$$J_s = C'J_w - D'(\delta C/\delta x) \qquad [1]$$

where J_s is the net salt flow, C' is the amount of salt being carried by the water flow, J_w, D' is the diffusion coefficient

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of salt in the soil moisture, C the concentration of salt in the soil moisture, and x is distance perpendicular to the air-water interface. Equation 1 assumes that the effect of the spontaneous thermal gradient developed across the evaporating site will have a negligible effect on the salt flux, i.e., the Soret coefficient will be small. The rate at which a salt will accumulate at the air-water interface should be affected by changes in the evaporation rate (i.e., J_w under steady conditions) and by changes in the salt's diffusion coefficient in the soil. The evaporation rate is controlled by the vapor pressure of the solution which may be varied by changing the temperature or the solute in solution. The diffusion coefficient varies with the salt and with temperature as shown in Table 1. Small concentrations of $AlCl_3$ are very effective in reducing the water vapor pressure whereas $ZnSO_4$ is relatively ineffective. On the other hand, $ZnSO_4$ has a very low diffusion coefficient when compared with $CaCl_2$. With these thoughts in mind the following experiment was conducted.

MATERIALS AND METHODS

A diagram of the equipment is presented in Figure 1. In the center of the apparatus an air chamber was formed by separating 2 porous ceramic plates with a lucite ring 8 inches in diameter. A thermal gradient was developed across the air space by maintaining a reservoir of warm water above the upper plate and a reservoir of cool water below the lower plate. A layer of Yolo loam soil was placed on the upper plate and brought to a given moisture suction by varying the vacuum pressure on the warm water reservoir. Moisture would then evaporate from the soil, diffuse down through the air space, and condense on the cool bottom plate. The condensation caused an outflow from the cool reservoir which was measured and was in effect the evaporation rate from the soil when steady state conditions were reached. The evaporation rate was varied by changing the temperature of the warm water reservoir. This was done by adjusting the A.C. potential across the 7-ohm insulated resistance wire in the reservoir. Settings from 2 to 6 volts were used which produced thermal gradients across the air space of 1 to 6° C. per cm., depending on the evaporation rate and the distances between the ceramic plates. The temperature of the lower reservoir was controlled by pumping water from a constant temperature bath through a copper coil inside the reservoir. The sides of the apparatus were wrapped in aluminum foil and placed in an airtight lucite container. The container was also covered with aluminum foil and placed in an air bath with temperature variations not greater than ±0.1° C.

The vapor flux across the air space in this system can be described, under steady state conditions, by Fick's first law,

$$J_w = -D(dc/dy) \qquad [2a]$$

where D is the diffusion coefficient of water vapor into still air, c is the concentration of water vapor in the air, and y is the distance across the air space.[3] In order to use this relation to calculate the vapor pressure of the soil, it may be written as

$$J_w = -(D/RT)(dp/dy) \qquad [2b]$$

or

$$p = (J_w RT\ l/d) + p_c \qquad [3]$$

where p is the vapor pressure at the soil moisture-air interface, R is the universal gas constant, T the absolute temperature, p_c the vapor pressure of the cool plate air-water interface, and l is the distance between the thermistors which are used to measure the temperatures at the upper and lower boundaries of the air space. The vapor pressure, p, may be calculated from the steady state outflow rate, J_w[4]. Knowing the saturated vapor pressure of the soil from the measurements of its temperature allows the

[3] Equation 2 assumes that the temperature gradient across the air does not become large enough to cause a significant thermal diffusion of water vapor (3).

[4] p_c is taken as the saturated vapor pressure of water at the cool plate-air interface temperature, R and D may be looked up in standard tables, and l is measured. T may be taken as the warm air-water interface temperature.

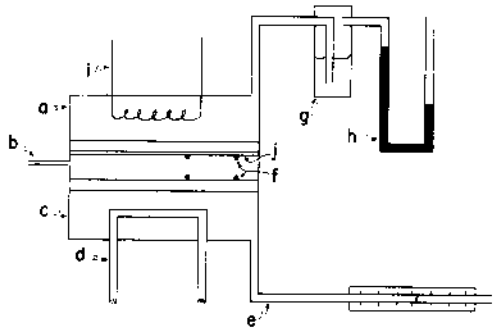

Figure 1. Diagram of the experimental apparatus: a is the warm water reservoir; b, a vent to the air space; c, the cool reservoir; d, the cooling coil; e, the outflow tube; f, the thermistors; g, the water supply; h, a mercury manometer; i, the heating coil; and j, the soil layer.

results to be conveniently expressed as the relative humidity at the soil moisture-air interface.

The experiment consisted then of finding the relative humidity of the soil under various evaporative rates, at different temperatures and with the soil solutions containing various solutes. The solutes used were $AlCl_3$, $CaCl_2$, $ZnSO_4$, sucrose, hexadecanol, and distilled water. To set up experiments with $AlCl_3$, H_2O, $CaCl_2$, and $ZnSO_4$ the apparatus was turned upside down and the moisture from a slurry of soil was drawn through the plate into the warm chamber. This left a 1-mm. layer of soil stuck to the plate's surface. Distilled water or a 0.4 molar solution of salt was then leached through the soil and plate into the warm reservoir. The reservoir was rinsed and filled with pure water or one of the 0.4M salt solutions. The same procedure was used for the sucrose solution except that a little phenol was added. When hexadecanol was used, 1% by weight hexadecanol was mixed into a dry sample of soil. The soil was then spread on the warm plate and wet up, but not leached.

After preparing the soil sample and filling the warm reservoir, the apparatus was set in place and a constant voltage applied to the heater. Twelve to 16 hours were allowed for the system to arrive at steady state temperatures. After the evaporation of 2 or 3 mm. of water, steady rates appeared to develop and the observed relative humidities are shown in Figures 2 and 3. Random variations due to experimental errors appeared to be around ±1% relative humidity when the average temperature was 35° C. and double this amount when the temperature was lowered to 12° C.[5]

[5] The thermal parameters of 35 and 12° C. are average temperatures of the warm air-moisture interface over the range of evaporation rates used.

The increase in variation developed primarily from the low vapor pressures at 12° C. Experimental error arose from uncertainties in the exact temperatures of the air-water inteface, the exact distance between the air-water interfaces, the effect of the lucite boundary of the air space on the diffusion of vapor, the use of average values of T and D associated with the thermal gradient in the air and the neglect of the thermal diffusion term in equation 2. In this experiment the temperature of each surface was measured in two places. Since small horizontal gradients were noted from the center to the edge of the plate, average temperature values were used for the calculations of relative humidity. Distances between the plates were varied from 1.25 to 3.50 cm. The closer spacing reduced the possibility of boundary effects and, as may be seen from equation 2, increased the evaporation rate for a given temperature difference. However, close spacing had the disadvantage of increasing the error arising from the measurement of the distance across the air space which was needed for equation 3. In order to compensate for as many of these problems as possible, the evaporation was measured with no soil in the system and with pure water feeding the upper plate. The vapor pressure, p, was then taken as the equilibrium saturated pressure (3) and the distance, l, was calculated from equation 2. This value was then used as the chamber constant to calculate vapor pressures when the soil was in place during the various treatments. The value of l arrived at in this way did not vary more than 1 or 2 mm from physical measurements of the distance between the upper and lower thermistors. Since the thermistors were imbedded in the thin layer of soil, their spacing remained constant.

RESULTS AND DISCUSSION

When distilled water was allowed to evaporate from the Yolo soil, there was no significant decrease in the relative humidity as shown by the upper curve in Figure 2. When 0.4M $CaCl_2$ was supplied to the soil for evaporation there was a gradual decrease in the relative humidity as the evaporation rate was increased. This effect resulted from increasing amounts of salt at the air-water interface, not from a drying of the soil due to the failure of water to be transported to the surface. It is evident that the soil remained moist at all times since the suction was never greater than 45 cm. Hg, the soil was only 1 mm. thick, the evaporation rates were low and the plate supporting the soil remained saturated and was highly permeable to water. Since the decrease in relative humidity was due to the increase in salt, it was possible to get the apparent concentration of salt in the air-water interface as a function of the evaporation rate (Figures 2 and 4). This was done with standard tables which give the vapor pressure or relative humidity of saline solutions at various concentrations.

For a given evaporation rate of the $CaCl_2$ solution, say 0.6 mm. per day, the concentration at the air-water interface was about double the concentration of the bulk solution when the temperature was 35° C. When the temperature was lowered to 12° C. and the evaporation was 0.6 mm. per day, the concentration at the interface rose to about 4 times that of the bulk solution. Equation 1 and Table 1 suggest that this was due to a sharp decrease in the diffusion coefficient of $CaCl_2$ as the temperature dropped. Changing the soil moisture content by changing the suction from 8 to 42 cm. of Hg appeared to have little effect on the concentration of salt at the interface though at 35° C. there appeared to be a tendency for the concentration to rise at the lower moisture content. The insensitivity to moisture content suggests that either D′ was much less sensitive to this moisture content change than it was to temperature changes or that C′ decreased with decreasing soil moisture, i.e., salt sieving developed.

The dependence of the soil's relative humidity on the evaporation rate for 0.4M solutions of $AlCl_3$, $ZnSO_4$, and a 1% mixture of hexadecanol is shown in Figure 3. The hexadecanol gave no significant decrease in the soil's vapor pressure at temperatures of 12 or 35° C. or at suctions of 8 or 42 cm. Hg. Thus its ability to reduce drying of soil columns at low application rates must be due to some other phenomenon as suggested by Olsen et al. (4). The $AlCl_3$ was slightly more efficient in reducing the relative humidity, and thus the evaporation rate, than was the $ZnSO_4$. One might have suspected this from the vapor pressure lowering data given in Table 1.

The apparent concentrations of $CaCl_2$, $AlCl_3$, and $ZnSO_4$ in the air-water interface as a function of evaporation rates at 12° C. are given in Figure 4. It is striking that the $ZnSO_4$ in the air-water interface reached concentrations of nearly ten times the concentration of the bulk solution. This was evidently due to the low diffusion coefficient of the salt in water, Table 1, and thus its inability to move against the flow of soil moisture.

The data presented in Figures 2, 3, and 4 appeared to be essentially steady state values, i.e., the salt was diffusing away from the air-water interface at the same rate it was being carried up to the interface by the evaporating moisture. Some transient-type observations were also made. At the beginning of one experiment using $CaCl_2$, the system was leached with 0.4M $CaCl_2$ solution and 16 hours

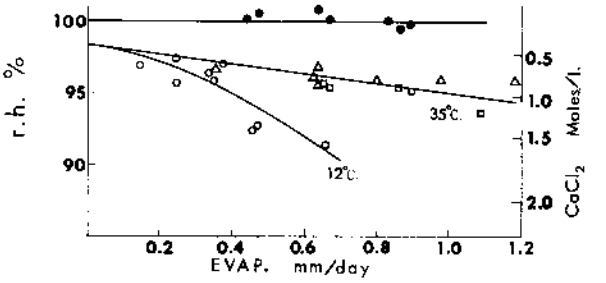

Figure 2. The relative humidity and the apparent salt concentration of the soil moisture-air interface as a function of the evaporation rate. The symbols indicate: ● pure water at 8 cm. Hg suction and 35° C.; △ $CaCl_2$ at 8 cm. Hg suction and 35° C.; □ $CaCl_2$ at 42 cm. Hg suction and 35° C.; ○ $CaCl_2$ at 12° with suctions of 8 or 42 cm. Hg.

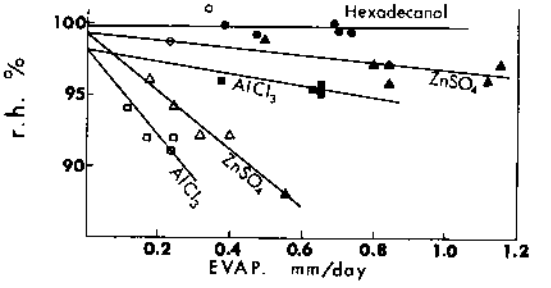

Figure 3. Relative humidity of the soil as it responded with the evaporation rate, temperature, and type of solute. The open symbols indicate 12° C. and the solid symbols indicate 35° C.

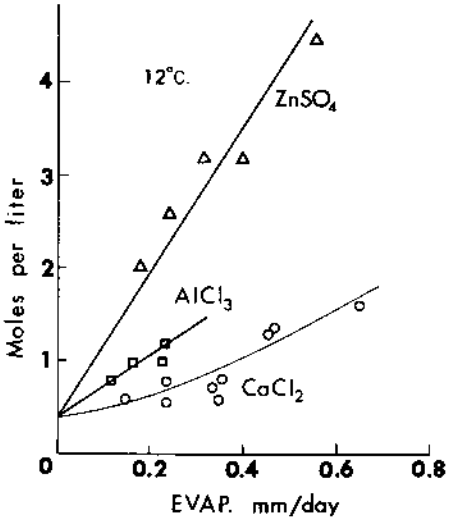

Figure 4. The apparent concentration of salt in the air-water interface as a function of evaporation rate at 12° C. with the bulk soil solution at 0.4M.

Table 1. Approximate diffusion coefficients and relative humidities of several solutions as listed in the International Critical Tables and the Handbook of Chemistry and Physics.

Solute	Relative humidities of 1M solutions, %	Moles per liter	Temp., C	D $cm^2/sec \times 10^6$
$CaCl_2$	94.7	1	0	0.65
		1	30	1.48
$ZnSO_4$	98.6	4	0	0.14
		3	20	0.38
$C_{12}H_{22}O_{11}$	98.3	1	12	0.30
		1	29	0.50
$AlCl_3$	92.1			

later, after about ½ mm. of water had evaporated, the interface concentration was from 0.5 to 0.6M. After 3 days and the evaporation of 2 mm. of water, the interface concentration was up to nearly 0.8M and seemed to be at steady state as long as the temperature and soil suction were maintained constant.

Short-term changes in vapor pressure were noted with abrupt changes in suctions. For example, at 35° C. under a suction of 42 cm. of Hg the evaporation rate was observed to be 0.65 mm. per day during the morning hours, which indicated an air-water interface concentration of 0.7M $CaCl_2$. Over the noon hour the suction was reduced to 8 cm. of Hg. For the first few hours during the afternoon the apparent concentration rose to around 0.8M, but by the next morning it had dropped to a little over 0.6M and was evidently at a steady state again. Possibly when the suction was decreased the salt at the air-water interface was temporarily concentrated in the smaller surface area exposed to the air. The $AlCl_3$ and $ZnSO_4$ showed similar short-term reactions to suction changes.

Heat flux across the air-water interface during evaporation was analysed, though the data are not presented in detail here. Of the net heat flux crossing the interface, the fraction utilized to provide latent heat for evaporation was significantly affected by both the temperature of the interface and the concentration of solutes in the moisture. The results followed the same general pattern reported earlier (3).

Even though the experimental data reported here were associated with a soil surface, the results are related to processes which occur in the soil-plant-moisture system. Shimshi (6) has recently suggested again that transpiration may not be entirely controlled in turgid plants by the stomata. More specifically, transpiration is controlled by the vapor pressure of water at the leaf's surface. As shown here the vapor pressure can be affected by the solutes much more than is indicated by equilibrium measurements of concentration. It seems likely, though, that dissolved salts could not cause a large effect in plant leaves since they are normally present in concentrations less than 0.4M. However, as suggested by Boon–Long (2) the possibility of organic solutes significantly affecting the vapor pressure remains. For this reason a 0.4M solution of sucrose (with a little phenol) was allowed to evaporate from the warm porous plate without soil. After about 2 mm. of water had evaporated over a period of 3 days at 35° C., the apparent concentration of sucrose in the air-water interface was 3 times that of the bulk solution. The temperature was then lowered to 12° C. and at an evaporation rate of only 0.26 mm. per day the concentration rose to nearly 2 molar or about 5 times that of the bulk solution. This suggests that similar conditions could occur with organic solutes in plant leaves, but the degree of concentration would depend on the mobility of the solute in the region behind the air-water interface inside the leaf stomata. Such a mechanism could account for some of the observations reported by Shimshi (6) and Boon–Long (2).

These results are also of interest when one considers the transfer of solutes across semipermeable membranes. If moisture is passing through a membrane which is more permeable to water than to dissolved materials in the water the system becomes somewhat analogous to evaporation from an air-water interface. Under these conditions, which are thought to be common in plants, a small transfer of water could cause the concentration gradient of dissolved materials across a semipermeable membrane to be significantly greater than equilibrium measurements of concentration would indicate (see the results presented by Barber (1) for instance). The solute gradient across the membrane would rise as the water flow increased and as the diffusion coefficient and membrane permeability of the solute decreased. For example, since sulfates tend to have lower diffusion rates in water than chlorides, one might expect that a given transpiration rate would cause a greater concentration of preferentially excluded ions around the outside of roots when sulfate was the principal anion, i.e., as opposed to chloride as the principal anion—all other factors being the same.

CONCLUSIONS AND SUMMARY

A method has been developed to measure the vapor pressure or relative humidity of a moist surface during steady state evaporation. This technique should prove useful in studies concerning the physical chemistry of air-water interfaces and in the investigation of properties of evaporation retardants.

The method was used to measure the relative humidity of a loam soil during evaporation rates up to 1 mm. per day, at temperatures of 12° C. and 35° C., and at moisture suctions of 8 and 42 cm. Hg. The data were interpreted in terms of the degree of salt accumulation in the air-water interface. An increased concentration of salt in the air-water interface of twice that in the bulk soil solution was easily obtained at evaporation rates of less than 1 mm. per day at 35° C. At 12° C. this apparent interface concentration often rose to more than 4 times that of the bulk solution at evaporation rates of less than 0.5 mm. per day.

The implication of results obtained using the loam soil are of possible significance in some plant-water relations. The interface accumulation as related to the evaporation of water from leaves and as related to the transport of solutes across semipermeable membranes warrants further study.

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