Salt and Water Movement in Unsaturated Frozen Soil[1]

J. W. CARY AND H. F. MAYLAND[2]

ABSTRACT

Salt and water movement was measured in unsaturated frozen soil columns incubated under a thermal gradient for 3, 6, or 9 weeks. Both water and salt moved from the warmer to cooler areas in the soil, creating a twofold concentration difference over a 24-cm distance. Movement of $CaCl_2$, LiI, and K_2SO_4 was studied in detail. Cation exchange reactions and salt solubilities at high concentrations affected the movement. Although the results suggested that mass flow of dissolved salts in a liquid film of water was the principal transfer mechanism, both vapor and salt diffusion were sometimes significant. Thermal diffusion and salt sieving did not appear to be important.

Since the vapor pressure of ice controls the water potential in frozen soil, the amount of unfrozen water and matric suction could be calculated from a water release curve and data from ice suspensions in salt solutions. These results led to the conclusion that mass flow in the liquid phase is described by Darcy's law. Thus, salt flow as well as net water transfer can probably be predicted in unsaturated frozen soil using information available from unfrozen systems.

Additional Index Words: salinity, salt diffusion, thermal diffusion, salt separation, frost heaving.

M OIST UNSATURATED SOIL freezes downward from the surface in the fall and is subject to varied thermal gradients throughout the winter (Benz et al., 1968). As the soil water freezes, small ice crystals form in the pore spaces. Not all of the water freezes under temperatures commonly experienced in the field. A liquid-like film 10 to 40Å thick remains at the ice-air interface. Liquid films of varying thicknesses also remain in the soil particle-ice interfaces and in the soil particle-air interfaces (Anderson, 1970).

Since ice crystals freeze out of a solution in a pure state, all soluble salts are forced into the unfrozen water films and may form relatively concentrated brines. The vapor pressure of ice is less than that of pure liquid water. Consequently, water will continue to crystallize from the soil solution until the combined osmotic and matric forces reduce the solution's vapor pressure to that of the ice (Hoeckstra, 1966; Low et al., 1968). Under natural conditions in the field, temperature gradients always exist, and liquid water tends to move from warmer to cooler areas (Fergusen et al., 1964). A spontaneous vapor pressure gradient in this same direction is fixed by the temperature of the ice phase. While some movement is in the vapor phase, most of the flow is in the unfrozen liquid films (Hoeckstra, 1966; Benz et al., 1968). Since the films may contain high concentrations of soluble salts, it is apparent that salt will also move from warmer to cooler areas in the unsaturated frozen soil.

Most of the liquid phase movement occurs along the water films adsorbed to the soil particles. While there are liquid films in the ice crystal air interfaces, they comprise a small fraction of the total unfrozen water in unsaturated soil because of the relatively small surface area of the ice crystals compared to that of the soil particles (Anderson, 1970). As the water moves from the warmer to the cooler areas, the ice crystals in the cooler areas grow as the arriving water freezes out. This may continue until the ice crystals completely fill the pore spaces. At this stage, the continuous liquid films along the soil particle surfaces begin to separate as the soil particles are pushed apart by the continued ice crystal growth. This is the beginning of an ice lens that leads to frost heave (Hoeckstra, 1969). Although the water may still move from warmer areas to these large ice lenses, little water can move past them so the lenses continue to grow.

A number of transport mechanisms may be involved in this mass flow toward the surface. The water in the soil may move in both the liquid and vapor phases, with the liquid phase responding to gradients of osmotic, matric, and possibly electrical potentials, as well as thermal diffusion (Hoeckstra, 1966). The soluble salts may be carried by mass flow in the liquid film subject to electrostatic salt sieving by the soil mineral surfaces, as well as by diffusion along salt concentration gradients and by thermal diffusion along the thermal gradients (Dietz, 1963; and American Society of Agronomy Symposium—Abstracts of papers by G. R. Benoit and J. Bornstein; G. H. Brandt; W. O. Willis and H. J. Haas; J. Brown; R. S. Sartz; M. J. M. Romkens and R. Miller; J. K. Torrance and R. D. Miller; P. Hoeckstra; and D. Anderson are given in the 1968 Agronomy Abstracts. Reprints of the complete texts are available upon request from the individual authors).

While the preceding description forms a reasonable qualitative model of what happens in frozen soil, little is known about the relative importance of the various transport mechanisms. Such information must be available before the system can be described quantitatively. The purpose of the work reported here was to evaluate the relative effects of the possible transport systems and to suggest appropriate flow equations.

PROCEDURE

Air-dried soil was mechanically packed into lucite tubes 24 cm long and 3.7 cm inside diameter (Jackson et al., 1962). The tubes were made by taping 2-cm sections together. Each section had two 1-mm holes located on opposite sides. After packing the columns, the tops were sealed with paraffin. They were then laid on their sides in pans of water containing various concentrations of salt and allowed to wet to the desired water contents. The holes were sealed and the columns were positioned vertically for 2 to 4 weeks at 21C to allow equilibration. They were then placed vertically in a container which thermally insulated the walls of the column while maintaining the bottoms at −0.5C
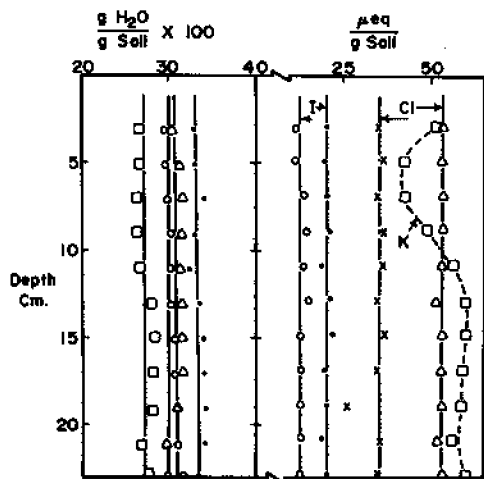
Fig. 1—Examples of water and salt distributions as a function of depth in several isothermal check soil columns.

and the tops at −6.5C. After 24 hours, the columns were completely frozen and a constant temperature gradient was established. Thermocouples were used in some of the columns to measure the temperature distribution. The columns were left under the temperature gradient for 3, 6, or 9 weeks before each was sliced into 2-cm sections and analyzed for water and salt contents.

Three salt solutions were used to wet the soil columns: $CaCl_2$, K_2SO_4, and LiI. Lithium iodide was chosen because the I salts are among the few with negative Soret coefficients (diffuse from cool to warm in aqueous solutions). Chemical potential data were needed for the analysis of transfer in soil, so the concentration of pure brine solutions in equilibrium with ice crystals at temperatures between 0 and −5C were measured. The solutions were allowed to freeze in separatory funnels suspended in a water bath which was controlled to ± 0.1C. After time for equilibrium, some of the unfrozen solution was drawn off from the ice slurry and analyzed.

Chloride was removed from the soil by exhaustive washing with water. Other salts were extracted by exhaustive washing with $1N$ NH_4Ac solution (pH 7.0). This method of extraction was chosen because of the inability to distinguish between added and native cations. Depending upon the test species, active exchange could occur during the treatment period. The subsequent cation extractability would, therefore, be a function of the solution salt concentration and exchangeable cationic species. Potassium and Li were determined by flame photometer, while Cl and I were measured by potentiometric titration. Sulfate was determined turbidmetrically after treatment with sized $BaCl_2$ crystals. Calcium was determined by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

As an illustration of how near the initial sample preparations came to uniformity, Fig. 1 shows the distribution of water and ions in several individual check columns, with no temperature gradient during the frozen period. The water content in these columns was generally uniform within ± 1% by weight. The distribution of ions was also reasonably uniform with the exception of K which may have been influenced by an exchange reaction with Ca.

The experimental results are summarized in Fig. 2. Each of the points shown in this figure is a mean of 2 or 3 replicated columns except for 2-G, which shows the results from a single column to which both K_2SO_4 and LiI were added. All of the results are for the Portneuf silt loam with the exception of results in Fig. 2-H, which are for a silty

clay. The bulk density of the soil in all columns was approximately 1.2 ± 0.05 except where specific curve parameters are shown. The Portneuf is a Ca-saturated soil with a surface area of 97 m^2/g and a CEC of 20 meq/100 g. It has a saturation extract conductivity of about 1.5 mmhos/cm (approximately equivalent to 15 μeq of salt/ml).

As predicted by the qualitative theory presented in the introduction, both the water and the salt moved toward the colder soil surface even though the entire column was frozen. The changes in concentration of the salts in the water from the original concentrations (dashed lines) indicate that the salt and water must have moved somewhat independently during the frozen period. Several mechanisms might account for this behavior. The basis of one is illustrated in Fig. 3, where liquid salt concentrations in equilibrium with ice are shown as functions of temperature. Since each degree decrease in temperature corresponds to approximately a 12-bar water potential drop in ice, the osmotic pressure of the brine solutions are known and shown on the left axis of Fig. 3. The break in the K_2SO_4 curve is caused by its solubility limit at about 800 μeq/ml. The curve from this point to −5C is an extrapolation of handbook values for the solubility change of K_2SO_4 with temperature. The $CaSO_4$ curve is also an extrapolation of handbook solubility values. It is obvious from this figure that as the temperature decreases, the concentration of soluble salts in the brine solution will increase. Thus, as the brine solution moves upward toward the colder soil surface, each unit volume of flow carries an increasingly greater amount of salt. In other words, as the soil solution moves up toward the colder surface, water continually freezes out along the way, leaving the soluble salts to move on in the more concentrated brine. Then upon melting, the amount of salt per milliliter of water near the surface will be higher than before freezing.

Another possible mechanism for separating salt and water flow is salt sieving. This should show up in the curves of salt per gram of water as an increase in the concentrations in the deeper portions of the soil. The only apparent possibilities appear in Fig. 2-A as the knee at the 17-cm depth, or as the two tails on the K curves in 2-C and 2-F. However, the tails on the K curves are largely a result of ion exchange and, in general, while the knee in 2-A may have occurred from a small amount of salt sieving, the high concentration of soluble salts in the brine films suggests the double layer was very compressed and salt sieving should be slight.[3]

Ions could also move independently of the liquid phase by diffusing along their own concentration gradients in the brine, as well as by diffusion under the thermal gradients. Thermal diffusion should appear as an increased concentration of salt near the surface for positive Soret coefficients, and as an increased concentration of salt in the warmer soil for negative Soret coefficients. Increases in salt concentration in the colder areas are evident in the $CaCl_2$ systems (Fig. 2), but the reverse was not observed for the LiI, which has a negative Soret coefficient.

[3] See, for example, *Soil Water*, edited by D. R. Nielsen, being published by the American Society of Agronomy, 1972.
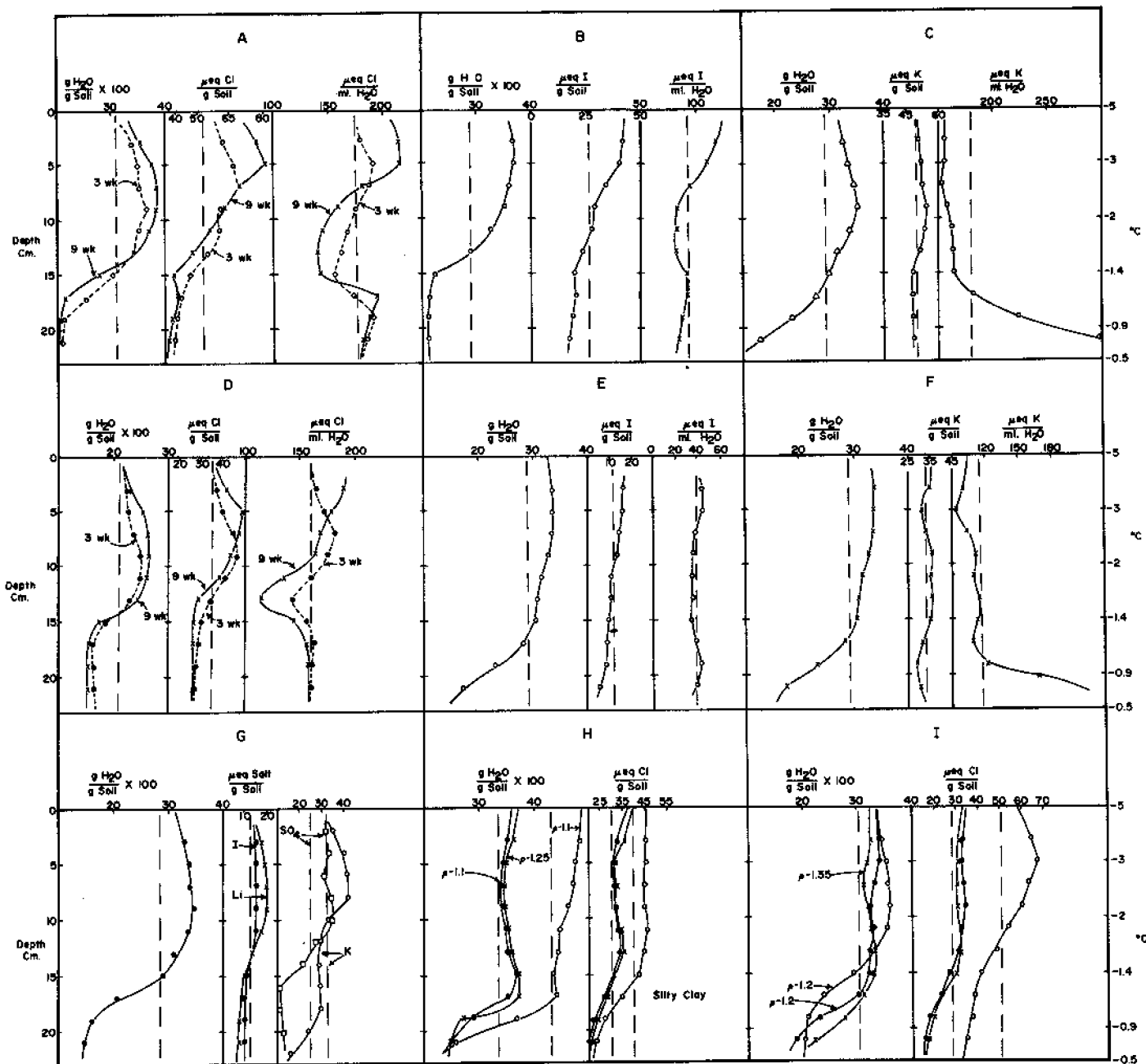
Fig. 2—Moisture and salt distributions as a function of soil depth at the end of various experimental tests. The dashed lines show the average concentration of salt and water at the start of each test. The temperature distribution with soil depth is shown on the right axis. All soils were incubated for 6 weeks except as specifically shown on curve parameters. All columns were filled with silt loam except for section H where silty clay was used. The bulk density "ρ" was approximately 1.2 except as noted by specific curve parameters.

Salt diffusion can be estimated from the relation

$$J_s = -\gamma \phi D_s \left(\frac{dn_s}{dz} + n_w n_s s_T \frac{dT}{dz} \right) \qquad [1]$$

where J_s is the flux of salt at depth z, γ the fraction of unfrozen water in a cross section at depth z, ϕ the tortuosity, D_s the diffusion coefficient of salt in water, n_s and n_w the mole fractions of salt and water, s_T the Soret coefficient, and T the temperature (deGroot and Mazur, 1962).

Soret coefficients for $CaCl_2$, LiI, and K_2SO_4 in pure

solutions are approximately 1×10^{-3}, -1.4×10^{-3} and 5.8×10^{-3} °C^{-1} (Snowdon and Turner, 1961; von Halle, 1959), while handbook values for diffusion coefficients of these salts range from 0.6 to 1.0 cm^2/day.

The fraction of unfrozen water needed in equation [1] can be estimated from the information given in Fig. 3 and 4 and the relation

$$\psi = \tau + \pi \qquad [2]$$

where ψ is the total soil water potential fixed by the vapor pressure of ice, τ is the soil's matric potential, and π is
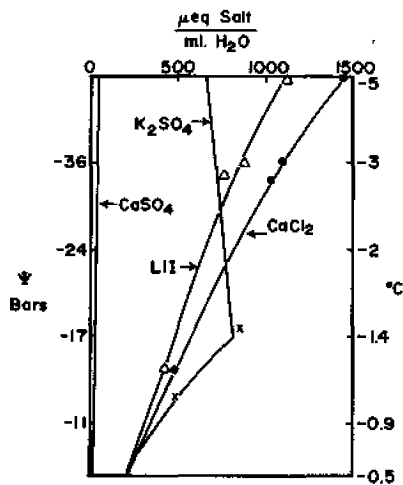
Fig. 3—The equilibrium concentrations of soluble LiI, K_2SO_4, $CaCl_2$, and $CaSO_4$ in ice slurries at different temperatures. The temperatures are scaled to the temperature distribution with depth in the incubated soil columns, and the total potential is known from the vapor pressure of ice at the various temperatures.
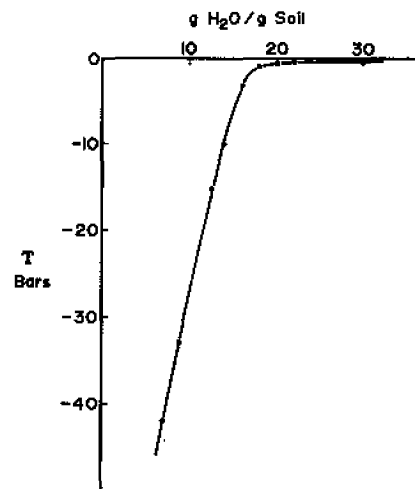

Fig. 4—A moisture desorption curve for Portneuf silt loam at 23C.

the osmotic potential. The matric potential can be calculated for any given amount of salt in the brine solution at any specific soil temperature by finding the single water content in Fig. 3 and 4 that allows equation [2] to sum to the total water potential fixed by the ice temperature. This type of calculation leads to the information shown in Fig. 5, where the soil matric potential and percent of unfrozen water is shown as a function of soil depth.

Equations [1] and [2], used with handbook values for diffusion coefficients and Soret coefficients, give an average downward salt diffusion flux at the 15-cm depth of Fig. 2-A as approximately 0.15 $\mu eq/(cm^2 day)$ for the concentration component of diffusion flux, and a value less than 0.015 for the Soret or thermal diffusion flux.

Since it is possible to calculate the concentration of soluble salt in the unfrozen brine film, the net transfer of salt may be estimated from measurements of the net water flow. Choosing the soil depth where the water content began to rise during the frozen period, generally between 13 and 16 cm, the average water increase per gram of soil can be measured by graphically integrating the curves in Fig. 2. The total amount of upward liquid water flow may be calculated by subtracting the vapor diffusion component. This component, across a plane at depth z, is given by:[4]

$$J_v = -\beta \frac{D\,p\,H}{R^2 T^3} \frac{dT}{dz} \qquad [3]$$

where β is a dimensionless constant $\simeq 2.5$, D the diffusion coefficient of water vapor in air, p the vapor pressure of ice, H the latent heat of vaporization, and R the universal gas constant. Finding the average vapor flux to be approximately 0.013 mm/day upward at the 15-cm depth, leads to the average liquid phase flux in mm/day shown in the first column of numbers in Table 1. This, multiplied by the average concentration of salt in the brine film,

gives the net salt movement shown in the second column of numbers. As previously noted, there was a small downward diffusive flux of salt along its own concentration gradient, which must be accounted for, giving the predicted salt flow shown in the third column of numbers in Table 1.

The actual amount of salt that moved upward was calculated by graphically integrating the curves showing the μeq salt/g soil. Results of these graphical integrations are shown in the last column of Table 1. The predicted values of salt movement are reasonably close to the observed values with the exception of the K_2SO_4 system, though in all systems there may be a systematic error that makes the calculated values higher than the actual observations. This could be due to an underestimate of vapor flux, or salt diffusive flux, or an overestimate of the concentration of soluble salts, as well as the problem of assuming average concentrations and concentration gradients in the transient systems.

The failure of the prediction in the case of K_2SO_4 arose from not accounting for the exchange of K and Ca between the soil particle surfaces and the brine solution. From Fig. 3, it is apparent that the K concentration in the brine solution may have approached 0.5N which should have resulted in a significant exchange of K for Ca, followed by precipitation of $CaSO_4$. Consequently, most of the K was held by the soil particles and did not move with the liquid film. The result is shown in the curves (Figs. 2-C and 2-F) of K concentration in the soil and is why the water concentration in the soil and K concentration in the water are mirror images of each other.

The possibility also exists that there was some exchange of Li for Ca in the LiI system. Since CaI_2 is soluble, the I was able to move toward the soil surface with either Li or Ca ions which does raise some question as to the correct value of s_T to be used in equation [1].

As already noted, part of the water flux was in the vapor phase and may be calculated from existing theory. Water in the liquid phase, i.e., the brine solution, may move as a result of hydraulic head gradients, by thermal diffusion, or by effects of osmotic concentration gradients and electrical potentials. Since the data and theory indicate that
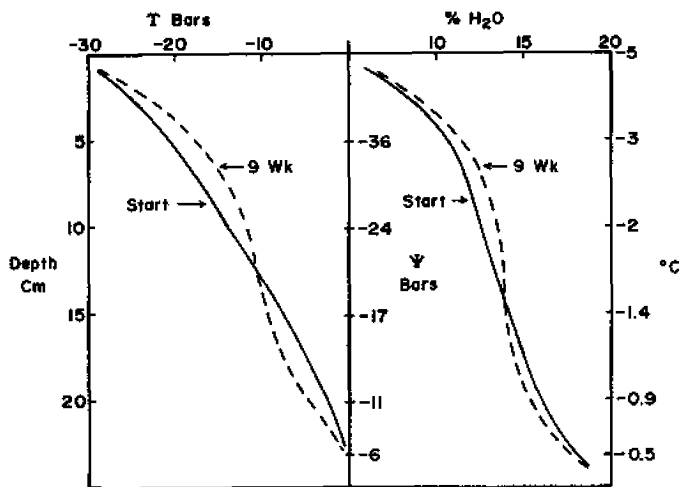
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[4] Ibid.

Fig. 5—The soil matric potential and unfrozen water content shown as a function of depth for the experimental test, Fig. 2-A. Temperature distribution with depth is shown on the right-hand side, while the center ordinate shows the total potential as required by the vapor pressure of ice.

salt sieving was small, it follows that water flow in response to osmotic gradients was also small. Both salt sieving and osmotic pressure flow require a system with semipermeable membrane characteristics, and, in fact, both phenomena are uniquely linked through the Onsager reciprocity relation.[5]

The net liquid flow was much greater than can be accounted for from thermal liquid-phase water flow,[5] thus the bulk of the liquid phase flow must have occurred along a pressure potential gradient arising from the matric potential effects on the unfrozen water film. Taking the average matric potential gradient from Fig. 5, and dividing it by the net flux of water found by graphical integration of Fig. 2-A at the 13-cm depth, gives a hydraulic conductivity of approximately 1×10^{-5} cm/day. This value occurs at a matric potential of -10 bars (Fig. 5), which is in reasonable agreement with experimental observations reported for other similar soils in an unfrozen state (Gardner, 1960).

A QUANTITATIVE THEORY

In view of the preceding discussion, it appears that the flow of soil solution and salt in unsaturated but frozen soil may be approximately described by the relations

$$J_{w} = -K \frac{d\tau}{dz} - \beta \frac{D \, p \, H}{R^2 T^3} \frac{dT}{dz} \quad [4]$$

and

$$J_{s} = -n_{s} K \frac{d\tau}{dz} - \gamma \, \phi \, D_{s} \frac{dn_{s}}{dz} \quad [5]$$

where K is the hydraulic conductivity and τ is the matric potential written in terms of cm of water, i.e., approximately bars $\times 10^3$.

To use these equations for predictive purposes, one needs to know the hydraulic conductivity of the soil at a

Table 1—Calculated and observed fluxes of soil solution and salt which moved upward in some of the systems shown in Fig. 2

| Case | Average liquid flux | Salt accumulation predicted | | Observed salt accumulation |
		Net moved	Corrected for back diffusion	
	mm/day	———— μeq/g soil ————		
Fig. 2-A High CaCl₂ – 9 weeks	0.13	17.3	15.8	14.2
Fig. 2-D Low CaCl₂ – 9 weeks	0.08	8.4	6.9	6.8
Fig. 2-A High CaCl₂ – 3 weeks	0.27	14.0	13.5	9.1
Fig. 2-D Low CaCl₂ – 3 weeks	0.18	6.3	5.8	5.5
Fib. 2-I High CaCl₂ – 6 weeks	0.14	12.0	11.0	8.2
Fig. 2-E Low LiI – 6 weeks	0.20	3.7	3.1	2.6
Fig. 2-B High LiI – 6 weeks	0.22	10.6	9.6	7.9
Fig. 2-F Low K₂SO₄ – 6 weeks	0.13	7.6	7.3	1.4
Fig. 2-C High K₂SO₄ – 6 weeks	0.13	9.7	9.3	2.5

water content or matric potential corresponding to either the unfrozen water content or matric potential of the liquid film in frozen soil. This moisture content or potential may be found from the type of information given in Fig. 3 and 4, utilizing equation [2]. Values for unsaturated hydraulic conductivity may be approximated by values from unfrozen soil. A reasonable value of β may be chosen from tabulated values previously published,[6] and the other constants may be estimated from handbook values and information on soil exchange reactions and salt solubilities. Since these equations give the flux of salt and water through a cross section at any depth at any given time, it should be possible to use a computer to construct complete salt and soil water profiles as a function of time beginning with any set of conditions under a known temperature profile. These equations are, of course, suggested only for unsaturated conditions. As soon as the water content approaches the saturation point, further growth of the ice lens will disrupt the soil particle arrangement (Hoeckstra, 1969), and the conductivity values from nonfrozen conditions will not be valid estimates. However, the theory might still be used to predict the rate of water transport to a growing ice lens.

Flow equations [4] and [5] are a natural consequence of the thermodynamic theory of soil water transport,[7] combined with the qualitative model of the unsaturated frozen soil water system presented in the introduction of this paper. These equations require no new concepts of salt and water transport, nor do they require any new parameters that soil scientists are not already familiar with from studying unsaturated flow in unfrozen soil systems.

The proposed theory is in accord with the general flow behavior in unsaturated frozen soil as shown in Fig. 2 and other reports of similar research (Sartz, 1969; Fergusen et al., 1964; and Benz et al., 1968). For example, the rate of upward water flux increases as the amount of soluble salt in the soil increases because the thicker unfrozen water films provide a greater hydraulic conductivity. The decreasing rate of upward movement with time (Fig. 2-A and 2-D) results from a decreasing water matric potential gradient (Fig. 5), combined with the effects of a changing

⁵ Ibid.

⁶ Ibid.
⁷ Ibid.

unfrozen water content on the hydraulic conductivity. Moreover, as positions in the soil approached local saturation, the ice crystals began pushing the soil particles apart, further reducing the conductivity. The separation of salt and water is accounted for in the theory by salt diffusion, ion exchange, and solubility limits in the unfrozen water film, as well as by the increasing concentration of the brine solution as the temperature falls.

Under some field situations where the soil surface is wet and undergoing daily freeze-thaw cycles, large ice crystal development may be observed at or just below the surface (Outcalt, 1969). The ice crystal growth may be associated with frost heave of small plants and suggests a large upward movement of soil water to the surface. The proposed theory does predict this type of flow. For example, suppose that conditions were such that the soil froze to a depth of 5 cm. If it were very wet, the continuing release of heat of fusion would hold the temperatures near zero, say —0.2C at the surface and 0C at the 5-cm depth. Even with very little dissolved salt in the soil solution, a matric potential of about —0.4 bar would exist at the 2.5-cm depth. The conductivity would then be about 0.1 mm/day in a silt loam. The average gradient between the surface and the 5-cm depth would be approximately 300 cm H_2O/cm, resulting from the temperature gradient in the ice phase. This gradient would develop a flux of 3 cm/day upward through the 2.5-cm plane. To maintain this large flow overnight, a high initial water content is required to buffer the temperature near zero and to make water readily available at the 0C soil temperature plane. A flow of 1 cm/night to the surface with subsequent ice formation would release 80 cal/cm^2, which is in the general neighborhood of nighttime heat loss from a bare soil (Gradwell, 1968).

Provided there is at least enough water present to allow the ice phase to form, the theory suggests that initial soil water content will not be too important in steady-state situations lasting a number of days, other than its effect on the temperature distribution in the soil profile. If the soil is initially so dry that the ice phase does not form, the water movement will decrease very rapidly with time in accord with the general theory of soil water transport in unfrozen soil.

Small changes in density may not be too important, Fig. 2-H and 2-I. Flow in frozen soil may at first be increased by increasing the soil bulk density since greater densities could increase the hydraulic conductivity at low water contents. However, increasing the density reduces the size of the pores, causing them to fill with ice sooner and create ice lens which terminate further transport of water.

The kinds of salt dissolved in the soil solution may interact to give varying results as shown in Fig. 2-G. Here it was obvious that none of the ions moved at the same rate, and the end result was no doubt affected by the soil exchange of Ca for K and Li compounded by the solubility product of $CaSO_4$ in the concentrated brine solution. If the exchange and solubility constants for the Ca, Li, K, SO_4, and I were known in the unfrozen film, their final distribution could presumably have been predicted.
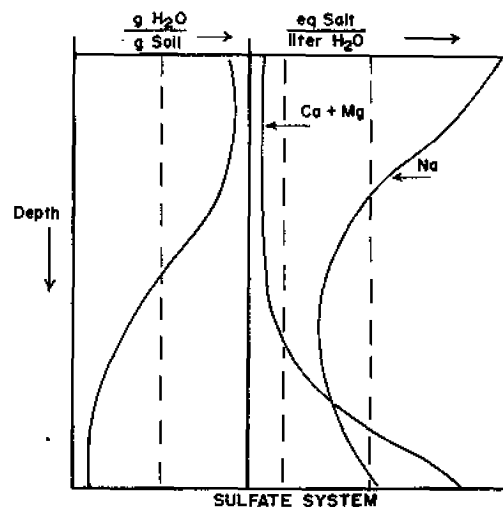

Fig. 6—Hypothetical changes in soil water, Ca, Mg, and Na distributions in a SO_4 soil system following a period of downward freezing from the surface.

PRACTICAL ASPECTS

The proposed theory suggests a number of practical applications, some of which are obvious from the preceding discussion. One of these is the possibility of predicting water and salt movement in frozen soil from data already available from unfrozen soil. Other possibilities are seen in recognizing the effects of bulk density, salt concentration, salt solubilities, and exchange reactions on the transport of liquid to the colder soil planes and the subsequent degree of frost heaving. These concepts provide a reasonable explanation for the upward movement from a water table observed by Benz et al., 1968; the affect of water potential on upward flow in the winter reported by Fergusen et al., 1964; and the infiltration into frozen soil (assuming periods of slight surface warming) observed by Sartz, 1969.

Another area of interest is the efficiency of the unsaturated frozen soil system in moving salt toward the coldest plane. Accumulation of NO_3 at the surface in the wintertime has been observed in the field by Campbell et al. (1970). Movement of herbicides, pesticides, and a variety of soluble salts toward the soil surface during frozen periods may also be important.

The ability of brine flow in the frozen soil to separate ionic species is particularly interesting. Suppose, for example, one had a sulfate soil system such as that sketched in Fig. 6. In the fall, the soil is uniformly wet as shown by the dashed line. After freezing, the water would migrate toward the surface, and the curved line would approximate the water distribution just before thawing in the spring (Fergusen et al., 1964). Further suppose that the [Na]/[Ca + Mg] ratio in the fall, was such that the soil was just on the borderline of becoming a problem. Upon freezing, the $CaSO_4$ and $MgSO_4$ would largely precipitate from the brine solution, while the very soluble Na_2SO_4 could, depending on the exchange reaction between the soil and brine, move toward the surface with the wintertime migration of liquid phase water. Melting in the spring, then, could result in an unfavorable Na/[Ca + Mg] ratio

near the surface, leading to dispersion of the clay minerals, a sharp decrease in infiltration, and all the associated problems. The salt and water movement in the frozen soil would have acted, then, to trigger a series of salt problems.

In any case, one must realize that frozen unsaturated soil in the wintertime is not a static system either with respect to water movement or to salt movement, and we should be aware of the possible consequences of these actions in the field.

ACKNOWLEDGMENT

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