

Thermally Driven Electrical Coupling Effects and Pore Water Advection in Soils

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Measurements of near-surface temperature fluctuations during a period of night frost were used in conjunction with a surrogate measure of soil water ion concentration to attempt to trace inflections in these time series to soil water advection effects. Major inflections in the ion concentration time series were traceable to water and water vapor processes as a freeze-thaw front propagated vertically through a soil profile at shallow depths. Relative ion concentration was related to the electrical potential measured between a probe at different depths of interest and a ground spike. The field probe electric circuit was modeled as an electrolytic cell without transference. Field time series data illustrated that effects of water migration toward near-surface evaporation/freezing fronts, solute expulsion from a freezing region, internal evaporation, and clean melt water release could be detected by variations in the electric potential or its surrogate, the relative ion concentration index. The spatial/temporal pattern of temperature and relative ion concentration helps to explain interactions or coupling between induced hydraulic, osmotic, and electrical gradients during the propagation of a thermal disturbance through a soil.

Electro-osmosis and streaming potential are manifestations of isothermal coupling of flows of water and electricity in a soil. Coupling effects become more complex when a thermal gradient or disturbance (e.g., freezing and thawing) are present. Passive generation of electrical potential gradients in soils by thermal gradients has been reported in a number of laboratory experiments (1–3). Measurements of electric potential variation across the freezing isotherm have been reported from permafrost regions in recent years (4–6). Those measurements demonstrated significant changes in electric potential near the freezing front. Outcalt et al. (7) propose that those electrical potential variations during soil freezing and thawing events may be interpreted as the product of soil electrolyte concentration variations resulting from phase changes and advection.

A primary purpose of this paper is to present additional evidence in support of this hypothesis based on soil-water potential and temperature measurements during a night frost event in the field. Another objective is to test the significance of electrical potentials associated with soil freezing and thawing. For example, Kelsh and Taylor (8) have claimed that freezing potentials depend in complex ways on so many different variables that it is hard to sort out their individual

effects. Accordingly, they assert that although freezing of water may indeed influence water migration and modify pore water ion concentrations freezing potential is not a useful measure of such effects.

An opposite view is that thermally induced concentration changes appear to explain best the gross features of the measured electrical potentials, which does not preclude, however, the presence of other coupling effects similar to those noted by Elrick et al. (9). Several types of coupling effects could conceptually manifest themselves during freeze-thaw events in a soil-water-electrolyte system as a result of complex interactions between the flows of matter and energy. If present, those effects would tend to modulate but not dominate concentration-induced potentials associated with freezing and thawing.

As an example of a secondary coupling effect, freezing of soil water can give rise to a large soil-water suction with a strong advective flow of water into the freezing region. This advective flow in turn can produce an electrokinetic streaming potential. However, the “electrokinetic potentials” cannot account for the magnitude and pattern of the observed electric potentials associated with frost-thaw events. Gray and Mitchell (10) measured streaming potential by using reversible Ag-AgCl electrodes on either side of homoionic clays and silty clays saturated with sodium chloride solutions varying from 10^{-3} to 10^{-4} N in concentration. The measured streaming potentials varied from 1 to 60 mV/atm with potentials decreasing sharply as either the concentration of the pore water electrolyte or the exchange capacity of the clay soil increased. Those potentials are an order-of-magnitude lower than the electric potentials measured between our near-surface probes and reference ground spike.

Other types of induced electrical potentials associated with freeze-thaw events (diffusion potentials, phase boundary potentials, and freezing potentials) have also been cited from time to time in the technical literature. So-called “freezing” potentials in the range of 1 to 25 mV have been reported by Drost-Hansen (11) in dilute aqueous solutions (10^{-4} – 10^{-3} N KCl) between the advancing ice front (negatively charged) and unfrozen water (positively charged). This potential is alleged to arise as the result of the incorporation of ions into ice and the crystallographic rearrangement of water molecules as freezing occurs. However, gentle stirring obliterated this potential. Stirring would also have eliminated ion concentration differences and suggests that the “freezing” potential is caused in large part by ionic concentration differences near the ice interface.

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EXPERIMENTAL PROGRAM

A field study was conducted in a grass lawn area at the University of Michigan Matthaei Botanical Gardens northeast of Ann Arbor, Michigan. The soil at the site is a pebble-rich upland sandy loam of glacial origin with a plow zone approximately 10 cm deep. A mixture of loess and sandy loam is present in the disturbed plow zone.

The data were collected by using copper probes (electrodes), each with an enclosed thermistor, and were installed in a vertical array or stack at shallow depths (0, 3, 6, and 9 cm) in the sandy loam. The surface probe was placed at the base of the grass mat, or organic-mineral soil interface, and the deeper probes were centered at the indicated level. The electric potential measurements were made relative to a 2-m-long copper-plated ground spike driven vertically into the soil and separated horizontally from the probe array by a distance of 2 m. A detailed description of the field installation, data system, and derivation of the C-index (a linear surrogate measure of relative ion concentration) is presented in an earlier publication (7).

Because the use of the C-index is critical, the derivation will be repeated here. The electrical potential developed by an electrolytic cell without transference is given by Equation 1. The basis for this equation may be found in Glasstone (12).

$$\Delta E = -2K \log C_p/C_s \quad (1)$$

where the electric potential (ΔE) in mV is measured and used to calculate the natural logarithm of the ratio of the probe/ground spike soil water ion concentrations (C_p/C_s). The parameter (K) is the product of the gas constant and absolute temperature divided by the Faraday constant and has a value of approximately 23.5 mV near the ice point. The mid-range value of potentials was 500 mV at the experimental site. By using 500 mV, the (C_s/C_p) ratio is 4.17×10^4 . Substituting 4.17×10^4 for (C_s) in Equation 1 and solving for the probe concentration (C_p) yields a relative index of soil water concentration on a linear scale (Equation 2).

$$\text{C-index} = 4.17 \times 10^4 \exp(-\Delta E/47) \quad (2)$$

The C-index is normalized to unity at 500 mV and corresponds to a (C_s/C_p) ratio of 4.17×10^4 . The C-index calculation assumes that the ion concentration at the ground spike is quasi-constant during a single data acquisition period. This assumption appears valid, because all data sets show a rapid attenuation in C-index variation with depth at the shallow near-surface probes. During the summer drought of 1988, in the U.S. middle west, the C-index of the surface probes increased nine orders-of-magnitude and returned to near mid-range values with drought-terminating rains. No attempt is made to update the quasi-constants in Equation 2, because only relative change is of interest.

A table-top analog of the field probe electric circuit is two glass jars filled with a low concentration brine (probe) and high concentration brine (ground spike) "jumped" by a copper wire and connected to a voltmeter by copper electrodes in the two jars. Brine solutions need not be in physical contact because the electric potential is generated only by the concentration contrast. In the soil the "jump wire" is the soil

water. Use of the electrolytic cell model without transference is based on the rapid response of the probes to ice nucleation and thaw. However, all models of electrolyte cells are based on the same general algebraic expression where the electrode potential is a function of the logarithm of the concentration ratio regardless of the absence or presence of transference. Therefore, in a strict sense, this model is equally applicable to both conditions. Reservations have been expressed (13) concerning the application of equilibrium thermodynamics to electrolyte cells. However, after the C-index transfer has been applied to the electric potential data, a lengthy series of soil frost and thaw events can be interpreted in terms of well-known processes (14).

The laboratory data described by Kelsh and Taylor (8) were collected by using methods that differed significantly from those employed here. Those differences are summarized:

1. Kelsh and Taylor reported electric potential across the freezing isotherm, and the system used in the present study yielded probe potential relative to a ground spike.
2. The Kelsh and Taylor test cell appears to be a closed hydraulic system, and the configuration used in the present study was open. Measurement in a closed cell may generate masking effects in the freezing region where pore water is mobile and tends to circulate as the freezing front advances.
3. Kelsh and Taylor reported their data as electric potential rather than converting to a relative measure of ion concentration, which was possible with the configuration in the present study.

EXPERIMENTAL RESULTS

Temperature and electric potential readings were collected at 10-min intervals by using an automatic acquisition system during a 1-day period from 14:00 EST on March 12, 1987, to 14:00 EST March 13, 1987. Figure 1 is a time series record

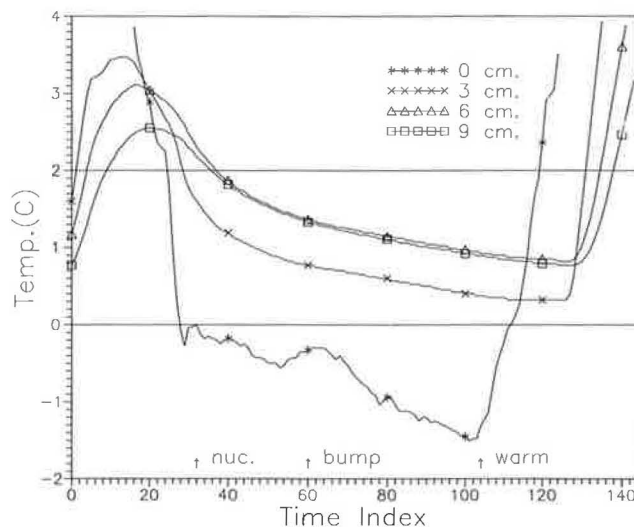


FIGURE 1 Temperature plotted on a linear scale. Time index divisions represent observations at 10-min intervals for a 24-hr period. The labels "nuc.," "bump," and "warm" indicate ice nucleation, warm water advection, and the onset of warming.

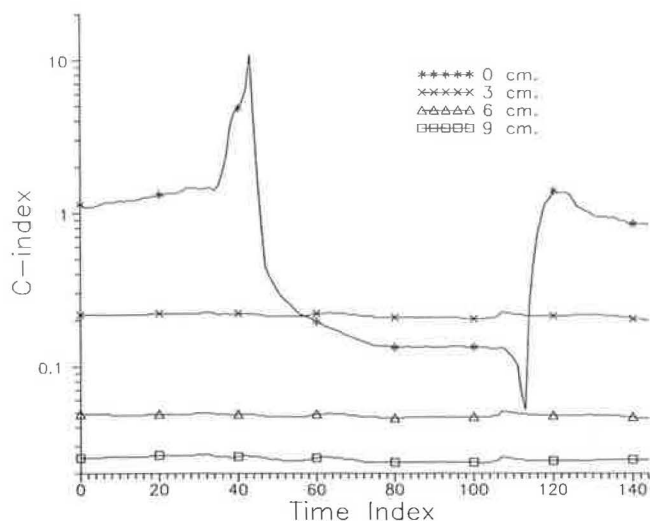


FIGURE 2 C-index plotted on logarithmic scale.

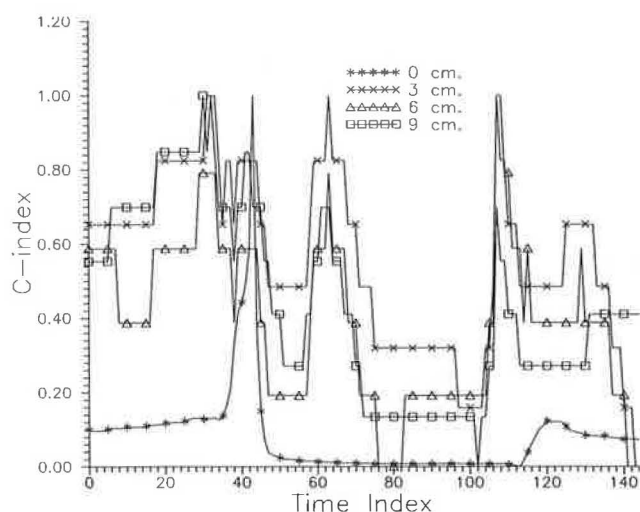


FIGURE 3 C-index plotted on a linear scale after adjustment to 0-1 range.

of the temperature at different probe depths. Figure 2 is a time series record of the C-index plotted on a logarithmic scale. Figure 3 is a time series plot of C-index values that have been normalized to a 0-1 scale to provide a more detailed perspective of fluctuations over time.

Interpretation of Time Series

The interpretation of events in the temperature and C-index plots is given in Table 1. Different events and their manifestations in either the thermal or C-index record at the 0-cm probe are referenced by their corresponding 10-min time observation index. Each of those events will be discussed in turn.

Hallet (15) described the expulsion of solute toward the warm side of the freezing region. Accordingly, as the temperature of the 0-cm probe declines while the freezing isotherm moves downward, the typical undercooling-nucleation pattern in the temperature record and steep increase in the C-index followed by a purification decline would be expected (see Figures 2 and 3 at time index 41). This pattern appears after ice nucleation (labeled "nuc." in Figure 1).

As the surface temperature declines, an increase in temperature at 0 cm exists that interrupts the smooth parabolic decline curve. This region near time index 60 is labeled "bump" in Figure 1 and can be interpreted as a consequence of a sudden and steep increase and decline in solute concentration from 3 to 9 cm. The increased ion concentration in the pore water can only be produced by two mechanisms in the absence of frost or a local solute source/sink. Those mechanisms are the advection of relatively solute rich soil water or, alternatively, the evaporation of water, both of which produce a concentration increase. Water advection or vapor condensation or both also can produce a decrease in ion concentration in an analogous manner.

The 0-cm level begins to warm near time index 108 (marked "warm" in Figure 1). The solute concentration or its surrogate, the C-index, increases after the thaw is completed at time index 113 after a slight drop owing to melt water dilution (see Figures 2 and 3). Strongly correlated ion concentration variations at the 3-, 6-, and 9-cm levels are evident as well when the C-index values are normalized to a 0-1 scale (as indicated in Figure 3). Because of the rapid propagation of

TABLE 1 EVENTS AT THE 0-cm PROBE BY TIME INDEX NUMBER

Event	Time Index	Record Manifestation
Undercooling-Nucleation	30	Temp. trough (-0.25°C)
Pre-Freezing Upturn	35	C-index upturn
Solute Expulsion Start	44	C-index peak
Warm Water Advection	54-79	Temp. convex "bump"
Melt Start	102	Temp. upturn
Thaw Downturn	108	C-index downturn
Melt End	113	Temp. $> 0^{\circ}\text{C}$
Post-Thaw Upturn	114	C-index upturn

those disturbances, they may be produced by internal evaporation and distillation processes strongly modulated by both the total (matric and osmotic) potential-vapor pressure variations near the surface [as discussed by Henry (16)].

In the case of those field measurements, relatively slow soil water migration toward the freezing-thawing or evaporating regions or both near the surface would bring relatively pure soil water into the near-surface zone as the solute concentration decreases downward below the freezing-thawing region. The tendency for local dilution by soil-water advection from 3 cm downward is countered by evaporation concentration events. Those events are initiated by changes in the near-surface water vapor pressure gradient, which in turn is modulated by the water potential. The C-index at the lower levels increases when there is strong evaporation below the surface. At times, when the vapor flux toward the surface is reduced the lower levels are diluted by the upward movement of relatively pure liquid water. As was observed previously by Outcalt (17), the vertical velocity of liquid water flow reaches maximum values of about 2 cm/hr under night-frost conditions. Therefore, the rapid propagation of surface disturbances downward must occur in the vapor phase.

A final demonstration of the detail available in C-index records is provided by a logarithmic plot of the 0-cm probe presented in Figure 2. Interpretation of this record indicates that thaw is complete at the level of this probe at time index 113. An initial release of melt water exists that lowers the C-index. As melting begins at the 0-cm probe, the solute-rich water below the lower boundary of the freezing isotherm is hydraulically separated by a subfreezing ice-rich zone. Because this cold zone warms toward the ice point and thaws the water (thereby increasing the hydraulic conductivity in the subfreezing zone), a solute-rich "pool" is advected toward the evaporating organic mat surface and thus reduces the C-index at the probe.

Role of Water Advection

If the position is accepted that the C-index is a good surrogate for solute concentration, then observations indicate that the solute concentration of the near-surface layers is strongly modulated by both liquid water and water vapor advection. The strongly correlated and rapid solute concentration fluctuations (C-index readings) in the upper 9 cm of the mineral soil must be initiated by changes in the water system state owing to phase transitions and meteorological variation near the surface. Those rapid fluctuations are transmitted to depth by fluctuations in the water vapor pressure gradient and alter the magnitude of internal evaporation/condensation. Evaporation increases the local solute concentration, and condensation reduces solute concentration. In those data there may have been a continuous liquid water migration toward the surface that varied in magnitude but not direction.

Pressure on both the liquid and the vapor phases of water is decreased with increased solute concentration [as pointed out by Henry (14)]. The soil water potential is composed of both the gravitational, the matric, and the osmotic potentials. The osmotic potential, produced by solute concentration gradients, is usually neglected. However, Hallet (13) indicated that osmotic effects may be significant near an advancing frost

front owing to the high solute concentration of the soil water on the warm side of the freezing region. An advancing freezing front will increase both the water and the vapor pressure gradients, which in turn favor liquid and vapor advection from depth toward the freezing region.

CONCLUSION

The preceding interpretation of these data demonstrates that Kelsh and Taylor (8) are to some degree correct, because the time series variations they measured are indeed the products of several interacting natural processes. However, the predictable response of the probe at the organic-mineral soil interface to the passage of the freezing isotherm (during both freezing and thawing) and the strong correlation of the solute concentration (C-index) patterns between the 3- and 9-cm levels indicates that electric potential variations follow the concentration cell model.

Variations of the vertical electric potential gradient in the near-surface soil is traceable to a finite group of well-documented physical-chemical processes that increase or decrease the local solute concentration. The spatial-temporal variations in soil electric potential are produced by variations in solute concentration and can be interpreted by the calculation of a relative index of solute concentration called the C-index.

Constrained horizontal dimensions of typical laboratory test cells can complicate the analysis of electric potential data because frost-expelled water may tend to migrate vertically along cell walls. Therefore, it may be prudent to carry out future laboratory tests in cells where the cell horizontal diameter/vertical depth ratio is much greater than unity.

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