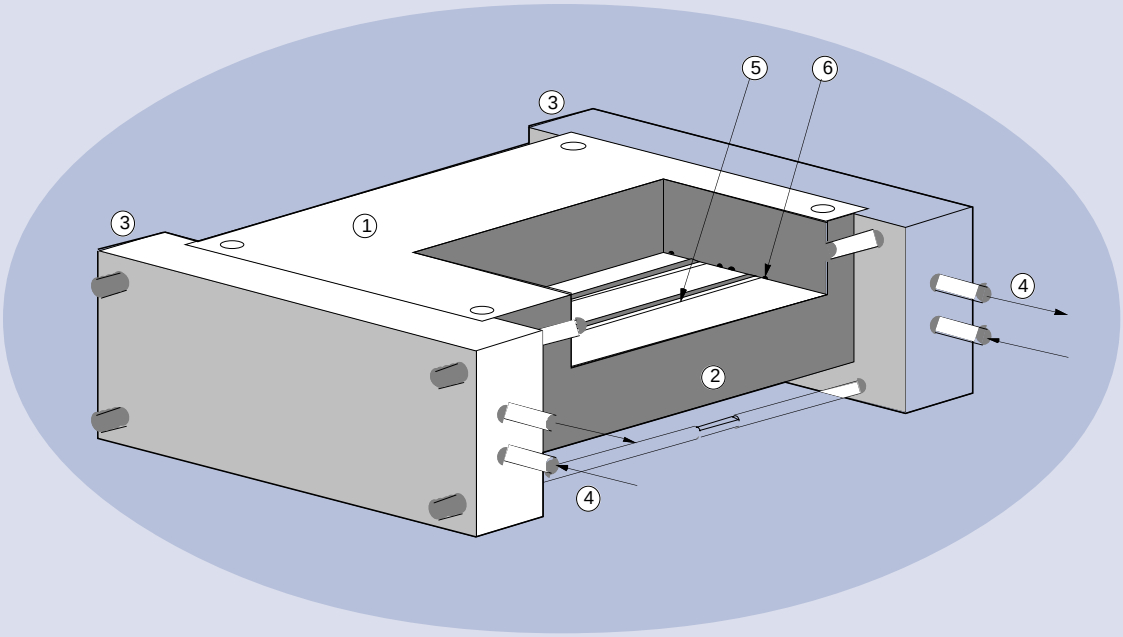
CRREL REPORT 95-3

Transport of Tracer Br^- in Frozen Morin Clay in Response to Temperature Gradients

Yoshisuke Nakano

February 1995



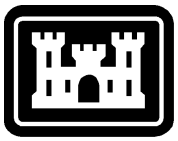
Abstract

The movement of water and Br^- was measured in unsaturated and partially frozen soil columns subjected to linear temperature fields. Both water and Br^- moved from the warmer to cooler parts in the columns. The data were analyzed under the assumption that Br^- is confined to unfrozen water. It was found that the negative adsorption of Br^- by clay surfaces plays a significant role in the transport of Br^- in frozen Morin clay and that Br^- tends to move faster than unfrozen water.

Cover: Experimental apparatus.

For conversion of SI metric units to U.S./British customary units of measurement consult *Standard Practice for Use of the International System of Units (SI)*, ASTM Standard E380-89a, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

CRREL Report 95-3



US Army Corps of Engineers®
Cold Regions Research & Engineering Laboratory

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Yoshisuke Nakano

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Prepared for
OFFICE OF THE CHIEF OF ENGINEERS
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PREFACE

This report was prepared by Dr. Yoshisuke Nakano, Chemical Engineer, of the Applied Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by DA Project 4A161102AT24, *Research in Snow, Ice and Frozen Ground*; Work Package 125, *Frozen Ground Processes*; Work Unit AT24-SC-F01, *Physical Processes in Frozen Soil*; and the Strategic Environmental Research and Development Program (SERDP).

The author thanks P.H. Miyares, formerly of CRREL, for his work in analyzing the concentration of Br^- by ion chromatography. He also thanks Dr. Thomas Jenkins and Dr. Yin-Chao Yen, both of CRREL, for technically reviewing this report.

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TABLE

Table

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NOMENCLATURE

B_i	loss of Br from a part V_i of a soil column
b	positive constant
C	concentration of Br in unfrozen water
C^+	C/C_0
$C_a(i)$	average concentration of Br in unfrozen water removed from a part V_i of a soil column during the experiment
C_a^+	$C_a(i)/C_0$
C_0	concentration of Br in distilled water that was mixed with dry soil to make soil columns
C_0^+	concentration of Br in unfrozen water divided by C_0 at the beginning of the experiments
C_i	concentration of Br in unfrozen water for segment i
C_ℓ	solute concentration in the liquid phase
C_s	solute concentration in the solid phase
$\hat{C}$	Br content, weight of Br per unit weight of dry soil
$\hat{C}^+$	$\hat{C} / \hat{C}_0$
$\hat{C}_0$	initial Br content
$F_B(i)$	mass flux of Br from segment i to segment $i + 1$
$F_w(i)$	mass flux of water from segment i to segment $i + 1$
k	effective segregation coefficient
k_0	value of k when $u = 0$
T	temperature
T_c	temperature at the cold end of a soil column
T_w	temperature at the warm end of a soil column
t	time (days)
t_0	22 days
u	growth rate of a solid phase
V_i	part of a soil column consisting of segments 1 through i
v	volume of each segment
W_i	loss of water from a part V_i of a soil column
w	content of water (including ice) based on the dry weight of soil
w^+	w/w_0
w_0	initial water content
w_i	content of water (including ice) of segment i based on the dry weight of soil
ρ	dry density of soil
ρ_a	average ρ over all segments
ρ_i	dry density of soil in segment i
σ	standard deviation

Transport of Tracer Br^- in Frozen Morin Clay in Response to Temperature Gradients

YOSHISUKE NAKANO

INTRODUCTION

The transport of solutes in frozen or freezing soils is important for both engineering and scientific reasons. The presence of salts is known to drastically alter the mechanical properties of frozen soils (Sego et al. 1982, Hivon 1991). It is also known that the presence of salts tends to reduce the rate of frost heave in fine-grained soils (Konrad 1990). The migration of fertilizer and pesticides during annual freezing is a subject of considerable interest in agronomy (Gray and Granger 1986).

The phenomenon of freezing soils that contain solutes is complex and poorly understood. Inasmuch as solutes tend to be excluded from growing ice, they are confined to the domains of unfrozen (interfacial) water. The transport process of solutes depends mainly on the transport of unfrozen water, but it also is influenced by the diffusion or dispersion of solutes and complex interactions of solutes with the surfaces of soil particles and ice. The amount of unfrozen water in frozen soils generally increases with the increasing concentration of solutes (Banin and Anderson 1974). Since the mobility of unfrozen water tends to increase with the increasing unfrozen water content (Nakano 1991), the two transport processes of solutes and unfrozen water mutually depend on each other. Because of this mutual dependence, the transport of solutes in frozen soils is more complex than that in unfrozen soils.

The rate of solute transport is anticipated to be great where the rate of water transport is great. Since the transport of water is closely coupled with the phase change of water in freezing soils and solutes tend to be excluded from growing ice, the solute redistribution is expected to be most rigorous near a freezing front. Therefore, the solute redistribution near a freezing front has attracted the attention of researchers. Mahar et al. (1983) investigated salt redistribution during freezing of gravel saturated with a salt solution of a known concentration. They found that a distinct freezing interface did not exist. Instead, a zone of partially frozen gravel with a high unfrozen water content beginning at the depressed freezing point isotherm (freezing front) was observed. It was also found that the salt concentration in unfrozen water increases toward the lower temperatures and that the content of salt in the frozen part of gravel was less than the initial content (Mahar et al. 1983).

When the solidification occurs from the melt containing impurities, the composition of the solid phase generally differs from that of the coexisting melt. This phenomenon, called segregation or redistribution among researchers of crystal growth, has been studied extensively. Analyzing the process of redistribution, Burton et al. (1953) obtained a quantitative description (BPS theory) of an effective segregation coefficient k given as

$$k = C_s / C_\ell = k_0 / \left[k_0 + (1 - k_0) e^{-bu} \right] \qquad (1)$$

where C_s and C_ℓ = solute concentrations in the solid and liquid phases, respectively, adjacent to the solid/liquid interface
k_0 = value of k when the growth rate u of the solid phase is zero
b = positive number that depends on a given system.

Weeks and Lofgren (1966) showed the validity of BPS theory applied to the problem of freezing salt so

lutions. By freezing columns of sand saturated with a NaCl solution at constant rates, Baker and Osterkamp (1989) found that BPS theory approximately holds true. Konrad and McCammon (1990) conducted step freezing tests on a saturated clayey silt with various salinities. They found that the rate of cooling is the main factor controlling solute redistributions and that there is a threshold rate of cooling of 3°C/day above which no redistribution takes place ($k = 1$).

The flow of aqueous solutions through unfrozen porous media has been investigated extensively (Nielsen et al. 1972). In saturated systems, the flow of a solute is described as the sum of a convective term and a diffusive term. The diffusive term is equivalent to Fick's law of diffusion where the diffusivity coefficient includes the effect of both molecular diffusion and hydrodynamic dispersion. Such a description is not accurate for fine-grained soils with small water contents because the interaction between solutes and surfaces of soil particles becomes significant. It has been shown experimentally that a soluble salt and water in which it is dissolved move at different rates through fine-grained soil (Biggar and Nielsen 1962, Krupp et al. 1972). For example, when a $CaCl_2$ solution containing ^{36}Cl and ^{3}H is passed through soils, the ^{36}Cl appears earlier in the effluent than the ^{3}H. This behavior can be explained by anion repulsion or negative adsorption of salt by the negatively charged soil particle surfaces.

While it has been anticipated that the phenomenon of anion repulsion is important in the transport process of solutes in frozen soils, no supporting data are available. The objective of this study is to examine experimentally the transport of the Br^- ion in unsaturated and partially frozen soil. The content of Br^- was intentionally kept low so that the transport of unfrozen water would not be altered significantly by Br^-. This study also aims to find the effect of interactions between Br^- and surfaces of soil particles.

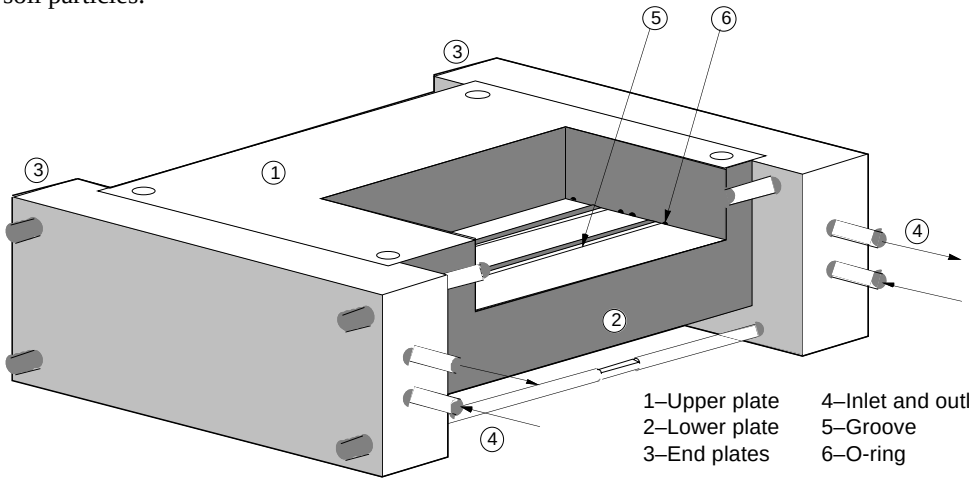
EXPERIMENTS

Experiments were conducted in which closed soil columns, initially with the uniform dry density and the uniform contents of water and Br^-, were subjected to a constant and linear temperature gradient. The apparatus used in the experiments is shown in Figure 1.

The apparatus consists of four parts made of aluminum: an upper plate, a lower plate and two end plates. The upper and lower plates are approximately 23 cm long × 20 cm wide × 5 cm thick. Four grooves with a rectangular cross section, 20.32 cm long × 1.27 cm wide × 0.625 cm deep, were machined on the upper surface of the lower plate. The center lines of these grooves, which are parallel to the longer side of the plate, are spaced 3.8 cm apart. Grooves for O-ring seals were also machined around each rectangular groove in the upper plate so that when the upper and lower plates are bolted together, four closed empty spaces of rectangular column shape are formed to be used as containers of soil.

Each of the two end plates has a 2.54-cm hole drilled into it, through which an antifreeze mixture from a temperature-controlled bath is circulated. The two end plates are positioned by four bolts. Two sides of the upper and lower plates bolted together have a small taper that matches the taper of the end plates so that the bolted upper and lower plates smoothly slide into the spaces created by the two end plates, with assured close contact. The four aluminum parts, when assembled, are thermally insulated by foam plastic. A row of 10 copper-constantan thermocouples is placed with equal spacing through the upper plate along the centerline of each groove to measure and record temperatures in a soil sample.

The soil selected for the experiment, called Morin clay, is a marine-deposited clay obtained from the Morin brickyard, Auburn, Maine. Morin clay is a non-swelling clay with a specific surface area of 60



1–Upper plate
2–Lower plate
3–End plates
4–Inlet and outlet of an antifreeze mixture
5–Groove
6–O-ring

Figure 1. Apparatus.

m^2/g and a specific gravity of 2.75 g/cm^3. This clay was used in the experiments reported by Nakano and Tice (1990). For a given dry density ρ and initial water content w_0, the exact amounts of oven-dry Morin clay and distilled water containing 400 μg/g of $B\bar{r}$ as KBr were weighed to be packed into a groove. Mixing thoroughly the weighed soil and water, we allowed the mixture to set for a few days to attain moisture equilibration. After all four grooves were packed with soil samples, we bolted together the upper and lower plates to seal each of four soil columns with a rectangular cross section and froze them down to about –15°C.

An experiment began by placing the bolted upper and lower plates into the space between the two end plates. A stable and linear temperature field was usually established within 1 hour by adjusting the temperatures of the two baths. After a specified time passed, the bolted upper and lower plates were brought into a coldroom with its temperature being set at –10°C. The two plates were separated and each sample was quickly sectioned into a total of 25 segments with equal lengths. Each segment was placed in a glass weighing bottle and oven-dried. The water content and the dry density of each segment were determined gravimetrically. The concentration of $B\bar{r}$ of each segment was determined using the Dionex Ion Chromatography Model 2010i.

RESULTS OF EXPERIMENTS

The test conditions of the experiments are presented in Table 1. For all of these experiments, we aimed to maintain the average dry density of the soil columns at about 1.45 g/cm^3, although the uniform packing of soil in each column was quite difficult. We examined the uniformity of the soil columns by using the measured dry density of all segments after each experiment. The mean ρ_a and the standard deviation σ of dry density ρ are given in Table 1. Although these values are affected by errors associated with rapidly sectioning a soil column into 25 segments with ideally equal lengths, they serve as an indicator of uniformity in packing and accuracy in sectioning.

In Table 1 T_w is the temperature at the warm end of a soil column while T_c is the temperature at the cold end of a soil column. For all the experiments, the same linear temperature field was applied; the duration of experiments was 22 days. In the last column of Table 1 is given the concentration of $B\bar{r}$ in distilled water C_0 that was mixed with dry soil to make the soil columns. In experiments 1–4, distilled water without $B\bar{r}$ was mixed with dry soil, while 400 μg/g $B\bar{r}$ was used in experiments 5–8. Experiments 1–4 were conducted to find the effects of $B\bar{r}$ on the transport of unfrozen water by comparison with experiments 5–8, where $B\bar{r}$ was used.

The results of experiments 5–8 are presented in Figure 2, where nondimensional quantities w^+ and $\hat{C}^+$ are defined as

$$w^+ = w / w_0 \tag{2a}$$

$$\hat{C}^+ = \hat{C} / \hat{C}_0 \tag{2b}$$

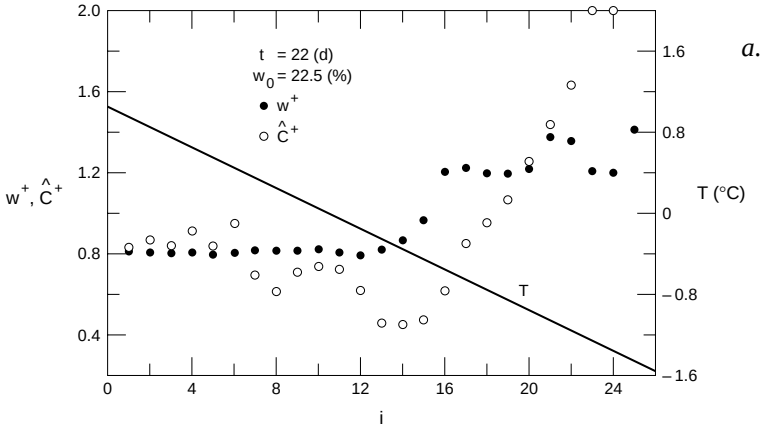
where w is the measured water (including ice) content at the end of experiments, while w_0 is the initial uniform water content. The unit of water content is the weight of water and ice per unit weight of dry soil. $\hat{C}$ is the measured $B\bar{r}$ content. The unit of $B\bar{r}$ content is the weight of $B\bar{r}$ per unit weight of dry soil.

In Figure 2 the nondimensional quantities w^+ and $\hat{C}^+$ are plotted versus the segment number i that is assigned 1–25 from the warm end to the cold end. The linear temperature field imposed is also shown in these figures. The 0°C isotherm is located at the interface between segments 10 and 11 so that the temperatures of segments 1–10 are positive while those of segments 11–25 are negative.

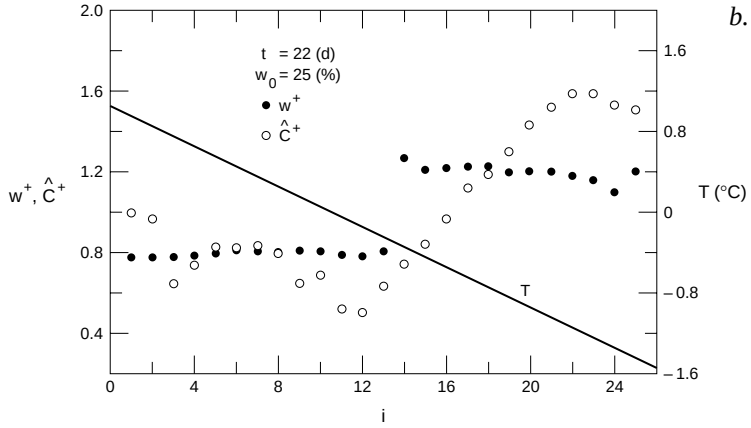
It follows from the definitions of eq 2a and 2b that w^+ and $\hat{C}^+$ would be one if unfrozen water and $B\bar{r}$ did not move at all during the experiments. It is clear

Table 1. Experimental conditions.

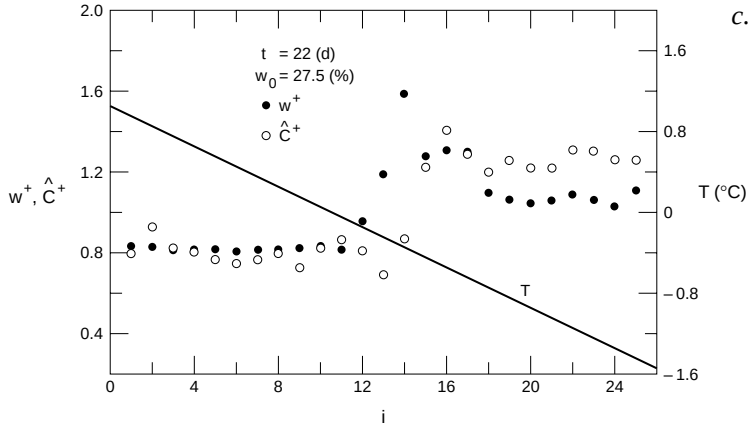
Experiment no.	w_0 *(%)*	ρ_a *(g/cm)*	σ	T_w *(°C)*	T_c *(°C)*	*Temperature gradient (°C/cm)*	*Temperature duration (days)*	C_0 *(μg/g)*
1	22.5	1.48	0.13	1.00	–1.50	0.120	22	0.0
2	25.0	1.45	0.10	1.00	–1.50	0.120	22	0.0
3	27.5	1.46	0.07	1.00	–1.50	0.120	22	0.0
4	30.0	1.45	0.12	1.00	–1.50	0.120	22	0.0
5	22.5	1.44	0.11	1.00	–1.50	0.120	22	400
6	25.0	1.46	0.14	1.00	–1.50	0.120	22	400
7	27.5	1.47	0.13	1.00	–1.50	0.120	22	400
8	30.0	1.43	0.08	1.00	–1.50	0.120	22	400



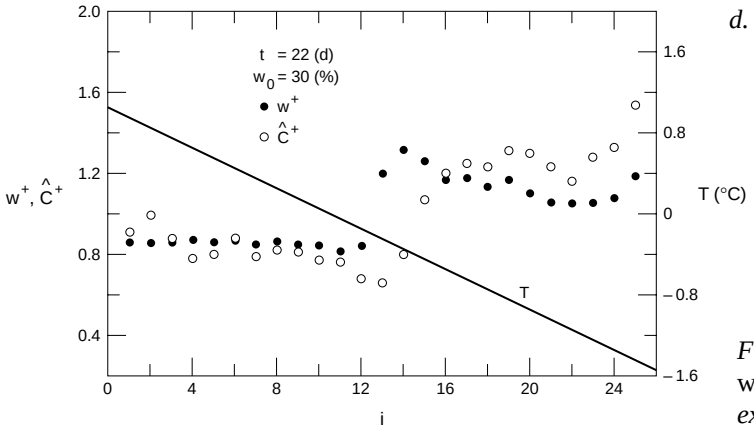
a. Experiment 5.



b. Experiment 6.



c. Experiment 7.



d. Experiment 8.

Figure 2. Nondimensional contents of water w^+ *and* $\hat{C}^+$ *versus the segment number* i *for experiments 5–8.*

from Figure 2 that both water and Br^- moved from the warmer to cooler parts in the soil columns. The unfrozen part (segments 1–10) of soil columns lost both water and Br^-. It is interesting that a few segments in the frozen part near the 0°C isotherm also lost both water and Br^- and that the minimum value of $\hat{C}^+$ appears in these frozen segments.

ANALYSIS OF DATA

We will consider the balance of water and Br^- in the part of soil columns V_i consisting of segments 1–*i*. We will assume that the initial dry density of each segment is equal to the final dry density of each segment measured at the end of the experiment. The loss of water W_i from the part V_i during the experiment is calculated as

$$W_i = v\sum_{j=1}^{i} \rho_j \left(w_0 - w_j\right) \tag{3}$$

where v is the volume of each segment and ρ_j and w_j are the dry density and the water content of segment j respectively. Similarly, the loss of Br^-, B_i, from the part V_i during the experiment is calculated as

$$B_i = v\sum_{j=1}^{i} \rho_j \left(\hat{C}_0 - \hat{C}_j\right) \tag{4}$$

where $\hat{C}_j$ is the Br^- content of segment j.

The calculated values of W_i for experiments 1–4 are plotted together with those for experiments 5–8 in Figure 3, where open circles are the data points from experiments 1–4, while solid circles are the data points from experiments 5–8. For instance, in Figure 3a the calculated values of W_i for experiment 1 are plotted together with those for experiment 5. Experiments 1 and 5 are conducted under the same conditions, except that Br^- is absent in experiment 1. Suppose that the soil was packed uniformly in each column and that Br^- does not affect the movement of unfrozen water. Then it is anticipated that the calculated values of W_i for experiment 1 should be equal to those for experiment 5. Since the uniform packing of soil is quite difficult, Figure 3 indicates that the level of Br^- content used in experiments 5–8 does not significantly affect the mobility of unfrozen water.

The calculated values of W_i and B_i for experiments 5–8 are presented in Figure 4. It is easy to see from these figures that both W_i and B_i attain their maxima and that the segment number of the maximum B_i is greater than that of the maximum W_i. Let $F_w(i)$ and $F_B(i)$ be mass fluxes of water and Br^-, respectively, from segment i to segment $i + 1$, then W_i and B_i are given as

$$W_i = \int_0^{t_0} F_w(i)dt \tag{5}$$

$$B_i = \int_0^{t_0} F_B(i)dt \tag{6}$$

where t_0 is the duration of the experiment (22 days).

If we assume that Br^- is transported mainly by the movement of unfrozen water, the mass flux F_B of Br^- is given as

$$F_B(i) = C_i F_w(i) \tag{7}$$

where C_i is the concentration of Br^- in unfrozen water for segment i. From eq 6 and 7 we obtain

$$B_i = \int_0^{t_0} C_i F_B(i)dt. \tag{8}$$

For a special case in which C_i remains constant at the initial value C_0, from eq 5 and 7 we obtain

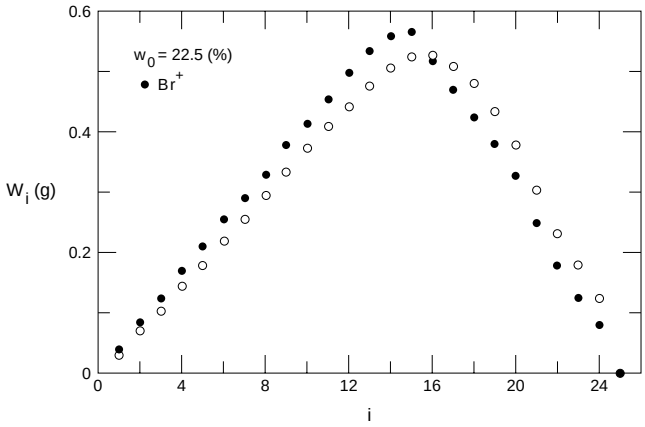
$$B_i = C_0 W_i . \tag{9}$$

It follows from eq 9 that both W_i and B_i attain their maxima at the same segment. This obviously did not occur in our experiments.

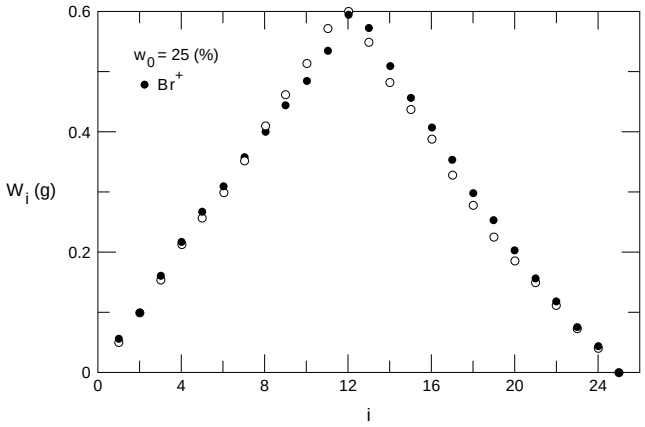
Since Br^- is excluded from growing ice and is confined to unfrozen water, the concentration of Br^-, C_i, must be a nondecreasing function of i for $i \geq 10$ when a linear temperature field is established at the beginning of experiments. Because of the Br^- exclusion from ice, C_i increases with i in segments where ice is present; as a result, the segment number of the maximum B_i becomes greater than that of the maximum W_i.

The Br^- ion may not be completely confined to unfrozen water. However, let us assume this complete confinement, as it appears to be a good approximation. We will also assume that the phase equilibrium of water holds true in the experiments. Then, the unfrozen water content is approximated by the equilibrium unfrozen water content determined by the nuclear magnetic resonance technique on a separate sample of Morin clay. Under these assumptions the concentrations of Br^- in unfrozen water at both the beginning and the end of the experiments were calculated.

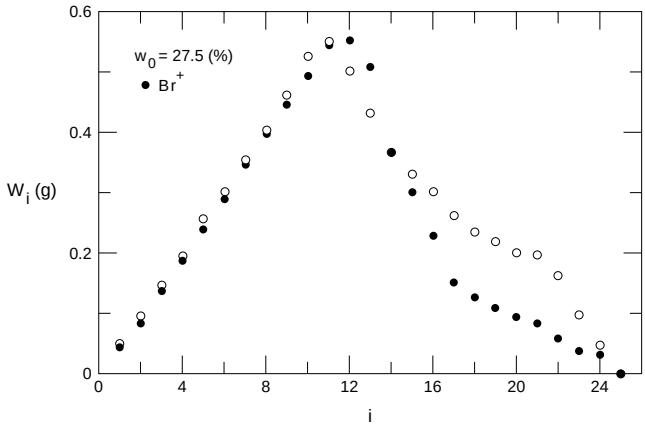
The results of calculations for experiments 5–8 are presented in Figure 5, where nondimensional quantities C_0^+ and $C^+(t)$ are defined as the concentrations of Br^- in unfrozen water divided by C_0 at the beginning and the end of the experiment respectively. For instance, the calculated values of C_0^+ and $C^+(t)$ for ex-



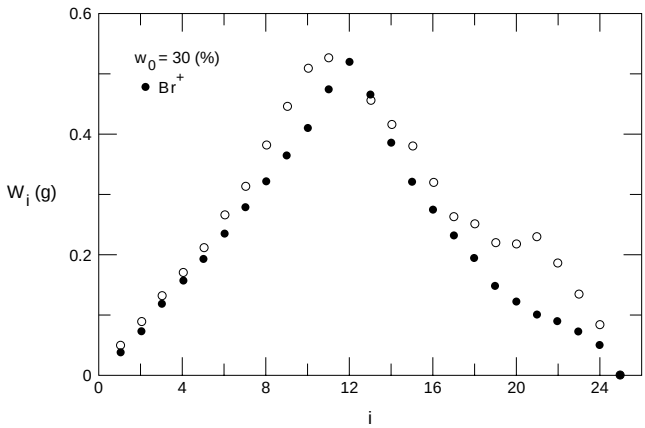
a. Experiment 1 with 5.



b. Experiment 2 with 6.

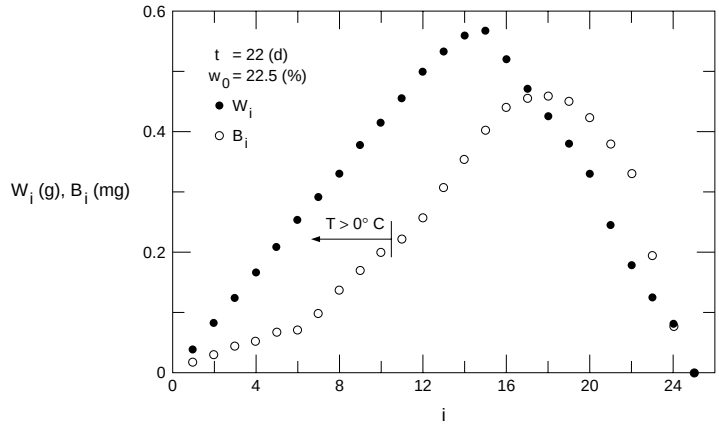


c. Experiment 3 with 7.

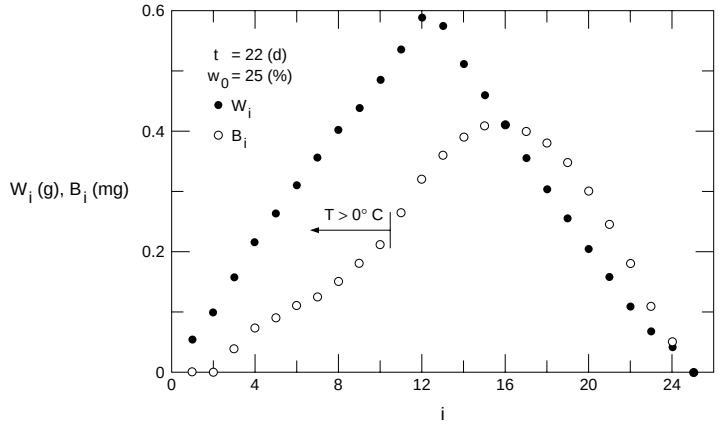


d. Experiment 4 with 8.

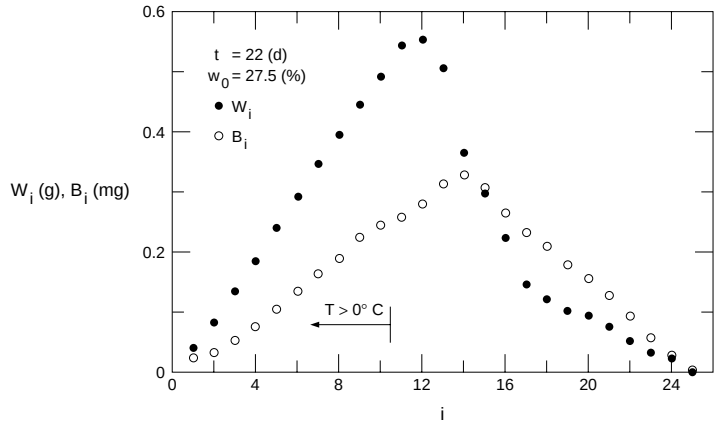
Figure 3. Comparison of W_i *values from experiments both with and without* $B\bar{r}$.



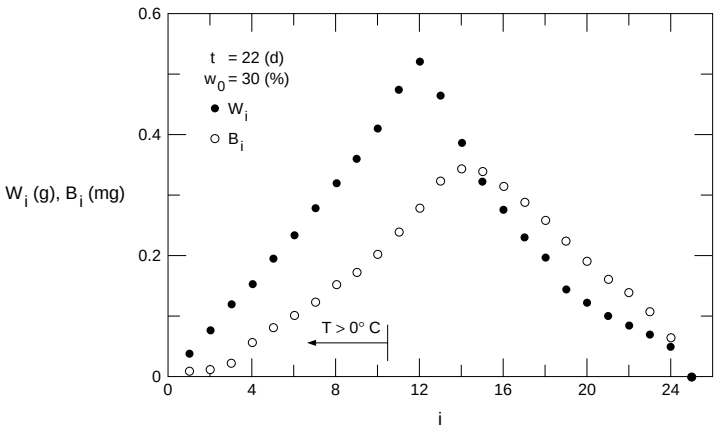
a. Experiment 5.



b. Experiment 6.

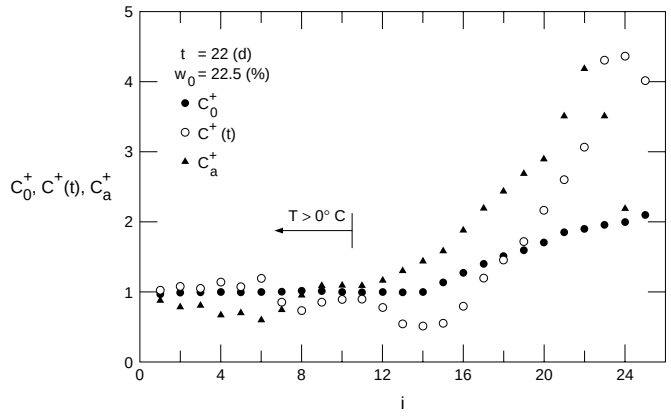


c. Experiment 7.

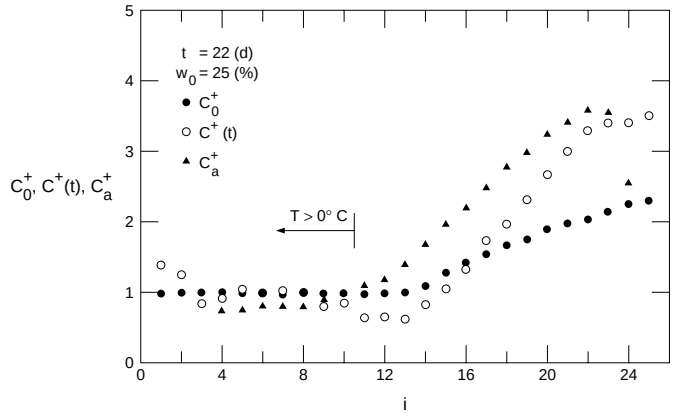


d. Experiment 8.

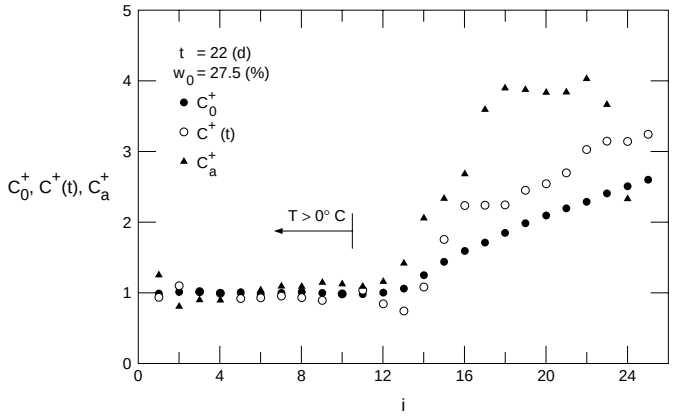
Figure 4. Calculated values of W_i *and* B_i *for experiments 5–8.*



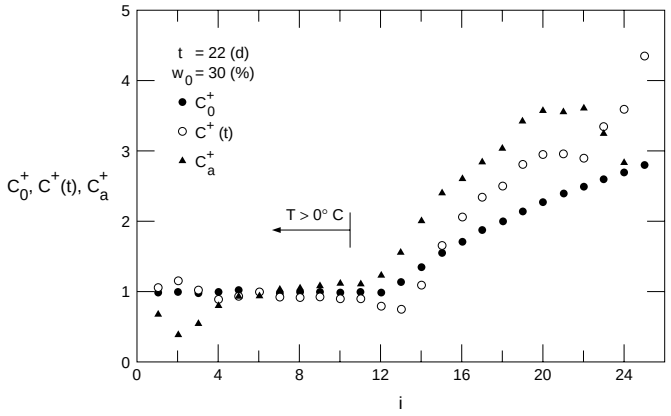
a. Experiment 5.



b. Experiment 6.



c. Experiment 7.



d. Experiment 8.

Figure 5. Values of C_0^+ , $C^+(t)$ *and* C_a^+ *of experiments 5–8.*

periment 5 are plotted vs. the segment number i in Figure 5a, where solid and open circles are the data points of C_0^+ and $C^+(t)$ respectively. The values of C_0^+ are nearly one in segments 1–14 because ice is absent while the C_0^+ increases with i in segments 14–25 as the content of ice increases.

The values of $C^+(t)$ vary in the unfrozen part (segments 1–10), but they are not very far from one. However, the $C^+(t)$ increases sharply from segments 15–23 in comparison with C_0^+ and as a result, the values of $C^+(t)$ become twice as great as the C_0^+ values near the cold end. There is an interesting trend that the values of $C^+(t)$ become less than C_0^+ in segments 12–17. The behaviors of C_0^+ and $C^+(t)$ described above can be seen also in Figures 5b–d, but become less pronounced as the initial water content w_0 increases.

In Figure 5 the values of $C^+(t)$ fluctuate about one in the unfrozen part, and the pattern of fluctuation appears to be more or less random. However, in the frozen part near the 0°C isotherm there is a common feature that $C^+(t)$ becomes less than C_0^+. It is clear from Figure 4 that both water and $B\bar{r}$ moved from the warmer to cooler parts in the soil columns. The common feature described above indicates that unfrozen water and $B\bar{r}$ may not move at the same rate.

We will introduce a nondimensional quantity C_a^+ defined as

$$C_a^+(i) = C_a(i) / C_0 \tag{10a}$$

$$C_a(i) = B_i / W_i. \tag{10b}$$

It follows from eq 10b that $C_a(i)$ is the (time) average concentration of $B\bar{r}$ in water removed from the part V_i of a soil column during the experiment. It is easy to see that the concentration of $B\bar{r}$ in water removed from V_i must be equal to C_0 at the beginning and $C(t)$ of segment i at the end of the experiment. The calculated values of C_a^+ are plotted in Figure 5 in comparison with C_0^+ and $C^+(t)$.

In Figure 5, we may consider that the concentration of $B\bar{r}$ in the unfrozen part did not change significantly from the initial concentration C_0 during the experiment. However, in the frozen part, except for a few segments near the cold end, C_a^+ is greater than both C_0^+ and $C^+(t)$ in all cases. Since the features of C_0^+, $C^+(t)$ and C_a^+ common to experiments 5–8 are the most pronounced in experiment 5, we will examine experiment 5 below.

We will consider a part V of the soil column consisting of segments 11–18 (Fig. 2a and 5a). Since $\hat{C}^+ < 1$ in V (Fig. 2a), every section of V lost $B\bar{r}$ during the experiment. Since $w^+ > 1$ in segments 16–18, these three sections gained water during the experiment. Segments 11–15 lost water, but $C^+(t)$ is still less than C_0^+. As a result $C^+(t)$ becomes less than C_0^+ in every section of V. The input of both water and $B\bar{r}$ to V must have come from the unfrozen part where the concentration of $B\bar{r}$ remained approximately at C_0 during the experiment. Suppose that unfrozen water and $B\bar{r}$ moved at the same rate. Then, $C(t)$ must not be less than C_0. However, it is easy to see from Figure 5a that $C^+(t)$ is less than one in segments 11–16. This is obviously contradictory. Therefore, we may conclude that $B\bar{r}$ must have moved faster than the unfrozen water in segments 11–16 where $C^+(t)$ is less than one.

The features of C_0^+, $C^+(t)$ and C_a^+ in experiment 5 described above are common to experiments 6–8. In experiment 6 (Fig. 5b) $C(t)$ is less than C_0 in segments 11–15, while in experiments 7 and 8 (Fig. 5c and d), $C(t)$ is less than C_0 in segments 12 and 13. In Figure 5 C_a^+ is greater than both C_0^+ and $C^+(t)$ in the frozen part except for a few segments near the cold end. These data strongly indicate that $B\bar{r}$ moved faster than unfrozen water in the frozen part of the soil columns. In other words, the repulsion or negative adsorption of $B\bar{r}$ by the negatively charged Morin clay must have moved $B\bar{r}$ faster than unfrozen water. Since the repulsion of anions is caused by the interaction between anions and surfaces of soil particles, the effect of anion repulsion on the transport of anions is expected to become less pronounced with the increasing unfrozen water content. This general trend can be seen in Figure 5 with the increasing initial water content w_0.

CONCLUSIONS

The movement of water and $B\bar{r}$ was measured in unsaturated and partially frozen clay columns subjected to linear temperature fields. Both water and $B\bar{r}$ were found to move from the warmer to cooler parts in the columns. The data were analyzed under assumption that $B\bar{r}$ is completely confined to unfrozen water in the frozen part of the columns.

The concentration of $B\bar{r}$ in water was found not to change significantly from the initial concentration in the unfrozen part of the columns. However, the data from the frozen part of the columns strongly indicate that $B\bar{r}$ moved faster than unfrozen water because of the repulsion of $B\bar{r}$ by the negatively charged surfaces of clay particles. The effect of anion repulsion on the transport of $B\bar{r}$ in the frozen part of the columns was found to become more pronounced with the decreasing initial water content. It may be concluded that the anion repulsion by clay surfaces plays a significant role in the transport of $B\bar{r}$ in unsaturated and partially frozen clay.

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The movement of water and Br^- was measured in unsaturated and partially frozen soil columns subjected to linear temperature fields. Both water and Br^- moved from the warmer to cooler parts in the columns. The data were analyzed under the assumption that Br^- is confined to unfrozen water. It was found that the negative adsorption of Br^- by clay surfaces plays a significant role in the transport of Br^- in frozen Morin clay and that Br^- tends to move faster than unfrozen water.

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