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**Evidence for
enhanced infiltration
of ion load**

G. Lilbæk and
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Evidence for enhanced infiltration of ion load during snowmelt

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Abstract

Meltwater ion concentration and infiltration rate into frozen soil both decline rapidly as snowmelt progresses. Their temporal association is highly non-linear and a covariance term must be added in order to use time-averaged values of snowmelt ion concentration and infiltration rate to calculate chemical infiltration. The covariance is labelled *enhanced infiltration* and represents the additional ion load that infiltrates due to the timing of high meltwater concentration and infiltration rate. Previous assessment of the impact of enhanced infiltration has been theoretical; thus, experiments were carried out to examine whether enhanced infiltration can be recognized in controlled laboratory settings and to what extent its magnitude varies with soil moisture. Three experiments were carried out: dry soil conditions, unsaturated soil conditions, and saturated soil conditions. Chloride solution was added to the surface of frozen soil columns; the concentration decreased exponentially over time to simulate snow meltwater. Infiltration excess water was collected and its chloride concentration and volume determined. Ion load infiltrating the frozen soil was specified by mass conservation. Results showed that infiltrating ion load increased with decreasing soil moisture as expected; however, the impact of enhanced infiltration increased considerably with increasing soil moisture. Enhanced infiltration caused 2.5 times more ion load to infiltrate during saturated conditions than that estimated using time-averaged ion concentrations and infiltration rates alone. For unsaturated conditions, enhanced infiltration was reduced to 1.45 and for dry soils to 1.3. Reduction in infiltration excess ion load due to enhanced infiltration increased slightly (2–5%) over time, being greatest for the dry soil (45%) and least for the saturated soil (6%). The importance of timing between high ion concentrations and high infiltration rates was best illustrated in the unsaturated experiment, which showed large inter-column variation in enhanced ion infiltration due to variation in this temporal covariance.

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1 Introduction

Underneath a melting snowpack, the infiltrability of the stratum, whether it is frozen or unfrozen, determines the partitioning of meltwater into ponding water, overland flow, infiltration to the organic layer and/or infiltration to the mineral soil (e.g., Hillel, 1998; Zhao and Gray, 1999). Infiltration excess water (i.e. overland flow and organic interflow) primarily ends up as rapid runoff, even where a well-developed organic layer exists (Carey and Woo, 2001; Quinton and Pomeroy, 2006). Water infiltrating the mineral layer often remains stored in the soil for a long period, eventually contributing to evaporation, percolating to groundwater, or ending up as slow interflow contributing to stream flow.

Partitioning depends on factors such as soil temperature, available pore space, macropores, hillslope gradient, depressional storage availability, hydraulic conductivity of the frozen organic layer, the infiltrability of the frozen mineral soil, the depth and nature of freezing, and the spatial variations in infiltration (e.g., Alexeev et al., 1972; Granger et al., 1984; Zhao and Gray, 1997; Gray et al., 2001). Macropores increase the rate at which water and its solutes can infiltrate and move through a stratum (Beven and Germann, 1982). They may originate from e.g. biological activity (e.g. decayed plant roots, worm holes, animals), geological activity (e.g. fractures, differences in media), freeze-thaw cycles, or farm management practice (e.g., Hillel, 1998). The fractional volume of macropores may be quite small, however, the effects that they may have on flow phenomena such as infiltration, drainage, and the transport of solutes in saturated or near-saturated conditions are huge. A sufficient heat flow into the soil due to frozen conditions underneath the melting snowpack (i.e. in cold regions) may cause ponding water to refreeze, forming a basal ice layer (Woo and Heron, 1981). Consequently, the rate and volume of snowmelt runoff depends not only on the melt intensity and amount of water in the snowpack, but also on the physical and thermodynamic properties of the underlying stratum.

The biggest difference between infiltration to unfrozen and frozen stratum is the presence of ice as a solid phase (e.g., Kane and Stein, 1983). Infiltration to frozen soil has

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been found to be governed by the structural, hydrological, and thermophysical characteristics of the soil (i.e. the initial moisture content (ice and water) and its distribution), meteorological conditions, the heat flux of the infiltrating water, the soil-ice-water system's temperature profile, and the induced freezing point depression due to solute concentrations (e.g., Kuznik and Bezmenov, 1963; Komarov and Makarova, 1973; Romanov et al., 1974). Changes in any of these parameters may lead to changes in the infiltration rate. Tao and Gray (1994) have shown that the infiltration process is least sensitive to frozen soil temperature.

Redistribution of soil moisture is important when quantifying the moisture content in frozen soil, as the changes in soil moisture over the course of winter directly affect the infiltration that can take place and thereby the soil water recharge from the snowpack (Kane and Stein, 1983; Granger et al., 1984). As the soil water freezes, formation of ice results in the water being confined in progressively smaller spaces. This causes a decrease in Gibb's free energy of water, which causes migration of water to the freezing zone (Williams and Smith, 1989). Thus, within the soil, water has been found to move from the unfrozen to frozen zone due to the pressure differences imposed by the temperature and local hydraulic gradients caused by the freezing process in frozen soils (Male and Gray, 1981; Kane and Stein, 1983; Gray et al., 1985). The magnitude of the migration is directly related to the moisture content; being greatest for light textured, wet soils (Gray et al., 1985). In soils that are dry at the time of freeze-up the migration of water is considered negligible. This migration occurs both above and below the freezing front observed as a decrease in moisture content in the upper part of the soil (0–0.3 m) and an increase in the lower part of the soil (Gray et al., 1985). This migration of water towards a freezing front has been found to complicate the computation of infiltration (e.g., Komarov and Makarova, 1973).

Over the course of winter, seasonal snowpacks accumulate ions as wet and dry deposition. Ion fractionation within snowpacks results in a two- to seven-fold enrichment of major ions in the initial meltwater (Johannessen and Henriksen, 1978). As melt progresses, ion concentrations decrease exponentially causing up to 80% of the snow-

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pack's solute to be released during the initial one-third of snowmelt (Tranter, 1991), making early melt a major chemical event in terrestrial and aquatic ecosystems (Jones, 1999). During infiltration of snowmelt water to the organic and mineral soil layer, inter-flow waters can become highly concentrated causing dramatic change to surface water chemistry (Peters and Driscoll, 1987). Changes in soil chemistry and microbiology (Abrahams et al., 1989) and episodic acidification of lakes and streams (Davies et al., 1987; Ikuta et al., 1999; Schindler, 1999) have been related to this rapid release of ions during spring freshet. Observed changes in ion retention and release in snowmelt runoff over frozen soil have been correlated with the frozen moisture content of soil and their infiltrability (Jones and Pomeroy, 2001). Thus, knowledge of the flow pathway of the snowmelt chemical load is important for determining the aquatic or terrestrial sink for these ions and the timing of ion delivery to water bodies (Lilbæk and Pomeroy, 2007).

Using Zhao and Gray's (1999) parametric relationship for the cumulative mass of water that infiltrates a frozen mineral soil, F (kg m^{-2}), and Stein et al.'s (1986) expression for meltwater ion concentration as a function of time, $C_i(t)$ (meq m^{-3}), Lilbæk and Pomeroy (2007) showed that the temporal association between infiltration rate, $f(t)$ ($\text{kg s}^{-1} \text{m}^{-2}$), and meltwater ion concentration, $C_i(t)$, is highly non-linear, even though both decline rapidly with time. The study showed that the cumulative infiltration of snowmelt ions is enhanced by initially higher ion concentration in meltwater and infiltration rate. However, time averaged ion concentration, \bar{C}_i , and infiltration, \bar{f}/ρ , where ρ (kg m^{-3}) is the solution's density, are far easier and more reliable to estimate than are concentrations and infiltration rates at any one time. Thus, in order to reliably calculate the cumulative ion load infiltrating a frozen soil, F_i (meq m^{-2}), the covariance between the instantaneous values of $C_i(t)$ and $f(t)$ has to be added to the mean terms (Eq. 1). The covariance was found to be positive as both meltwater ion concentration

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and infiltration rate decrease with time.

$$F_i = \int_0^t C_i(t) \cdot \frac{f(t)}{\rho} dt = \frac{\bar{C}_i \cdot \bar{f} \cdot t}{\rho} + \text{cov}[C_i(t), f(t)] = \frac{\bar{C}_i \cdot F}{\rho} + \text{cov}[C_i(t), f(t)] \quad (1)$$

The model by Lilbæk and Pomeroy (2007) assumes a limited infiltration regime as defined by Granger et al. (1984) in which there are neither substantial macropores nor impeding basal ice layers as well as that the meltwater solute is conservative and fully mixed at all times. The use of Zhao and Gray's equation to estimate infiltration to mineral soils under an organic layer was assumed appropriate when the organic layer rapidly transfers water to the mineral soil surface (Lilbæk and Pomeroy, 2007). A reasonable assumption where the organic layer is thin and porosity is high or organic layer macropores are abundant.

The covariance term is labelled *enhanced infiltration* and represents the additional ion load that infiltrates during snowmelt due to the combination of initially rapid infiltration rate and higher ion concentration in meltwater (Lilbæk and Pomeroy, 2007). Its magnitude was found to be governed by initial snow water equivalent, SWE (kg m^{-2}), average melt rate, \bar{M} ($\text{kg s}^{-1} \text{m}^{-2}$), and the meltwater ion concentration factor, CF [$(\text{meq m}^{-3}) (\text{meq m}^{-3})^{-1}$].

The objective of this paper is to examine whether enhanced infiltration can be identified in a controlled laboratory experiment. It is hypothesized that average initial soil saturation will not influence enhanced infiltration in a limited infiltration regime but the distribution of initial soil moisture may. Thus, soil columns with different initial soil moisture contents were used. It was assumed that solutions released to the soil surface were conservative, fully mixed within each time step, and that mass and energy were conserved.

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2 Methodology

Experiments were carried out in a temperature-controlled cryospheric environmental laboratory (CEL) containing a dual refrigerating system (Heatcraft, BZ series) with a stable cooling capacity from +7.5 to -30°C ($\pm 2^{\circ}\text{C}$). The room was sealed to prevent contamination of samples from dust and atmospheric particulates.

The experimental setup consisted of a 0.46 m long frozen soil column with a surface area of 0.004 m^2 (Fig. 1a). Each column consisted of an acrylonitrile butadiene styrene (ABS) pipe with a 1 mm mesh at the base. The column was filled with 30 mm of coarse quartz gravel (particle size was $\sim 2\text{--}3\text{ mm}$) to prevent the overlying soil from exiting the column, $\sim 0.32\text{ m}$ of homogenized, dried, and grinded loamy soil collected at a forested site in the Marmot Creek Research Basin, Kananaskis Valley, AB ($50^{\circ} 56' \text{ N}$, $115^{\circ} 08' \text{ W}$), and $\sim 0.11\text{ m}$ of an in-situ soil sample from the same field site. The column was placed on top of $\sim 70\text{ mm}$ of filter sand (particle size was $\sim 1\text{ mm}$) to allow air to escape freely during the infiltration experiments.

Type-E thermocouples (TC) were placed at two depths within the column to monitor the temperature of the soil: one at the interface between the in-situ soil sample and the homogenized soil and one towards the base of the column ($\sim 0.34\text{ m}$). The accuracy of the TC was $\pm 0.1^{\circ}\text{C}$ within the applied temperature range (Campbell Scientific, 2007). Temperatures were recorded every 10 s by a Campbell Scientific CR21X datalogger. In the first experiment the values were averaged and logged hourly; in the following two experiments, the values were averaged and logged every 10 min.

Copper pipe was coiled tightly around the ABS pipe and connected to a temperature-controlled refrigerated bath (RTE-DD8, Neslab). This allowed circulation of coolant, which was used to maintain frozen soil conditions during experiments. Filter sand was used to fill the voids between the coils. Insulation was wrapped around the outside of each column for further insulation.

Three experiments were carried out, differing with respect to initial average soil saturation, S_1 ($\text{mm}^3\text{ mm}^{-3}$), which was estimated from average volumetric soil moisture,

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θ ($\text{mm}^3 \text{mm}^{-3}$), and average soil porosity, ϕ , as $S_1 = \theta/\phi$. Each experiment was conducted simultaneously on three soil columns (Fig. 1b). One experiment was conducted on air-dried soil, which hygroscopic water content ($\sim 2\%$) was determined using standard oven-drying method (Levitt and Young, 2008). Average S_1 for the dry soil was $0.06 \text{mm}^3 \text{mm}^{-3}$ (dry conditions). Two experiments were conducted on wetted soil: an unsaturated and a saturated experiment. Wetting of the soil columns were done by allowing water to enter from the base, by capillary forces; the columns were placed on a layer of filter sand to ease the process. Water depth was $\sim 0.3 \text{m}$ for eight days. Hereafter, the columns used in the unsaturated experiment were allowed to drain by gravity at room temperature for three days. Time constraints dictated this time period and thereby the average initial soil saturation of $0.83 \text{mm}^3 \text{mm}^{-3}$. To ensure saturated conditions of the columns used in the saturated experiment, water was ponded on top of the columns 24 h prior to experimental use; average S_1 was $\sim 0.97 \text{mm}^3 \text{mm}^{-3}$. Volumetric soil moisture in the columns were determined by weight; assuming a density of the water of 1000kg m^{-3} .

The dry and saturated conditions were selected to represent the boundaries for the effect of enhanced infiltration during infiltration to frozen soil and the infiltrability cases described as “unlimited” and “restricted” by Granger et al. (1984). For the dry soil, infiltration was assumed unlimited because the pore space was free of ice. For the saturated soil, infiltration was presumed restricted as a result of ice in the pore spaces. The unsaturated conditions represented a situation in-between, where part of the pore space was filled with ice, limiting infiltration.

The soil columns were allowed to freeze for a minimum of 12 h at a room temperature of -2°C ($\pm 2^\circ\text{C}$). Circulation of coolant took place during this period too, allowing a rapid freezing ($< 4 \text{h}$); the temperature of the coolant was -2°C ($\pm 2^\circ\text{C}$). The experimental setup caused the freezing of the soil to occur from the sides as well as top and bottom. This is not like in nature, where freezing generally occurs from the top; in areas where permafrost exists, freezing of the soil can also progress from below. The method of soil freezing will influence the migration of soil moisture that takes place during freezing of

the soil (e.g., Male and Gray, 1981; Kane and Stein, 1983; Williams and Smith, 1989). However, redistribution of soil moisture is considered negligible in dry soils (i.e. the dry experiment) and only limited migration was expected in the unsaturated and saturated soil columns due to their high S_1 (e.g., Gray et al., 1984).

5 The temperature in the CEL was increased just prior to initiation of the experiments. Average room temperature during experiments was $+1.6^\circ\text{C}$ ($\pm 1.2^\circ\text{C}$). Small adjustments ($\pm 2^\circ\text{C}$) of the coolant temperature were made throughout the experiments to ensure frozen soil conditions; these adjustments were based on the TC readings within the soil columns. Total experimental time for each column was 12 h.

10 To simulate preferential ion elution from an overlying snowpack, chloride solutions with decreasing concentrations with time were added to the soil surface (Fig. 2). Burettes (100 ml) were used for the application; rates varied between $0.001\text{ kg s}^{-1}\text{ m}^{-2}$ (3.6 mm h^{-1}) and $0.020\text{ kg s}^{-1}\text{ m}^{-2}$ (72 mm h^{-1}); the average rate was $0.010\text{ kg s}^{-1}\text{ m}^{-2}$ (36 mm h^{-1}). This range of rates was strongly influenced by the burettes themselves; however, an overflow valve (4 mm in diameter) prevented ponding greater than $\sim 10\text{ mm}$. An increasing ponding depth, and thereby head, would result in changing infiltration conditions as time progressed (i.e. enhance the rate of infiltration for the water). Thus, the maximum head was chosen to resemble field conditions. The chloride concentration decreased exponentially from $\sim 81\,400\text{ meq m}^{-3}$ ($\sim 2890\text{ ppm}$)
15 to $\sim 4060\text{ meq m}^{-3}$ ($\sim 145\text{ ppm}$) during the 12 h. Solutions were spiked compared to normal snow concentrations to achieve an enhanced indication of changes in ion load. All solutions were at room temperature ($\sim 2^\circ\text{C}$) when they were added. In each experiment, initial addition of solute to the soil surfaces of column 2 and 3 were delayed 25 and 50 min, respectively, due to the timing of sample collection.

25 Infiltration excess water was collected using a syringe at increasing time intervals (Fig. 2). All water was collected each time to determine the mass of water that had infiltrated the soil as well as to avoid mixing of solutions once concentrations changed. Samples were stored at 3°C until analyzed ($< 24\text{ h}$).

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3 Results

The experimental conditions of the nine soil column experiments are listed in Table 1. Major differences between the three experiments were due to the initial soil saturation. Differences in average porosity (~ 0.05), dry bulk density ($\sim 125 \text{ kg m}^{-3}$), average room temperature (0.1°C), and average precipitation rates ($< 0.003 \text{ kg s}^{-1} \text{ m}^{-2}$; 11 mm h^{-1}) were considered minor. The rates of precipitation were generally higher than those found in nature. However, the overflow valve ensured a maximum constant head, which was comparable to natural conditions (10 mm), and minimized the influence of the high and highly variable precipitation rates on the infiltration rate. The greatest inter-column variability was observed for average soil temperatures, ranging between -0.7 and -1.4°C , with standard deviations ranging between 0.4 and 1.2°C . This variability was likely a result of the delay in additions of solute to columns 2 and 3, which allowed these columns to adjust to the room temperature increase for longer than did column 1. However, studies have shown that the effect of the soil temperature on infiltration is secondary to that of initial soil moisture (e.g., Komarov and Makarova, 1973; Granger et al., 1984; Zhao and Gray, 1997). In addition, the temperature at an advancing wetting front has been found to be rather independent of the initial temperature of a frozen soil (Zhao et al., 1997). Though, the variability may influence on the supply of latent heat as water refreezes, being greater in a colder soil, causing the soil temperature to increase faster (Zhao et al., 1997). In general, the soil temperatures were all within the range of melt period soil temperatures observed in many seasonally frozen soils.

Ponding occurred after approximately two hours in the dry experiment ($S_1 \approx 0.06 \text{ mm}^3 \text{ mm}^{-3}$), whereas it occurred instantaneously in the saturated experiment ($S_1 \approx 0.97 \text{ mm}^3 \text{ mm}^{-3}$). In the unsaturated experiment ($S_1 \approx 0.83 \text{ mm}^3 \text{ mm}^{-3}$), ponding took place almost instantaneously for two of the columns (1 and 3), and after 25 min for column 2. The mass of water added to the soil surface, P (kg m^{-2}), and the mass of infiltration excess water, R (kg m^{-2}), were recorded throughout the experiment. The mass of infiltrated water, F , was specified by mass conservation, $F = P - R$. The great-

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est F was observed for the dry soil, with an average of 119.7 kg m^{-2} (Table 2); for the unsaturated and saturated soils, average F were 25.2 kg m^{-2} and 8.7 kg m^{-2} , respectively.

Chloride concentrations in P and R confirmed the conservative behaviour of the solutions; differences between concentrations were $<10\%$ and were assumed to be a result of instability in electrode readings. The ion load infiltrating the frozen soil, F_i (meq m^{-2}), was estimated from conservation of mass too, $F_i = P_i - R_i$, where P_i and R_i are the ion load in, respectively precipitation (meq m^{-2}) and infiltration excess water (meq m^{-2}). All columns showed a rapid initial increase in F_i followed by a quasi-steady state, as described by Zhao et al. (1997) (Fig. 3). The transition occurred after $\sim 0.5 \text{ h}$ for the saturated soil, after $\sim 1.5 \text{ h}$ for the unsaturated soil, and after $\sim 2.0 \text{ h}$ for the dry soil. The greatest F_i was observed for the dry soil, with an average for the three columns of 5928 meq m^{-2} ; the lowest F_i was observed for the saturated soil, with an average of 750 meq m^{-2} . F_i ranged between 870 and 2375 meq m^{-2} for the unsaturated soil with an average of 1473 meq m^{-2} .

To assess the magnitude of enhanced infiltration, the normalized enhanced infiltration, NEI [$(\text{meq m}^{-2}) (\text{meq m}^{-2})^{-1}$], was calculated for each column. NEI is defined as the ratio between the cumulative enhanced infiltration and the cumulative ion infiltration estimated from only the time-averaged ion concentration and cumulative infiltration, with no covariance (Lilbæk and Pomeroy, 2007):

$$NEI = \frac{\text{cov}[C_i(t), f(t)]}{\left(\frac{\bar{C}_i \cdot F}{\rho}\right)} = \frac{F_i - \left(\frac{\bar{C}_i \cdot F}{\rho}\right)}{\left(\frac{\bar{C}_i \cdot F}{\rho}\right)} \quad (2)$$

Figure 4a shows how NEI increased almost linearly with infiltration time in all three experiments. The average rate of change was greatest for the saturated soil columns (slope= 0.22 h^{-1}) and least for the dry soil columns (slope= 0.12 h^{-1}). The average rate of change for the unsaturated soil columns was only slightly higher than that of the dry

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soil (slope=0.14 h⁻¹). Consequently, the greatest *NEI* were obtained for the saturated soil, with values ranging between 2.2 and 2.9 (Fig. 4a) indicating that, on average, 2.5 times more ion load infiltrated than if calculated from time-averaged ion concentration and cumulative infiltration alone (no covariance). For the dry soil, *NEI* ranged between 1.3 and 1.4 at the end of the experiment and for the unsaturated soil, *NEI* ranged between 0.9 and 1.9; average *NEI* were 1.3 and 1.5, respectively. One of the columns in the unsaturated soil experiment changed slope after approximately 6 h, ending up with the lowest cumulative *NEI* of all the experiments (0.9).

The impact of enhanced infiltration on infiltration excess ion load was assessed by normalizing the infiltration excess ion load, NR_i [(meq m⁻²) (meq m⁻²)⁻¹]. NR_i is defined as the ratio between R_i and the difference between P_i and F_i , due only to time-averaged ion concentration and cumulative infiltration (no covariance) (Lilbæk and Pomeroy, 2007):

$$NR_i = \frac{R_i}{P_i - \left(\frac{\bar{C}_i F}{\rho}\right)} = \frac{P_i - F_i}{P_i - (F_i - \text{cov}[C_i(t), f(t)])} = \frac{R_i}{R_i + \text{cov}[C_i(t), f(t)]} \quad (3)$$

Calculations showed that after the initial one-third of the experimental period (4 h), the ion load in the infiltration excess water was reduced due to enhanced infiltration (1- NR_i) by ~40% in the dry soil experiment, between 4% and 12% in the unsaturated soil experiment, and between 3% and 8% in the saturated soil experiment (Fig. 4b). A slight increase in the reduction, between 1% and 7%, was observed over the rest of the period. In general, ion loads in infiltration excess water over the dry soil columns increased the most and over the saturated soil columns the least. The variation in total R_i between columns was 3% in the dry soil experiment, 14% in the unsaturated soil experiment, and 6% in the saturated experiment.

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4 Discussion

Three experiments were conducted, each in three replicates, to assess whether enhanced ion infiltration to frozen soil could be recognized in controlled laboratory settings in addition to determining its magnitude. Each experiment differed from the others with respect to initial soil saturation; differences in porosities, average room and soil temperatures, and average precipitation rates were minor (Table 1). The results show that enhanced infiltration of a conservative ion takes place once partitioning of meltwater added to a frozen mineral surface occurs.

It has previously been suggested that the cumulative mass that infiltrates frozen soil is inversely related to the initial moisture content of the soil (e.g., Gray et al., 2001) and that the effect of soil temperature on the cumulative infiltration is secondary (e.g., Komarov and Makarova, 1973; Granger et al., 1984). This was also observed for the experiments carried out in this study. The greatest cumulative infiltrating mass was observed for the dry soil and the least for the saturated soil. The inter-column variation in cumulative infiltrating mass could not be correlated with the inter-column variation in soil temperature indicating that it was of little importance for the general observations in this study. From the three experiments it was demonstrated that there is a similarly inverse relationship between initial soil moisture content and cumulative infiltrating ion load; cumulative infiltrating ion load increased with decreasing initial soil moisture (Table 2). General ranking order for infiltration of snowmelt ions with respect to soil moisture was: dry \gg unsaturated $>$ saturated soil conditions. Over the course of the infiltration, about 60% of the total ion load added to the soil surface of the dry soil infiltrated, varying little ($\sim 1\%$) between the columns; only 10% to 28% of the added ion load infiltrated the unsaturated soil, and between 6% and 13% infiltrated the saturated soil.

The impact of enhanced infiltration increased with initial soil moisture content. The largest normalized enhanced infiltration ($NEI=2.90$) was calculated for the first column in the saturated experiment with $\sim 50\%$ difference to the other two saturated columns.

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This was most likely a result of the cumulative infiltrating mass being twice that of the other columns and that most of it infiltrated during the beginning of the experiment, while solute concentrations were high. The presence of soil macropores (i.e. cracks, roots) could account for the difference in infiltration, as the transport deeper into the soil would be more rapid than matrix flow alone (e.g., Beven and Germann, 1982). Consequently, the presence of macropores will enhance the effect of enhanced infiltration due to this fast transfer of water deeper into the soil. However, no visual observations of macropores were made in any of the soil columns in either experiment. On average, *NEI* in the saturated experiment was close to twice that of the other experiments, with 250% more ion load infiltrating compared to only 131% when the soil was initially dry and 145% when the soil was unsaturated. Overall, *NEI* with respect to initial soil moisture ranked the experiments: saturated>>unsaturated>dry soil conditions.

The change in slope of *NEI* for column 1 in the unsaturated experiment (Fig. 4a) was a result of the timing between high infiltration rate and meltwater ion concentration. During the second half of the experiment, the cumulative infiltrated mass increased by roughly 50% for this column, compared to only 10% for the other two columns. This continuous infiltration throughout the experiment, even though at a very low rate ($\sim 1 \text{ mm h}^{-1}$), causes the cumulative ion load to increase continuously throughout the experiments. For the other columns, the infiltration rates became 0.0 mm h^{-1} during parts of this period, limiting the ion load infiltration.

Even though enhanced infiltration had the greatest impact on the saturated soil, the reduction in normalized infiltration excess ion load ($1 - NR_i$; Fig. 4b) was almost negligible ($\sim 5\%$). In contrast, enhanced infiltration had the least impact on the dry soil ($NEI \approx 1.31$) but the reduction in infiltration excess ion load was almost 10 times greater than that of the saturated columns with a reduction between 44% and 47% (Fig. 4b). General ranking order for the reduction in infiltration excess ion load with respect to initial soil moisture content was: dry>>unsaturated>saturated soil.

An implication of enhanced infiltration is that formation of a basal ice layer will result in an alteration of both meltwater ion pathway and concentration. When basal ice is

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present, all meltwater runs off and further ion concentration enrichment occurs (Lilbæk and Pomeroy, 2008). Conversely, when partitioning occurs, enhanced infiltration of meltwater ion load can result in relatively dilute runoff water.

The unsaturated soil experiment showed the greatest inter-column variability in infiltration results (Table 2). Cumulative infiltrating mass for the second column (39.6 kg m⁻²) was twice that of the other columns, resulting in the greatest cumulative infiltrating ion load (2375 meq m⁻²) as well as greatest reduction in infiltration excess ion load (19%). Nevertheless, the third column had a cumulative infiltration ion load that was half that of the second column (1174 meq m⁻²), with less than half the cumulative mass infiltrating (16.7 kg m⁻²). The lowest cumulative infiltrating ion load was observed in the first column (870 meq m⁻²), even though its cumulative infiltrating mass was higher than that of the third column (19.4 kg m⁻²). This experiment showed the greatest range in normalized enhanced infiltration and normalized infiltration excess ion load (Fig. 4), demonstrating the importance of timing between high meltwater ion concentration and infiltration rate.

A factor that may have influenced on the experimental results was the high solute concentrations in the added water, as the presence of solute lowers the freezing temperature of the solution compared to the pure solvent (e.g., Masterton and Hurley, 1997). The depression (or lowering) of the freezing point, ΔT_f (°C), can be calculated for any solution as

$$\Delta T_f = k_f \cdot m \cdot i \quad (4)$$

where k_f is the molal freezing point constant [°C kg mol⁻¹], which is 1.86 °C kg mol⁻¹ for water, m is the molality of the dissolved solute (mol kg⁻¹), and i is the “Van’t Hoff factor” that is equal to the number of moles of ions per mole of electrolyte (e.g., Masterton and Hurley, 1997). For NaCl i is equal to ~ 2 for dilute solutions, decreasing as the molality of the solution increases; e.g. i is ~ 1.8 for $m=0.5$.

As water infiltrated the frozen soil, some refreezing occurred upon contact with the soil particles. As ice is formed, ion exclusion takes place, relocating some of the ions to

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a quasi-liquid layer on the surface of the ice (Davies et al., 1987). This leads to a further depression of the freezing point, as the concentration in this brine is greater than in the initially infiltrating solution. Figure 5 shows how the depression of the freezing point increases for each of the six solutions used in the experiments, as the volume of liquid water decreases. The calculations assume that all Na^+ and Cl^- in solution are excluded from the ice lattice, as the solubility of ions in ice is much less than in water (e.g., Smith and Haymet, 2004; Blackford et al., 2007); almost negligible. This assumption seems reasonable as reported solubility of HCl in ice range between 1 and 10^4 mmol m^{-3} (e.g., Dominé et al., 1994); a very small amount compared to the concentration of Cl^- in the here used solutions.

In this study, the solute concentrations added to the soil surfaces were greater than those typical of snowmelt water and rain; consequently, their freezing point depressions ranged from 0.03°C for the 145 ppm Cl^- solution to 0.6°C for the 2890 ppm Cl solution. These depressions are larger than what will normally be observed in nature and unfrozen water was most likely present within the soils even though the soil temperatures were below zero; however, no measurements were done to confirm this. With average soil temperature of -1.0°C , the freezing point depressions was most pronounced, and therefore of greatest influence, during the initial third of the experiment (Fig. 5). The result of this would therefore be a greater mass infiltrating the soil during this stage of the experiment, increasing the impact of enhanced infiltration. However, it was believed that the influence of the increased freezing point depression would be most pronounced for the dry soil, where infiltration was assumed unlimited, as refreezing would have been limited within the soil and thereby formation of limiting ice layers. The high initial saturations of the soils in the unsaturated and saturated experiments were believed to minimize the effect of the freezing point depression on cumulative infiltration.

5 Conclusions

Laboratory experiments with frozen loamy soil at different saturations showed that an enhanced infiltration of ions takes place during infiltration of meltwater to frozen soil due to the timing between initially higher infiltration rates and enriched ion concentrations in meltwater. The results demonstrated that the impact of enhanced infiltration was related to initial soil moisture content, with the greatest impact on saturated and near-saturated soil. Even infiltration into dry soils may result in an enhanced infiltration of solute; in the presented experiment, it was shown to cause the greatest reduction in infiltration excess water ion load. The results also show that synchronicity between the timing of high ion concentration and infiltration rate greatly influence enhanced infiltration and therefore the flow path of snowpack ions during the melt and spring runoff periods. Future work will focus on examining whether enhanced infiltration can be identified in the field.

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Table 1. Summary of experimental setup for each soil column.

Experiment Column #	Dry			Unsaturated			Saturated		
	1	2	3	1	2	3	1	2	3
Soil saturation, S_1 ($\text{mm}^3 \text{mm}^{-3}$)	0.06	0.06	0.06	0.85	0.83	0.81	0.97	0.95	0.98
Soil porosity, ϕ	0.46	0.47	0.47	0.42	0.45	0.42	0.43	0.43	0.43
Dry bulk density (kg m^{-3})	1441	1400	1407	1528	1463	1525	1514	1502	1513
Soil temperature ($^{\circ}\text{C} \pm \text{stdev}$)	-1.4 ± 1.1	-0.9 ± 0.8	-0.9 ± 0.8	-1.2 ± 1.2	-0.9 ± 0.6	-0.8 ± 0.6	-0.9 ± 0.9	-0.7 ± 0.4	-0.8 ± 0.5
Precipitation rate ($\text{kg s}^{-1} \text{m}^{-2}$)	0.011	0.010	0.011	0.009	0.009	0.010	0.009	0.008	0.010
(mm h^{-1})	38.5	37.6	40.2	32.9	31.6	36.4	32.0	30.2	36.2

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Table 2. Summary of infiltration results for each soil column.

Experiment Column #	Dry			Unsaturated			Saturated		
	1	2	3	1	2	3	1	2	3
Cumulative mass infiltrating, F ($\text{kg s}^{-1} \text{m}^{-2}$)	119.7	119.3	120.0	19.4	39.6	16.7	12.2	6.3	7.7
Cumulative ion load infiltrating, F_i (meq m^{-2})	5953	6189	5643	870	2375	1174	1172	478	600
$-F_i$ if no covariance (meq m^{-2})	2625	2721	2387	477	931	406	310	143	167
Normalized enhanced infiltration, NEI [$(\text{meq m}^{-2}) (\text{meq m}^{-2})^{-1}$]	1.27	1.27	1.37	0.87	1.56	1.92	2.90	2.21	2.42
Normalized infiltration excess ion load, NR_i [$(\text{meq m}^{-2}) (\text{meq m}^{-2})^{-1}$]	0.55	0.53	0.56	0.95	0.81	0.92	0.90	0.96	0.96

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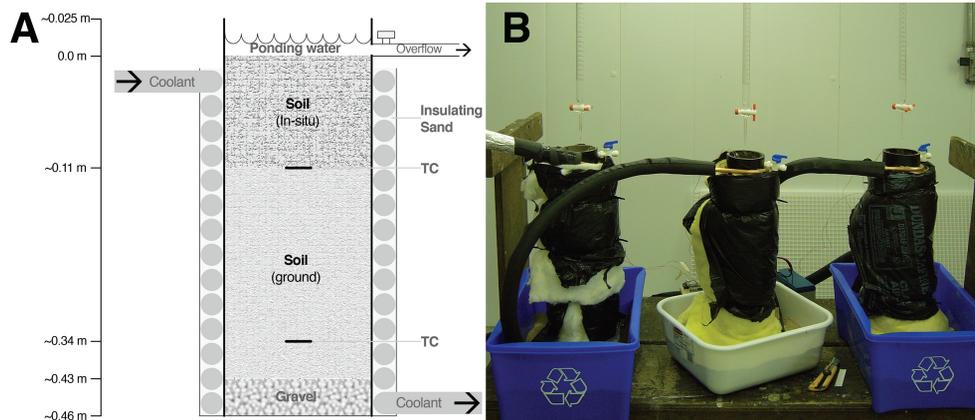


Fig. 1. (A) Schematic drawing of soil column setup (not to scale). (B) Three columns with burettes over top set up in the cryospheric environmental laboratory (temperature controlled room).

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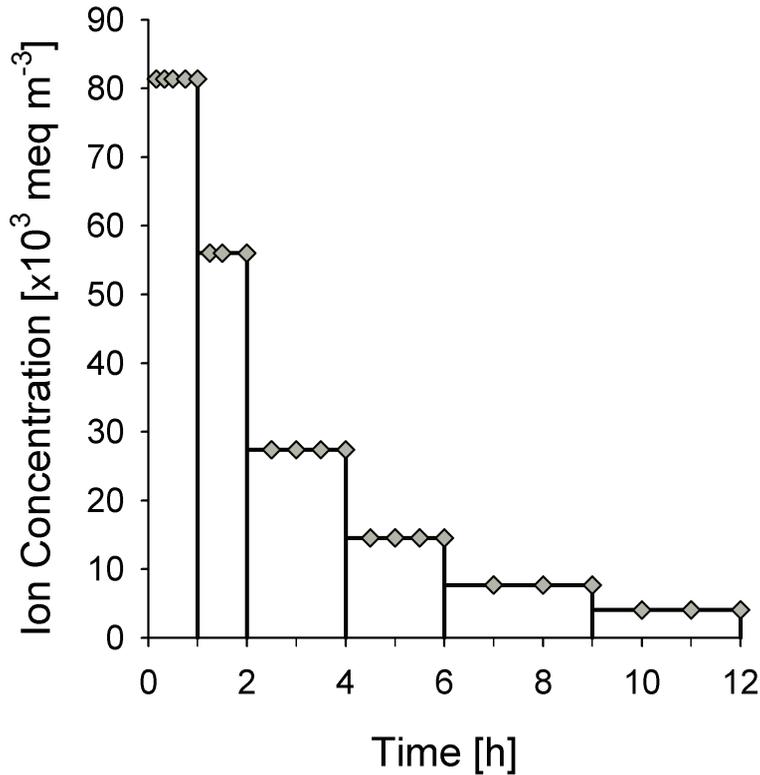


Fig. 2. Changes in the applied chloride concentration over time (line). The diamonds represents when sampling occurred.

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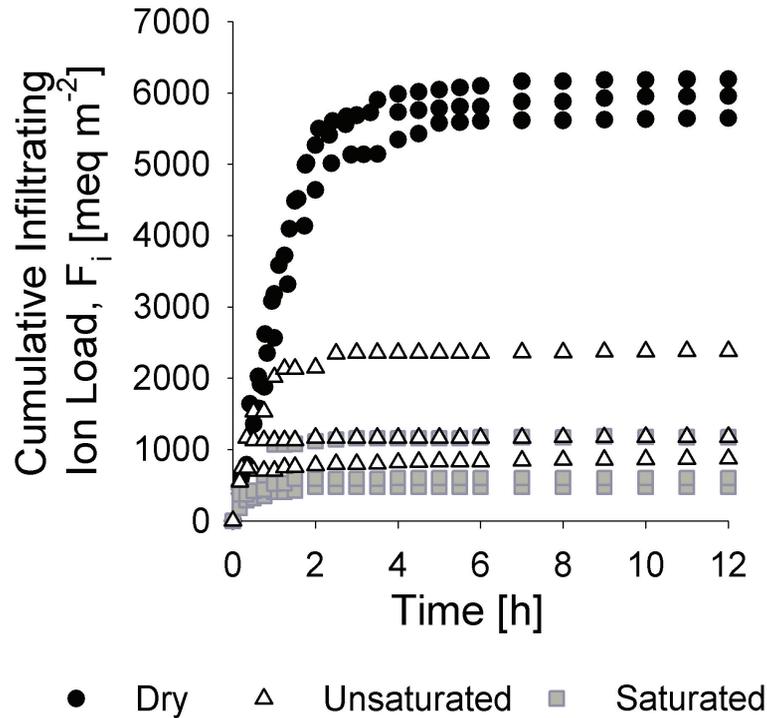


Fig. 3. Cumulative ion load infiltrating, F_i , for each soil column.

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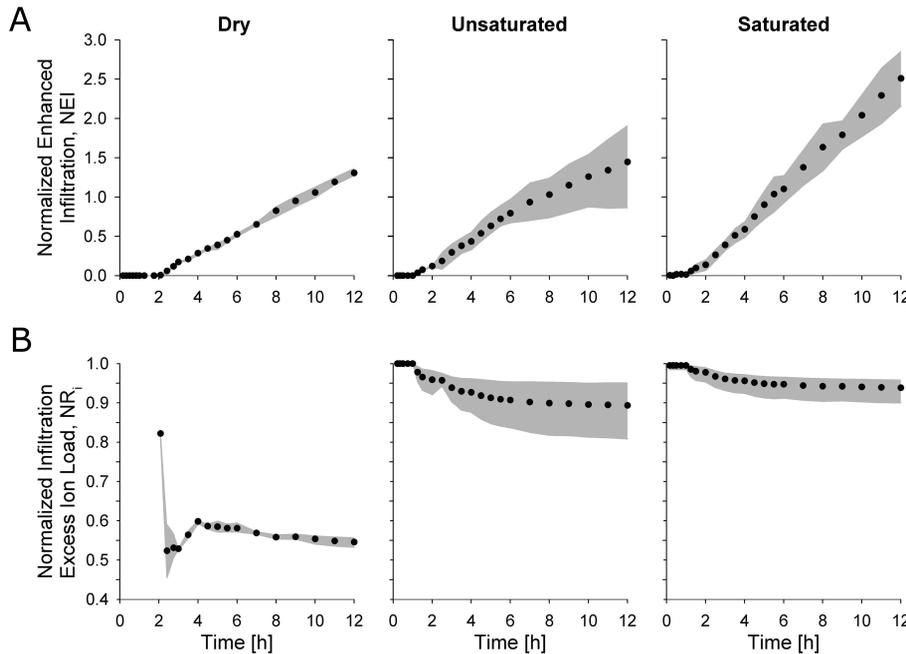


Fig. 4. Variation with time of **(A)** average normalized enhanced infiltration, NEI , and **(B)** average normalized infiltration excess ion load, NR_i , for each experiment. The grey area represents the range for the three columns.

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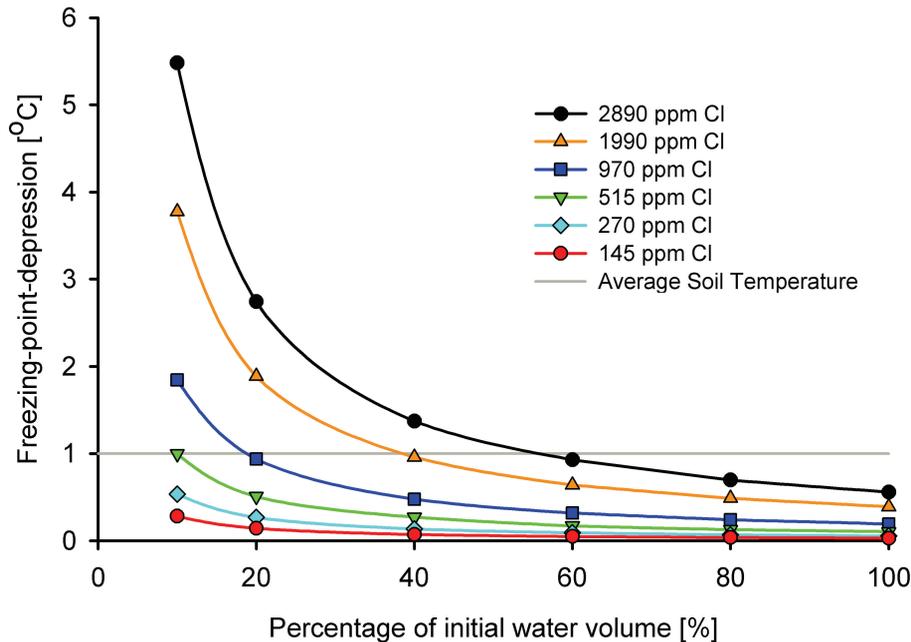


Fig. 5. The change in freezing point depression as the volume of water decreases. The change is shown for each of the solute concentrations used in the experiments. The horizontal line represents average soil temperature during the here presented experiments.

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