Quantification of Water Content during Freeze–Thaw Cycles: A Nuclear Magnetic Resonance Based Method

Huihui Tian, Changfu Wei,* Yuanming Lai, and Pan Chen

In analyzing the phase transition and water migration processes in multi-phase porous systems, it is helpful to properly evaluate the unfrozen capillary water content and adsorptive water content, respectively. In this study, an innovative procedure was developed to determine the total, adsorptive, and capillary water contents in frozen soils based on the nuclear magnetic resonance (NMR) technique. We found a threshold value of the proton spin–spin relaxation time, $T_2$, that separates the unfrozen pore water into two distinct regimes: the adsorptive regime for small $T_2$ values and the capillary regime for large $T_2$ values. We showed that the relationship between adsorptive (or capillary) water content and temperature is hysteretic for all three tested soils experiencing a freeze–thaw cycle. The hysteresis behavior of capillary or adsorptive water content during a freeze–thaw cycle is attributable to capillary effect, metastable nucleation, pore blocking, and variation of microstructure. In all the tested soils, the adsorptive water content was significantly larger than the capillary water content and was supported by the experimental evidence inferred from previous pore water potential measurements of various soils.

Abbreviations: CPMG, Carr–Purcell–Meiboom–Gill; NMR, nuclear magnetic resonance; RF, radio frequency.

Soil freeze–thaw cycles affect multitudes of physical, chemical, and biological processes in the sediments of cold regions. During the past two decades, increasing concerns about the potential impact of global warming on the spatial extent of permafrost and poor understanding of hydrological and ecological processes in frozen soils have prompted renewed interest in this subject. In addition, understanding the effect of freeze–thaw cycles on the hydromechanical behavior of soils plays a crucial role in designing infrastructure in cold regions and in evaluating the impact of engineering activities on permafrost zones. In characterizing the subsurface physical, chemical, and biological processes in cold regions, one of the challenges to address is to determine the amount of unfrozen water in soils, which provides passageway for melted snow infiltration, moisture transport, and nutrients leaching in the sediments.

The unfrozen water phase in unsaturated porous media has been well recognized to be retained by both capillary and adsorptive forces (Tuller et al., 1999; Tuller and Or, 2005; Lebeau and Konrad, 2010; Tokunaga, 2009, 2011). Accordingly, the matric potential of a porous medium can be decomposed into an adsorptive component and a capillary component (Nitaou and bear, 1996; Tuller et al., 1999). The capillary forces refer to the surface tensions on the interfaces between any two bulk phases, particularly, the air–water interface in an unsaturated soil or the ice–water interface in a frozen soil. The adsorptive forces include all the interfacial forces involved in adsorbing the water films onto the grain surfaces. Derjaguin et al. (1987) distinguished between two types of adsorptive forces: (i) long-range electrostatic forces (e.g., diffuse double layer repulsion) and short-range van der Waals and hydration forces and (ii) long-range forces stemming from the overlapping of two interfacial regions. Generally, thicker water films in angular pores or water retained in pendular rings of unsaturated porous media may be considered as capillary dominated, whereas thinner water films on flat or convex segments of grain surfaces are adsorption dominated. In simulating subsurface transport
...and fate processes, it is important to evaluate both the capillary and adsorptive water contents (Tuller and Or, 2005; Lebeau and Konrad, 2010; Tokunaga, 2009, 2011; Rempel, 2012).

Few experimental efforts have been undertaken to determine the amounts of capillary and adsorptive waters in unsaturated or frozen soils. Several relevant experiments have been performed with aims to obtain the thickness of adsorbed water films in porous media. Using an angle-averaging, refractive-index-matching technique, Beaglehole et al. (1991) monitored adsorption of water on molecularly smooth mica and determined the adsorbed water thickness. Asay and Kim (2005) used attenuated total reflection-infrared spectroscopy to determine the molecular configuration and thickness of water adsorbed on a hydrophilic silicon oxide surface at room temperature as a function of the humidity in the air phase. More recently, Bohr et al. (2010) used synchrotron X-ray reflectivity to measure the thickness of the water film adsorbed on a cleavage surface of calcite in a sample chamber where relative humidity was controllable. Although the above experimental data are divergent, they imply that the adsorbed water film thickness is not larger than 10 water layers, which accounts for only a small percentage of the total pore volume.

Analytical models developed from modern interface science provide an alternative approach to determining the thickness of adsorbed water films in porous media. For instance, based on the Derjaguin–Landau–Verwey–Overbeek theory, Tokunaga (2011) developed a theoretical model to examine the problem of adsorbed water film thickness in unsaturated geological media. This model predicts that the typical thickness of adsorbed water films ranges from ~1 to 20 nm in drained pores and fractures of unsaturated environments. Noticeably, the as-predicted thickness of adsorbed water films can significantly exceed the experimental data available in the literature (e.g., Beaglehole et al., 1991; Asay and Kim, 2005; Bohr et al., 2010).

Thus far, the adsorbed water film thicknesses (or adsorbed water content), determined either experimentally or theoretically, are all much smaller than those inferred from the results of matric suction measurements. Based on the analysis of the matric suction measurements on various types of clayey or clay-enriched soils, Baker and Frydman (2009) concluded that unless the water content is very high, the capillary component of the matric suction is insignificant compared with its adsorptive counterpart. For example, for kaolin (Tarantino and DeCol, 2008), the capillary component of matric suction became significant only when the water content was >32%, equivalent to 90% saturation, and for bentonite-enriched sand (Dineen et al., 1999), this water content was ~14%, equivalent to 80% saturation. Hence, based on the analysis of Baker and Frydman (2009), it is reasonable to expect that in clay-enriched soils with moderate or relatively high saturation, only a small portion of the pore water is dominated by capillary action, while most of it is indeed adsorbed.

To explore the mechanisms behind these inferred results, Baker and Frydman (2009) introduced a double-porosity model, originally proposed by Hueckel et al. (2001) for the geometry of pore spaces, in which the soil matrix was assumed to be composed of large aggregate pods (or clayey patches) containing clay platelets and water. The pore space within the pods is considered as micropores, while the pore space between the pods represents macropores. At common engineering water contents, the pods are assumed to be fully saturated and all the water in them is adsorbed. The macropores may be unsaturated, but all the surfaces of clay platelets are coated with a layer of adsorbed water. As such, interfacial (adsorbed) forces are likely to play a larger role in hydro-mechanical behavior than usually expected, especially for those soils of relatively large surface area. Although the double-porosity model explains the high adsorbed water content in clay-enriched soils, its direct experimental validation is yet to be performed.

The objective of this study was twofold: (i) to develop an NMR-based procedure for determining capillary and adsorptive water contents of soils during a freeze–thaw cycle, and (ii) to examine the physical models for the pore geometry as introduced by Baker and Frydman (2009). Because the transverse relaxation time ($T_2$), determined by the NMR relaxometry of targeted molecules, is a measure of the microscopic mobility of fluid molecules (Coates et al., 1999), the $T_2$ distribution reflects the structural arrangements of surrounding water molecules, shedding insight into pore water distribution and migration in soils during thermal or hydraulic cycles. Our working hypothesis was that the capillarity-dominated water and the adsorption-dominated water can be distinguished based on the $T_2$ measurement, since they are subjected to forces of different origins. A series of NMR measurements was first performed with incorporation of freeze–thaw experiments, and then the NMR measurements were performed together with a series of drying tests for comparison. In addition, the experimental results based on the procedure were used to examine the alteration of the soil microstructure and fabric during a freeze–thaw cycle.

Theoretical Background

A proton (e.g., H$^+$) bears a slight magnetic moment originating from its spin and thus can be viewed as a micromagnet. For a water-saturated porous material embedded in a fixed magnetic field ($B_0$), all the protons in it tend to align along the direction of the magnetic field, resulting in the initial magnetization $M_0$ (Ishizaki et al., 1996). The initial magnitude of $M_0$ is proportional to the number of nuclei per unit volume of the porous medium (denoted by $N$) and inversely proportional to the temperature, $T$. According to the Curie law for paramagnetic substances,

$$M_0 = \frac{I(I+1)N g^2 \mu_N^2}{3kT} B_0$$

[1]

where $I$ is the spin quantum number of the nucleus (for H, $I = 1/2$), $g$ is the Lande factor (for H, $g = 5.585$), $\mu_N$ is the nuclear...
magneton (for H, \(\mu_N = 5.05095 \times 10^{-27} \text{J T}^{-1}\)), and \(k\) is the Boltzmann constant.

If a magnetic pulse of a radio frequency (RF) \(\nu\) is applied, the magnetization can be temporarily oriented to a new, unstable direction. Once the pulse is removed, each proton spin emits the absorbed energy and returns to the initial equilibrium position through a series of relaxation processes, which can be characterized using NMR. These relaxation processes can be described by

\[
M(t) = M_0 \exp \left( -\frac{t}{T_2} \right)
\]

where \(T_2\) is the transverse relaxation time.

The \(T_2\) distribution curve is determined with the inversion of the relaxation decay curve monitored by the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence, which consists of a series of RF pulses. The \(M_0\) value is the initial amplitude of the decay curve derived from CPMG pulse sequence measurements. The first pulse rotates the nuclei 90° from the \(B_0\) direction. This is followed by a long series of equally spaced 180° pulses. When irradiated with such a series of pulses, a nuclear spin system will return a series of equally spaced spin echoes, one after each 180° pulse. The echo spacing, \(T_E\), is typically on the order of tenths of a millisecond. Measuring the decay of echo amplitudes \(M\) during the sequence can track the transverse magnetization relaxation. Based on the inversion, the transverse nuclear magnetization decay curve can be transformed to yield the \(T_2\) distribution curve.

The measured relaxation time is given by (Coates et al., 1999)

\[
\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}
\]

where \(T_{2B}\) is the proton relaxation time in bulk, \(T_{2S}\) is the surface relaxation time, and \(T_{2D}\) is the diffusion relaxation time. In some water-saturating porous media, such as rock, the water is confined in pores, and the relaxation process can be significantly accelerated by the solid–water interactions in the vicinity of pore surfaces. Because of this, rock materials are usually classified into the so-called fast-diffusion regime (Jaeger et al., 2010), in which \(T_{2S}\) is much shorter than \(T_{2B}\) and \(T_{2D}\) so that \(1/T_2 \approx 1/T_{2S}\). Noticeably, the diffusion of water molecules can also be significantly influenced by temperature. As made clear below, however, \(T_2\) for the adsorbed water is practically independent of temperature. Hence, the relaxation process of the adsorbed water is controlled only by the solid–water interactions and is practically independent of temperature.

For water-saturated spherical pores, \(T_{2S}\) is proportional to their characteristic radius, \(R\). Hence, it is assumed that \(T_{2S} = R/\rho_2\), where \(\rho_2\) is the surface relaxivity of pore walls in porous media. In more general cases, where the pores are not spherical,

\[
\frac{1}{T_2} \approx \frac{1}{T_{2S}} = \rho_2 \frac{F}{R}
\]

where \(F\) is a shape factor that assumes a value of 1, 2, or 3 for planar, cylindrical, or spherical pores, respectively. Equation [4] implies that the smaller the pore, the smaller the value of \(T_2\), that is, the adsorptive water or the water in the smaller pores relaxes faster than the free water or the water in larger pores.

### Materials and Methods

The NMR setup used in the experiments was a 23-MHz MiniMR system, developed jointly by the Institute of Rock and Soil Mechanics, Chinese Academy of Sciences, and Niumag Corporation, China. As shown in Fig. 1, the system consists of a sample tube, a magnet unit, the RF system, the temperature-controlling system, and the data acquisition and analysis system. The effective test area of the sample tube was 60 by 60 mm (height...
All the tested soil samples were compacted, layer by layer, in three layers to a targeted dry density of 1.7 g cm⁻³ in sample rings. Instead of using conventional steel oedometer rings, special Teflon plastic rings (45-mm i.d. and 20-mm height) were used to eliminate the influence of Fe in the magnetic field. All the samples were saturated using the vacuum method in the following procedure: (i) the soil sample was moved into a sealed chamber and vacuumed for 3 h, (ii) the chamber was filled with distilled, deionized water so that the sample was totally immersed and the system was vacuumed for one more hour, and (iii) the chamber was exposed to the atmosphere and the samples remained immersed in the distilled water for another 24 h.

Two groups of experiments (six samples in total) were conducted: one group (denoted by A, B, and C) for freeze–thaw tests and the other group (denoted by A-1, B-1, and C-1) for drying tests. The objective of the drying tests was twofold: to validate the results of the freeze–thaw tests and to characterize the amount of pore water retained in soils during a drying process, which is driven by increasing matric suction (by applying air pressure).

In the drying experiments, the saturated samples were first placed on the ceramic plate in a Tempe apparatus, which was tightly sealed, and then the air pressure was sequentially adjusted to some specified values such that the matric suction increased stepwise with the following sequence: 0, 10, 20, 50, 80, 120, 170, 270, 400, 650, 1300 kPa. After each suction step was applied, the sample was allowed to equilibrate; for each suction step, it took 4 h to 26 d for the sample to achieve equilibrium. The equilibrated sample was then weighed using an electronic balance with an accuracy of ±0.001 g to determine its moisture content. Finally, the sample was moved into the sample tube of the NMR apparatus for measurement. This procedure was repeated until all the suction steps were applied.

During the freeze–thaw experiments, the saturated samples were cooled in a closed-system cold bath, where the temperature was slowly changed stepwise from ~7.5 to −25°C. After each small temperature step (0.3–1°C) was applied, sufficient time was left for the sample to reach thermal equilibrium (usually 4–10 h). The samples were then moved to the NMR sample tube one by one to isolate them from the environment. In the experiments, the adopted freezing rate had to be slow enough so that the soil remained at thermal equilibrium during the freezing process. Under the specified experimental conditions, the soil samples experienced a three-dimensional freezing process in a closed system, and no ice lenses were visible to unaided eyes in the freezing samples. To prevent the pore ice from melting during the NMR measurements, the temperature of the NMR sample tube was controlled to approximately equal the temperature of the frozen sample. To this end, the cold N₂ gas cooled in a cold bath was circulated around the NMR sample tube. During the experiments, only one freeze–thaw cycle was applied.

Before starting the NMR measurement, acquisition parameters and sampling parameters were properly set. The CPMG pulse sequence used had an echo time of 240 μs, a repetition time of 1000 ms, and 10,000 echoes. After all the NMR measurements, the measured data were analyzed using an inversion procedure, and the T₂ distribution curves were determined.
Results and Discussion

The soil–water characteristic curves determined in the drying experiments are depicted in Fig. 3, showing that both the air-entry value and the residual saturation increased with the clay content of the soils. Clearly, a significant amount of pore water was trapped in all the tested soils during the drying process, resulting in the so-called irreducible saturation phenomenon. For soils with a dual-porosity structure, one of the important mechanisms behind the existence of irreducible saturation is associated with water blockage (Chen et al., 2016). For instance, in the soils of concern here, the clayey patches included small pores, while the sand matrix had large pores. During the drying process, drainage occurred first in larger pores and then in smaller pores. As a consequence, some interconnected large pores became unsaturated first, forming some poorly permeating closed boundaries surrounding fully saturated clayey patches. As such, some amount of pore water was trapped in the fully saturated clayey patches. The more the clay content, the larger amount of water was trapped.

Figure 4 illustrates the variation of the initial magnitude of magnetization, $M_0$, with the degree of saturation, $S_r$, for Samples A-1, B-1, and C-1. It is clear that variables $M_0$ and $S_r$ are very well correlated to each other, which can be characterized using a linear equation, $M_0 = \alpha S_r - \beta$, where $\alpha$ and $\beta$ are fitting parameters whose values are listed in Table 2. It is noted that when $S_r$ is smaller than a certain value, $M_0$ may become negative, implying that when the degree of saturation is lower than a certain value, the pore water has no response to the magnetic field.

In general, the physicochemical interactions between the grain surfaces and pore water are more significant in small pores than in large pores. Hence, the pore water in small pores relaxes faster than in large pores. For the same reason, for water that is more strongly adsorbed, the measured value of $T_2$ is smaller. As a general rule, for the pore water in micropores or tightly adsorptive water, $T_2$ is <60 ms; for the water in mesopores or loosely adsorptive water, $T_2$ ranges from 60 to 300 ms; for the water in macropores or bulk water, $T_2$ is >300 ms (e.g., Todoruk et al., 2003; Bird et al., 2005; Bayer et al., 2010). Recently, Jaeger et al. (2010) determined the range of $T_2$ for the adsorptive water in frozen soils and found that the $T_2$ of the adsorptive water was <5 ms (namely, 0.9–1.1 ms).

Because the dead time of the NMR device is relatively large (~70 $\mu$s), the NMR signal associated with the strongly adsorbed water may disappear within the dead time of the instrument. Thus, the observed $M_0$ is supposed to account only for the part of the pore water detectable in the soil, and the other part of the pore water is not detected by the NMR signal. To address this issue, it is useful to define the pore water content at which the NMR signal disappears as the undetected adsorptive water content. The volume fraction of undetected adsorptive water with regard to the total pore volume (denoted as $S_{a_u}$) is given in Table 2. It can be seen that $S_{a_u}$ increases almost linearly with the increase of silty clay content in the soil sample. This is understandable, since the soil of higher clay content has more specific area and pore water is absorbed. The specific area is an indicator of the intensity of the grain surface–pore water interaction in a soil (Tuller et al., 1999); that is, the larger the specific area, the more significant the adsorptive effect and the more intensive the physicochemical interaction between the pore water and the pore walls.

To determine the capillary and adsorptive water contents, one can first distinguish the detected adsorptive water from the capillary water based on the NMR measurements. Figure 5 depicts the distribution curves of $T_2$ for Samples A, B, and C at different temperatures during a cooling process. Clearly, the $T_2$ distribution

<table>
<thead>
<tr>
<th>Soil sample</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>Correlation coefficient</th>
<th>Fraction of undetected bound water</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>36.69</td>
<td>545.1</td>
<td>0.994</td>
<td>14.86</td>
</tr>
<tr>
<td>B-1</td>
<td>36.70</td>
<td>713.2</td>
<td>0.989</td>
<td>19.43</td>
</tr>
<tr>
<td>C-1</td>
<td>38.80</td>
<td>969.7</td>
<td>0.987</td>
<td>25.00</td>
</tr>
</tbody>
</table>
curves show three distinct peaks, which represent different energy states of pore water. This result is consistent with previous observations (e.g., Todoruk et al., 2003; Bird et al., 2005; Bayer et al., 2010): the two leftmost peaks are associated with the adsorbed pore water in the dual-pore structures mentioned above, whereas the right peak is related to the capillary pore water. During the cooling process, the amounts of adsorbed water and capillary water can change relatively. Figure 5 shows that for all three tested soils, there is a cutoff point around $T_2 = 5.8$ ms where the NMR signal intensity remains practically unchanged when the temperature varies. On the left-hand side of the cutoff point, the signal intensity generally increases with the decrease in temperature, whereas on the right-hand side of the cutoff point, the signal intensity decreases. Existence of the cutoff point implies that the range of low $T_2$ content (i.e., the left-hand side of the cutoff point) remains fixed as the temperature varies. Because the low $T_2$ content is closely related to adsorption, this result indeed implies that the effect of temperature on the $T_2$ of the adsorbed water is insignificant.

To identify the underlying mechanisms behind this phenomenon, it is helpful to explore the effect of temperature on the water adsorption and capillarity in the pores. Sufficient experimental results show that the activity of the pore water decreases with decreasing temperature, which, in turn, enhances water adsorption (e.g., Saravacos et al., 1986). Hence, in a closed body of fully saturated soil, where the total water content is constant, the adsorptive water content increases while the capillary water content decreases as the temperature decreases. When the soil is frozen, the surface tension on the interfaces between unfrozen pore water and pore ice increases (e.g., Domańska and Królikowska, 2010), and the interfaces become flatter (the curvatures decrease). In the case where the increase in surface tension is surmounted by the decrease of curvature, the capillary effect diminishes as the temperature decreases and the ratio of the adsorptive water content to the capillary water content increases. This is clearly shown in Fig. 5, illustrating that the peak area of the NMR signal intensity (denoted by $I$), which represents the amount of water (Gao et al., 2009), increases in the adsorptive regime (i.e., in the small-$T_2$ regime), while it decreases in the capillary and free-water regime (i.e., in the large-$T_2$ regime).

To further explore the significance of the cutoff point of $T_2$, a series of drying tests with NMR measurements was conducted on the three tested soils (named A-1, B-1, and C-1, respectively). The $T_2$ distribution curves at different applied matric suctions are given in Fig. 6 for all three soils. Clearly, in all cases, as the matric suction increases (drying), the right branch of the $T_2$ distribution curve shifts toward shorter relaxation times, and the content of large $T_2$ quickly disappears in the early beginning of the drying process until the matric suction rises to a certain value (20 kPa for A-1, 50 kPa for B-1, and 80 kPa for C-1). When the matric suction is further increased, the maximum value of $T_2$ approaches a constant. Because the above drying processes were all driven by the applied matric suction (through increasing the air pressure), the disappearing large $T_2$ content simply accounts for the amount of capillary water that was expelled out of the soil under the applied matric suction, while the remaining $T_2$ content represents the amount of adsorptive water in the soils. As shown in Fig. 6, the maximum values of $T_2$ for all the tested soils under large applied matric suction range from 5.5 to 7 ms, which is very close to the $T_2$ cutoff point, 5.8 ms. Hence, a $T_2$ value of 5.8 ms represents a threshold value that can be used to distinguish adsorptive water from capillary water in the soils.
The strength of physicochemical interactions between pore water and solid grains decreases as the distance away from the grain surface increases (Mitchell and Soga, 2005, Chapter 6). Hence, the interactions between adsorptive water (closer to the grain surfaces) and soil grains are generally stronger than those between capillary water (farther away from the surfaces) and soil grains. As a consequence, the chemical potential of the adsorptive water is lower than that of capillary water, so that the freezing (or melting) point of the adsorptive water is lower than that of the capillary water in a soil. Figure 7 demonstrates the $T_2$ distribution curves for Samples A, B, and C during the melting process. As the temperature increases, the $T_2$ distribution curve continues to expand (i.e., the pore ice is melting), and both the peak area and the maximum $T_2$ increase, although the maximum $T_2$ increases only slightly, until the temperature rises to about −3°C. For all three soils, the $T_2$ value at −3°C is very close to the cutoff point of $T_2$ at 5.8 ms. When the temperature becomes higher than −3°C, the maximum $T_2$ increases drastically and becomes significantly >5.8 ms, implying that capillary water starts to appear in the soil pores. This result is consistent with those of previous research. In

![Graphs showing $T_2$ distribution curves](Image)

Fig. 6. The proton spin–spin relaxation time, $T_2$, distribution curves during the drying process: (A) Sample A-1, (B) Sample B-1, and (C) Sample C-1.

Fig. 7. The proton spin–spin relaxation time, $T_2$, distribution curves during the thawing process: (A) Sample A, (B) Sample B, and (C) Sample C.
fact, Razumova (1965) showed that the freezing point of loosely bound water (approximately a distance of several water molecules away from the surfaces within the diffuse double layer) ranges from $-1.5$ to $-4^\circ C$, and Jaeger et al. (2010) chose $-5^\circ C$ as a criterion to determine the amounts of bound water in a frozen peat.

**Determination of Adsorptive and Capillary Water Contents**

Based on the above analysis, we suggest that there exists a threshold value of $T_2$ at which one can distinguish adsorptive water from capillary water in soils. When $T_2$ is smaller than the threshold value, the pore water is considered as adsorptive water; when $T_2$ is larger than the threshold value, the pore water is retained mainly by capillary forces. For the three soils tested in this study, the threshold value of $T_2$ is $\sim 5.8$ ms. For an open body of an unsaturated soil at constant temperature, the content of capillary water may vary, whereas the adsorptive water content remains unchanged. Hence, one can first determine both the adsorptive water content and the total pore water content and then obtain the capillary water content by subtracting the adsorptive water content from the total pore water content.

To start with, the total unfrozen water content at each temperature in the soil is first calculated. The NMR measurements can be used to determine $M_0$, which represents the current amount of the unfrozen pore water (under either the frozen or unfrozen condition). To determine the fraction of the unfrozen pore water based on the NMR measurements, one needs to calculate the total amount of pore water before freezing, when the soil is fully saturated with the unfrozen water. This can be done simply by making a temperature correction to the NMR signal according to the Curie law. Figure 8 presents the fit of the relationship between the temperature $T$ and $M_0$. Clearly, a linear relationship exists between $T$ and $M_0$ before freezing for all three soils:

$$M_0 = \alpha - \beta T$$  \[5\]

The corrected $M_0$ based on Eq. [5] represents the total amount of pore water existing in the fully saturated soil at a specified temperature. Therefore, at a specified temperature, the total fraction of unfrozen pore water (denoted by $S_r$) is related to the ratio of the measured $M_0$ to the value calculated from Eq. [5]:

$$S_r = \frac{M_0(\text{measured})}{M_0(\text{calculated})}(1 - S_u^a) + S_u^a$$  \[6\]

Once the unfrozen water content is determined, the adsorptive water content (and thus the capillary water content) can be calculated based on the $T_2$ measurements. For convenience, the area under the $T_2$ distribution curve is termed the peak area (Gao et al., 2009). It is noted that the peak area represents the population of water molecules. Let $A_a$ and $A_c$ be the peak areas for the adsorptive and capillary water, respectively; then the total adsorptive water fraction ($S_a$) is given by

$$S_a = S^a_u + \frac{A_c}{A_a + A_c}(S_r - S^u_a)$$  \[7\]

where $S_r$ and $S^u_a$ are the total fraction of unfrozen water and the undetected fraction of adsorptive water (given in Table 3), respectively. It is noted that quantity $A_a$ plus $A_c$ accounts for the detected unfrozen water content, which is equal to $S_r$ minus $S^u_a$. The fraction of capillary water, $S_c$, is given by

$$S_c = \frac{A_c}{A_a + A_c}(S_r - S^u_a)$$  \[8\]

Figure 9 depicts the variations in the total fraction of adsorptive water ($S_a$) and the total fraction of unfrozen water ($S_r$) with temperature for the three tested soils during a freeze–thaw cycle. Noticeably, for all the tested soils, a significant amount of unfrozen water can still exist, in the form of adsorptive water, in the soil pores even when the temperature is lower than $-15^\circ C$. For instance, in Sample C, the total fraction of unfrozen water is up to 28% even at a temperature lower than $-20^\circ C$. In general, the amount of remaining unfrozen water at low temperature increases.

<table>
<thead>
<tr>
<th>Soil sample</th>
<th>Fitting parameters</th>
<th>Correlation coefficient</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>3900.44</td>
<td>11.03</td>
</tr>
<tr>
<td>B</td>
<td>3689.79</td>
<td>22.03</td>
</tr>
<tr>
<td>C</td>
<td>3470.70</td>
<td>15.72</td>
</tr>
</tbody>
</table>
with the increase in the clay content. The reason that such a significant portion of pore water remains unfrozen in the soil has not been fully understood, and research in this regard needs to be pursued in the future. Nonetheless, such a phenomenon may be partially attributed to metastable nucleation (e.g., Watanabe and Mizoguchi, 2002; Bittelli et al., 2003). In metastable nucleation, the pore water in a metastable state can remain unfrozen far below the thermodynamic freezing point.

It is clear that both the variations of $S_a$ and $S_r$ with temperature are hysteretic during the freeze–thaw cycle. Several mechanisms may account for the hysteresis of the total unfrozen water content including capillary effect, metastable nucleation, and pore blocking (Watanabe and Mizoguchi, 2002; Bittelli et al., 2003; Drotz et al., 2009; Anderson et al., 2009). The capillary effect originates from pore geometry, which induces curvature in confined water and lowers the water activity. The effect of pore geometry becomes dominant in the capillary regime. Metastable nucleation is a common thermodynamic phenomenon occurring in the crystallization process of pore water in a metastable state. The crystallization process starts with nucleation, which appears first in larger pores where the water potential and freezing point are higher and the capillary effect is dominant. Hence, the nucleation occurs mainly in the capillary regime. The nucleation of capillary water can induce the delay of phase transition and thus results in the hysteresis of the adsorptive water content. The pore-blocking effect is associated with the process in which pore ice invades the liquid-filling pores, which is analogous to the process of the gaseous phase displacing the pore water during a drying process. Hence, pore blocking occurs also mainly in the capillary regime.

Unlike the hysteresis of the unfrozen water content, the hysteresis of the adsorptive water content is unexpectedly significant. Also, the adsorptive water content after the freeze–thaw cycle is smaller than its original value before freezing. These phenomena cannot be explained simply by introducing the above-mentioned mechanisms, and some other mechanisms may have come into play. One of these mechanisms is related to the structural change of the soils during the freeze–thaw cycle (Chamberlain and Gow, 1979; Chamberlain et al., 1990; Wang and Wang, 1998). To illustrate such a mechanism, consider two extreme types of soils with idealized packing structures as shown in Fig. 10. In the first case (Fig. 10a), coarser grains make up the packing structure, with macropore spaces filled with small clay particles. In the second case (Fig. 10b), the coarser grains have no contact with each other and instead they float in a flocculated clay matrix.

Fig. 9. Variations in the adsorptive water ($S_a$) fraction and the total unfrozen water ($S_r$) fraction for three soils during a freeze–thaw cycle: (A) Sample A, (B) Sample B, and (C) Sample C.

Fig. 10. Schematic of two idealized packing structures: (a) coarser grains make up the packing structure, with macropore spaces filled with small clay particles, and (b) the coarser grains have no contact with each other and instead they float in a flocculated clay matrix.
In the first case, clay particles control the micropore distribution, and the small particles can move in the macropores within the skeleton. The clay particles in the macropores can be arranged into packets with a flocculated structure. With this arrangement, the coarse-grained particles control compressibility, while the finer grained clay particles control the permeability. When the soil freezes, ice crystals first form in the macropores where the water potential and freezing point are higher, sucking pore water from the surrounding clay packets into the macropores. As a consequence, the adsorbed water films around the particles become thinner, and the clay particles become closer and more aggregated. Hence, after a freeze–thaw cycle, the adsorptive water content in the soils decreases significantly.

In the second case, both the compressibility and the permeability are controlled by the arrangement of the clay particles. When the soil freezes, ice crystals first form in the preexisting small fissures where the water potential and freezing point are higher than the adsorbed water. As the temperature decreases, the volume of the fissures may increase because of crystallization, resulting in a more heterogeneous structure in the soils. Because the volume of the preexisting fissures is much less than that of the large pores in the first case, less water is adsorbed from the surrounding clay particles, and dehydration of clay particles is not as significant as in the first case. Hence, it can be expected that the difference in adsorptive water content before and after the freeze–thaw cycle is smaller than that in the first case.

Sample A has a first-type structure, as evidenced by the significant difference between the adsorptive water contents before and after the freeze–thaw cycle, whereas Samples B and C behave more like the second type of soil.

For comparison, both the variations of the adsorptive water fraction ($S_a$) and the capillary water fraction ($S_c$) with temperature are given in Fig. 11. In addition to the hysteresis appearing in both $S_a$ and $S_c$, a soil with higher clay content has more adsorptive water. This result is expected, since the adsorptive effect, and thus the physicochemical interactions between clay and water, is more significant in a soil with higher clay content.

In all three tested soils, the capillary water content is significantly less than the adsorptive water content. Although this result is somewhat surprising, it is supported by limited experimental evidence available in the literature. By analyzing the experimental results of Speswhite kaolin (Tarantino and De Col, 2008), Boom clay (Romero, 1999), Barcelona silt (Gens et al., 1995), and bentonite-enriched sand (Dineen et al., 1999), Baker and Frydman (2009) concluded that the pore water potential (i.e., matric potential) in a compacted soil remained practically independent of the dry density of the soil up to a very high water content. For example, in the compacted Speswhite kaolin, with a dry density ranging from 0.96 to 1.45 Mg m$^{-3}$ (1 Mg = 1000 kg), the matric potential was practically independent of the dry density until the water content increased to 0.32 (w/w), corresponding to a saturation of $\geq 90\%$; in the bentonite-enriched sand, the matric potential varied significantly with the dry density only when the saturation was $>80\%$. Because the capillary effect becomes significant only when the matric potential significantly depends on both water content and dry density (or void ratio), the above experimental results imply that a very significant portion of pore water is adsorbed.

To explain the phenomena, first note that soils usually have angular or slit-shaped pores, and the corners and crevices of such pores can store some amount of capillary water (Tuller et al., 1999). Although this part of the pore water is capillarity dominated, it stays in the pores as adsorbed. In addition, the soils tested here
A new procedure based on the NMR technique is proposed to determine the total unfrozen water content, adsorptive unfrozen water content, and capillary unfrozen water content in frozen soils. In this procedure, the total water content and the adsorptive water content in the soil are first determined based on the NMR relaxometry measurements, and the amount of capillary water is obtained by subtracting the adsorptive water content from the total water content.

For all the tested soils, the measured $T_2$ distribution curves showed three distinct peaks corresponding to the different energy status of pore water. A threshold value of $T_2$ exists, below which the NMR signal intensity became stronger, and above which the NMR signal intensity became weaker as the temperature decreased. As such, the threshold value separated $T_2$ into two distinct regimes: the adsorptive regime for small $T_2$ and the capillary regime for large $T_2$, from which the adsorptive unfrozen water content could be exactly determined.

The relationship between adsorptive water content or capillary water content and temperature showed clear hysteretic behavior for all three tested soils during a freeze–thaw cycle. Microscopic mechanisms underlying the hysteric phenomena were analyzed and identified. It was suggested that the hysterisis behavior of the capillary water content or adsorptive water content was attributable to a capillary effect, metastable nucleation, pore blocking, and variation of the microstructure. It was found that in all the tested frozen soils, the adsorptive water content was significantly more than the capillary water content. This result is supported by the experimental evidence inferred from the pore water potential measurements of various soils.

The proposed procedure can be used not only to analyze the state of pore water but also to determine the amount of pore water in different states in a soil, providing an alternative way to investigate the microstructural alteration and the hydromechanical behavior of unsaturated and frozen soils. The tested soils adopted in this study were artificially made, and naturally deposited soils should be used to validate the proposed procedure. In addition, the effect of soil composition, solution pH value, and cation exchange capacity on the experimental results also needs to be addressed. All these are the subjects of our future research.

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References


