

PHYSICAL AND CHEMICAL PROCESSES IN FROZEN GROUND AND ICE

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APPLICATION OF WATER POTENTIAL METHOD FOR UNFROZEN WATER CONTENT DETERMINATION IN DIFFERENT FROZEN SOILS

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The paper presents results of the unfrozen pore water content determination from measured water potential (activity). The water potential method is applied to frozen soils with different particle size distribution, chemical and mineral compositions, salinity and organic matter contents (peat). The unfrozen water content in frozen soils correlates with specific surface area at different negative temperatures. The method is applicable to saline and peat-bearing soils.

Frozen sediments, unfrozen water, soil, pore water activity, water potential method, specific surface area, particle size distribution, mineral composition, salinity, organic matter

INTRODUCTION

The first experiments on pore moisture freezing in Russia dated back to the 1930s [Andrianov, 1936]. The idea that some pore moisture in artificially frozen soil and in natural permafrost may remain liquid appeared already in the fundamental treatise “General Geocryology” by Sumgin *et al.* [1940]. The idea led to the phase equilibrium principle of pore water formulated on the basis of experimental evidence [Tsytoovich, 1945; Are, 2014]: frozen ground at any low negative temperature always bears some amount of residual liquid water which varies as a function of temperature and pressure.

Further instrumental advances in the 1950–1970s provided a wealth of experimental constraints on the sensitivity of the pore water phase composition to grain size, mineralogy, and salinity of soils [Nersesova, 1953; Ananyan, 1961; Tyutyunov, 1961; Nersesova, Tsytoovich, 1963; Tyutyunov, Nersesova, 1963; Tsytoovich, 1973; Votyakov, 1975; Ershov *et al.*, 1978]. Unfrozen pore water in frozen soils was found out to exist in capillary, film, adsorbed, or other forms [Ershov *et al.*, 1979a; Ershov, 1986; Komarov, 2003; Cheverev, 2003a,b, 2004]. Its content was studied in terms of effect on thermal, mechanic, and electrical properties of permafrost, as well as on various physicochemical processes [Grechishchev *et al.*, 1980; Ershov *et al.*, 1987, 1999; Ershov, 1995, 1996; Frolov, 1998; Vyalov, 2000; Roman, 2002; Andersland,

Ladanyi, 2003; Komarov, 2003; Cheverev, 2004; Starostin, 2008; Sun *et al.*, 2015; Xu *et al.*, 2016, Liao *et al.*, 2017; Zhao *et al.*, 2017].

Experimental methods for studying the phase composition of pore water in frozen ground include direct cryoscopic, sublimation, and contact measurements of liquid water contents [Ershov *et al.*, 1979b; Komarov, 2003; Cheverev, 2004], as well as the methods of hygroscopic absorption, desorption [Cheverev *et al.*, 2005], nuclear magnetic resonance (NMR), time-domain reflectometry (TDR) [Tice *et al.*, 1978, 1982; Patterson, Smith, 1981; Spaan, Baker, 1995; Ishizaki *et al.*, 1996; Watanabe, Mizoguchi, 2002; Suzuki, 2004; Yoshikawa, Overduin, 2005; Watanabe, Wake, 2009; Chai *et al.*, 2018; Tang *et al.*, 2018], calorimetry [Williams, 1964; Anderson, Tice, 1972; Kozłowski, 2016], thermometry [Starostin, Petrov, 2013], and ultrasonic measurements [Frolov, 1998]. The applicability of different methods depends on soil type and temperature range, required instrumental facilities, and time, but most of them are labor and time consuming. In this respect, the techniques for determination of unfrozen pore water in permafrost are to be updated and innovated.

Alternatively, the amount of unfrozen pore water can be estimated by thermodynamic calculations from measured water potential (activity). The measured pore water potential (ϕ) is related with the

thermodynamic water activity (a) as [Campbell et al., 2007]:

$$\varphi = \frac{RT\rho}{M} \ln a, \quad (1)$$

where R is the universal gas constant (8.314 J/mol·K); T is the sample temperature (K); M is the water molecular weight (18.015 g/mol); ρ is the water density (1.0 g/cm³).

This approach lied at the base of the desorption method [Cheverev, 2004; Cheverev et al., 2005] in which the contents of water remaining liquid at negative Celsius temperatures were inferred from relative vapor pressure over the pore water at a positive (room) temperature. The same principle works in the water potential method which was grounded theoretically more than ten years ago [Istomin et al., 2008, 2009, 2017a,b]. In fact, the desorption and water potential methods measure the same parameter (vapor pressure over pore fluid in a soil system), but differ in the way and time of measurements. Water potential sampling is faster due to advanced automatic facilities [Istomin et al., 2017a,b]. Furthermore, pore water contents remain invariable during the run while equilibrium in a small volume can be achieved tens of times faster than in the desorption technique which requires drying of samples.

The potential method (called *potentiometric* in Russia) was used to estimate the amount of unfrozen pore water in model soil samples within a large range of negative temperatures (till -15 °C). The contents of equilibrium liquid pore water calculated from water potential data fit well the results of direct contact measurements in natural clay [Istomin et al., 2017a,b].

This study focuses on the applicability of the water potential method to frozen soils of different mineralogical and chemical compositions.

METHOD

The method consists in measurements of pore water potential in freezing soil samples at each step of progressively decreasing contents of unfrozen water, with subsequent thermodynamic calculations to convert the potential values to equivalent temperatures

at which pore water is in equilibrium with ice in free volume [Istomin et al., 2009].

The water potential of pore water is measured on WP4-T or WP4-C modifications of a WP4 meter [Istomin et al., 2009] designed by METER Group (formerly *Decagon Devices*), USA [Campbell et al., 2007]. The instrument samples the pressure of water vapor over wet soil by the dew point method [Campbell et al., 2007] in a range of 15 °C to 43 °C, to a precision of ± 0.05 MPa at 0 to -5 MPa and ± 1 % at -5 to -50 MPa, as estimated with reference to calibration on standard solutions. The accuracy of the activity values depends on their range: 0.0025 at 0.7 to 0.85; 0.0015 at 0.85–0.9, about 0.001 at 0.9–0.95, and within 0.0005 at 0.9–1.0.

The water potential is measured in natural soils or in laboratory-made model samples of known moisture content prepared as 0.5 cm thick pellets in a round sample cup 3.8 cm in diameter, the size being tailored to the instrument specifications. The measurements are first applied to wet natural or model samples (the latter approach the total moisture capacity). Then the samples are dried stepwise to 1–2 %, and their moisture content and water potential are determined at each of six or seven steps. The bulk moisture content is determined by weighing the soil samples on analytical scales, to a precision of ± 0.003 g, before and after the water potential sampling. The acquisition commonly takes 20 to 30 min (60 min the longest for dry mud): the time required for soil moisture and vapor-bearing air in the sample chamber to reach full equilibrium. The WP4 system is connected to a PC using *Hyper Terminal* for automation of data acquisition and processing.

The pore water activity in the range from 0.75 to 1.0 is related to the temperature of bulk ice – pore water equilibrium (t_{eq} , °C), in a sample with the specified water content (W , %), as [Istomin et al., 2017a,b]

$$t_{eq} = 103.25 \ln a + 5.57(1-a)^2. \quad (2)$$

The equation actually relates the pore water activity with the negative temperature of the sample [Istomin et al., 2017a, 2018]. The total water content of the sample (W , %) corresponds to the amount of

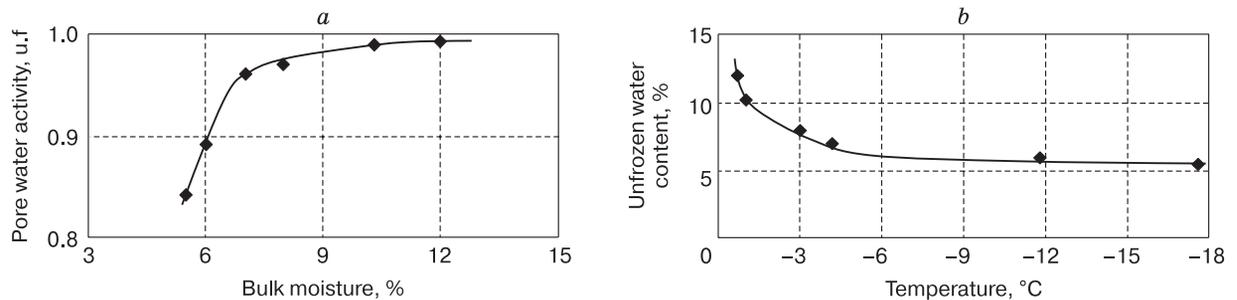


Fig. 1. Bulk moisture dependence of pore water activity (a) and temperature dependence of unfrozen water content (b) for a polymineral clay sample.

Table 1. Properties of soil samples

Lithology	Sampling site	Mineralogy*, %		D_{sal} , %
1	2	3		4
Montmorillonite clay	Djembel, Turkmenistan	montmorillonite andesine biotite	93 3 3	1.99
Kaolinite clay	Novokaolinovo (Chelabinsk area)	kaolinite quartz muscovite	92 6 2	0.04
Polymineral clay	Kudinovo (Moscow area)	quartz microcline illite kaolinite X-ray	45 9 9 5 28	0.10
Clay silt-1	South Tambey gas-condensate field (Yamal)	quartz albite chlorite muscovite kaolinite orthoclase	46 25 10 7 5 7	0.34
Clay silt-2	East Messoyakh oil-gas-condensate field (Gydan)	quartz montmorillonite albite-oligoclase orthoclase muscovite kaolinite amphibole	38 20 15 11 6 4 2	0.06
Clay silt-3	East Messoyakh oil-gas-condensate field (Gydan)	quartz montmorillonite albite-oligoclase orthoclase kaolinite muscovite amphibole chlorite	41 15 13 11 5 4 3 2	0.06
Clay silt-4	Erkuta gas explosion crater (Yamal)	quartz albite microcline illite chlorite amphibole kaolinite	45 22 10 9 5 3 3	0.05
Clay silt-5	East Messoyakh oil-gas-condensate field (Gydan)	quartz albite-oligoclase montmorillonite orthoclase muscovite kaolinite	52 18 10 9 3 2	0.04
Silt-1	East Messoyakh oil-gas-condensate field (Gydan)	quartz montmorillonite albite-oligoclase orthoclase muscovite kaolinite	30 25 15 12 4 2	0.04
Silt-2	Vorkuta	microcline + albite quartz illite montmorillonite x-ray	45 38 9 3 <5	0.09
Silt-3	Tiksi, Laptev Shelf, BH 2D-13, core depth 12–19 m	quartz albite microcline chlorite illite smectite	37 24 17 7 6 5	0.64

Table 1 (continued)

1	2	3		4
Silt-4	East Messoyakh oil-gas-condensate field (Gydan)	quartz albite-oligoclase orthoclase	41 17 16	0.02
Sand	Lubertsy	quartz	>90	0.01

Note. X-ray = X-ray amorphous matter; D_{sal} = salinity.
*Element contents >1 %.

pore water that remains unfrozen at negative temperatures, which is converted from the empirical pore water activity.

Some examples are shown in Fig. 1 for a polymineral clay sample: the moisture dependence of pore water activity (panel *a*) and temperature (t , °C) dependence of the amount of unfrozen water (panel *b*).

In the same way, the bulk moisture dependence of pore water activity is obtained for soil samples of different compositions and particle sizes. Then the temperature at which pore water in a sample of a given bulk moisture is in equilibrium with bulk ice is found by thermodynamic calculations.

SAMPLES

The water potential measurements were applied to soil samples of different particle sizes and compositions (Tables 1 and 2). The mineralogy was analyzed by X-ray diffractometry (XRD) and the particle sizes were determined by aerometry according to *State Standard [2015]* (Document 12536-2014). The contents of dissolved salts were estimated by decanting [Trofimov, Korolyov, 1993]. The amount of organic matter was measured by ignition till constant weight

according to *State Standard [2017]* (Document 23740-2016). The specific surface area of the samples was determined on a SORBI-MS analyzer, by nitrogen adsorption following the BET method based on the Brunauer–Emmett–Teller theory of 1938 explaining physical adsorption of gas molecules on the solid surface. The samples had either natural or laboratory-made salinity. In the latter case, 0.2, 0.5 and 1.0 mol/L aqueous solutions of NaCl and CaCl₂ (NaCl and CaCl₂ crystals dissolved in distilled water) were added to air-dry soil specimens with a pipette and mixed carefully in a glass bowl.

Water potential method against other methods for determination of unfrozen water content

Previously, the water potential-based estimates of unfrozen water contents were checked against the results of the contact method [Ershov *et al.*, 1979*b*] for kaolinite and polymineral clay, which showed good agreement [Istomin *et al.*, 2017*a*]. We additionally compared our results with those of the contact and NMR methods for soil samples of different compositions and particle sizes (Fig. 2): both methods for clay silt-2 (Fig. 2, *a*) and NMR only for clay silt-1 and clay silt-4 (Fig. 2, *b*, *c*, respectively). Nuclear mag-

Table 2. Particle-size distribution of soil samples

Lithology	Lithology and grain size*	Particle-size distribution, %			Organic matter content, %	Specific surface area, m ² /g
		1–0.05 mm	0.05–0.001 mm	<0.001 mm		
Montmorillonite clay	Heavy clay	0.3	46.2	53.5	<1	~70**
Kaolinite clay	Light silty clay	4.5	70.9	24.6	<1	11.7
Polymineral clay	Light silty clay	31.0	49.0	20.0	<1	26.6
Clay silt-1	Heavy silty clay	21.1	63.9	15.0	2.4	14.1
Clay silt-2	Light silty clay	24.5	56.2	19.3	3.1	23.1
Clay silt-3	Light silty clay	27.4	62.3	10.3	6.2	9.5
Clay silt-4	Light silty clay	16.2	78.8	5.0	0.4	18.0
Clay silt-5	Sandy silt	50.5	36.3	13.2	2.7	12.9
Silt-1	Fine silt	43.4	47.4	9.2	5.3	8.1
Silt-2	Fine silt	41.8	53.7	4.5	4.1	5.0
Silt-3	Fine silt	34.0	60.0	6.0	2.2	8.8
Silt-4	Inhomogeneous silty sand	74.2	18.1	7.7	1.0	5.1
Sand	Medium-fine homogeneous sand	94.8	3.1	2.1	<1	0.2

* According to *State Standard [2013]* (Document 25100-2011).

** Surface of montmorillonite particles, without regard to interlayer surfaces.

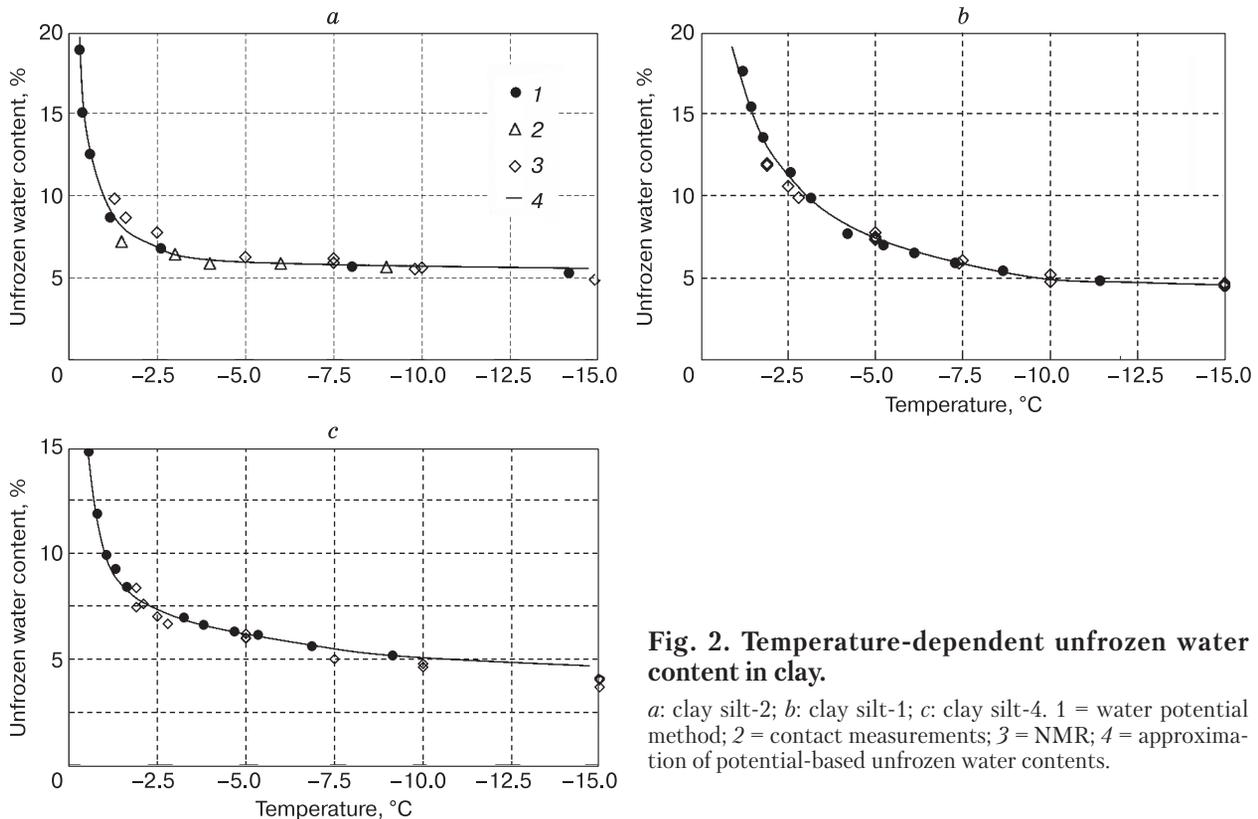


Fig. 2. Temperature-dependent unfrozen water content in clay.

a: clay silt-2; *b:* clay silt-1; *c:* clay silt-4. 1 = water potential method; 2 = contact measurements; 3 = NMR; 4 = approximation of potential-based unfrozen water contents.

netic resonance (NMR) spectroscopy was performed on an Oxford Instruments *Geospec 2-53* spectrometer. The NMR spectroscopy is based on interaction of hydrogen nuclei with external magnetic fields. The frozen sample placed in a constant magnetic field is exposed to radio-frequency pulses intermittent with sampling of NMR responses. The relaxation times T_1 and T_2 estimated from spin echo amplitudes provide integrated parameters of the sample, such as the amount of free and bound pore fluids (including liquid water). The total volume of unfrozen pore water (cm^3) in frozen soil is calculated from processed T_2 relaxation times (ms). The NMR spectrometer operated at a frequency of 2 MHz, with a magnetic field of 0.05 T, was additionally equipped with a set of gradient coils on each side of the magnet. This configuration allowed measuring the total amount of unfrozen water and yielded a 1D vertical profile of liquid water contents along the sample axis, as fast as in 60 s.

Good fit between the water potential method and the results of contact and NMR measurements was obtained at warm and cold negative temperatures (till -15°C), with a misfit no more than 0.5°C in temperature and 0.5 % in water content, or generally within the precision of the two methods.

RESULTS

The pore water potential was measured in soil samples that differed in particle size, mineralogy, sa-

linity, and organic matter contents, and the measured values were then converted to the contents of unfrozen water. Thus obtained liquid water contents were tested for sensitivity to the various soil properties: particle size distribution, clay mineralogy, salinity (contents and composition of salts), and relative contents of organic matter.

The sensitivity to particle sizes was investigated in natural soils (Fig. 3, *a*) and in sand-clay mixes with different percentages of kaolinite or montmorillonite (bentonite) in a mainly quartz matrix (Fig. 3, *b, c*). Soils with smaller grain sizes contained more unfrozen pore water. In sand, almost all pore water froze already at -1.4°C , while the unfrozen water contents at -10°C increased from 1.6 % in silt-2 to 6 % in clay silt-2, and on to 11.5 % in polymineral clay. The pore moisture froze at progressively lower temperatures as the samples became finer-grained: at -1°C in sand, -3°C in silt, and -7°C to -8°C in clay silt (Fig. 3, *a*).

The mixes of sand with different clay percentages (Fig. 3, *b, c*) contained notably more liquid pore water, and the effect of montmorillonite was stronger than that of kaolinite, especially at low temperatures. The difference in unfrozen water contents between the mixes with kaolinite and montmorillonite particles was greater at higher percentages of the clay component. The sensitivity of the unfrozen water contents in the sand-clay mixes to clay mineralogy is due to the fact that kaolinite-bearing samples have

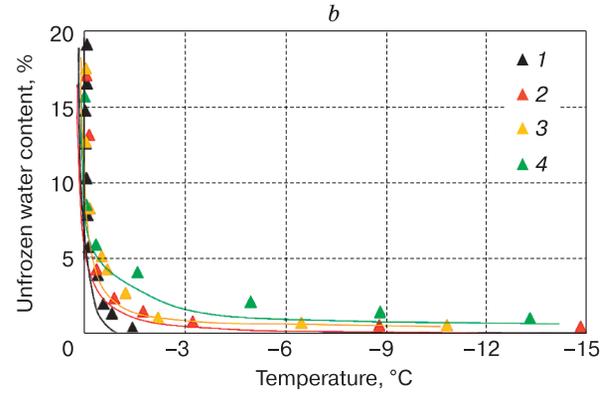
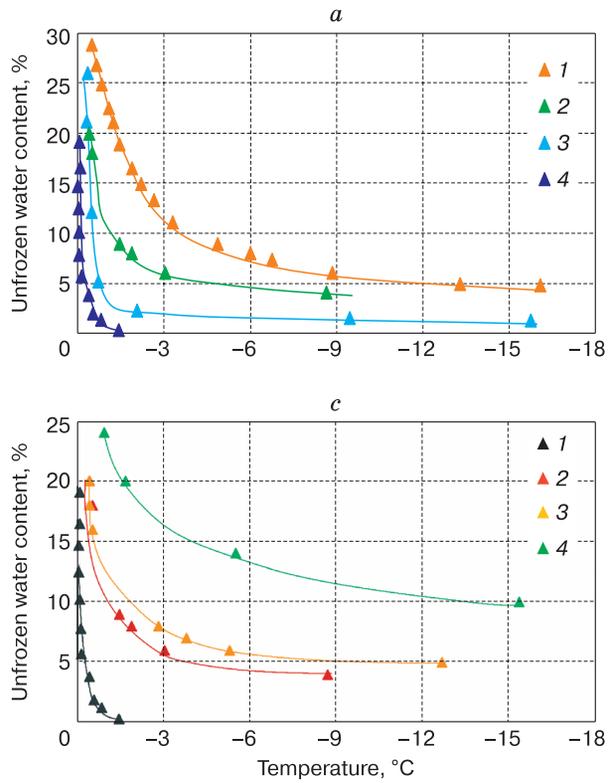


Fig. 3. Temperature-dependent unfrozen water contents in soils of different grain sizes (a) and in sandy soil with different contents of kaolinite (b) and montmorillonite (bentonite) (c) clay.

Symbols in panels a–c: 1 = clay silt-1; 2 = silt-1; 3 = silt-2; 4 = sand (a); 1 = sand; 2 = sand with 15 % kaolin; 3 = sand + 25 % kaolin; 4 = sand + 40 % kaolin (b); 1 = sand; 2 = sand with 15 % bentonite; 3 = sand + 25 % bentonite; 4 = sand + 40 % bentonite (c).

times smaller specific surface areas than those with montmorillonite particles: 11.7 m²/g against 70 m²/g in the samples we used (Table 2; Fig. 4). The correlation between the contents of unfrozen pore water and the specific surface area depended on temperature: the data points of the water content increasing from 1.5 to 6 % proportionally to the area increase from 5.1 to 26.6 m²/g (Fig. 4) fitted closely the trend line ($R^2 = 0.9603$) at -10 °C, but showed a worse R-square fit at -5 °C ($R^2 = 0.8876$). Furthermore, the two parameters lost any correlation at -2 °C, as a result of pore space changes.

Thus, the specific surface area is a key control of the unfrozen pore water content at temperatures below -4 or -5 °C, while the pore space structure, which affects the amount of capillary water, is more important at warmer negative temperatures [Ershov et al., 1978, 1979a; Cheverev, 2004].

Salinity is another major control of pore moisture composition in frozen soil. Its effect varies with the content and chemistry of dissolved salts. Saline soils have lower freezing points, and thus more pore water remains liquid. See Fig. 5 for the temperature dependence of unfrozen water contents in the presence of saline polymineral (Fig. 5, a) and kaolinite (Fig. 5, b, c) clay components, at above-eutectic temperatures. The contents of unfrozen water in polymineral clay at -5 °C were 8 % in the case of NaCl salinity ($D_{\text{sal}} = 0.17$ %) but 6 % in non-saline samples (Fig. 5, a). As the salinity increased to $D_{\text{sal}} = 0.4$ %

and then to 0.8 %, the liquid water amount increased correspondingly to 9.5 % and 12 %. The freezing point values shifted to colder temperatures from 0 °C in non-saline clay to -3 °C at a higher salinity (Fig. 5). The trends in the case of kaolinite were the same (Fig. 5, b).

The behavior of unfrozen pore water turned out to be poorly sensitive to salt composition, which is evident in the patterns for kaolinite clay with NaCl and CaCl₂ pore fluids (Fig. 5, b, c). The patterns for CaCl₂ and NaCl salinity are quite similar (Fig. 5, b, c): e.g., the amount of liquid pore water in kaolinite clay

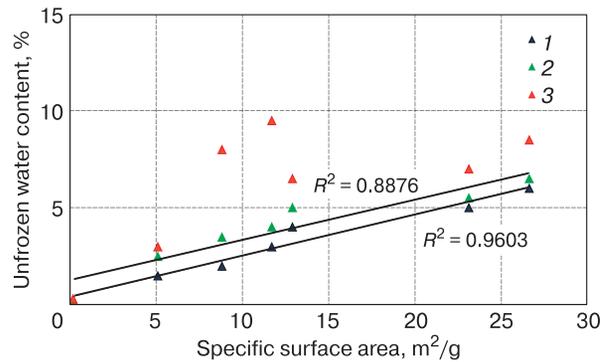


Fig. 4. Unfrozen water content in non-saline soils of different particle sizes as a function of specific surface area at fixed negative temperatures: -10 °C (1), -5 °C (2), -2 °C (3).

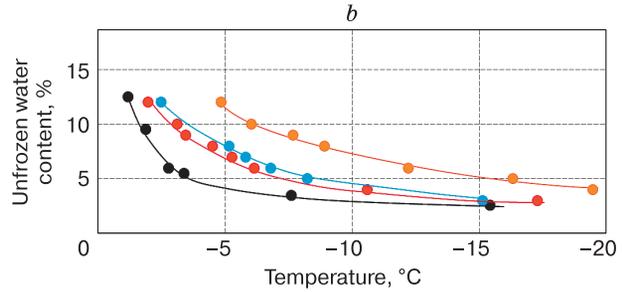
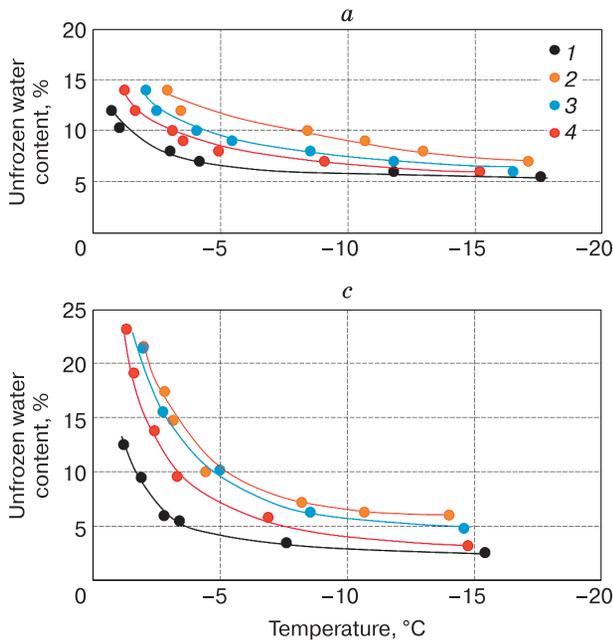


Fig. 5. Temperature-dependent unfrozen water content in soils of different salinities (D_{sal}):

a: polymineral clay, NaCl; *b*: kaolinite clay, NaCl; *c*: kaolinite clay, CaCl_2 ; 1–4 are salinity values (D_{sal}): 0 (1), 0.8 % (2), 0.4 % (3), 0.17 % (4).

at -5°C increased from 4 % in a non-saline sample to 7.5 % at $D_{\text{sal}} = 0.17\%$ and from 0.8 to 10 % at higher salinities ($D_{\text{sal}} = 0.4$ and 0.8). The difference is still smaller at cold negative temperatures, since the two saline solutions have similar activity. The similarity of NaCl and CaCl_2 effects on the amount of liquid pore water was also reported earlier [Ershov *et al.*, 1979a, 1999; Cheverev, 2004].

The liquid phase of pore moisture is also sensitive to the content of organic matter (peat) which is highly hydrophilic and can hold water. The effect of organic contents on the amount of unfrozen water in frozen soils was studied in natural clay silt samples with relative contents of organic matter (I_r , %) increasing from 0.4 % to 6.2 %. The liquid water content was higher in the presence of a greater organic component at -5°C (3.5 % at $I_r = 0.4\%$; 5 % at

$I_r = 2.7\%$; 6 % at $I_r = 3.1\%$; and 8 % at $I_r = 6.2\%$) and increased linearly as a function of I_r within the temperature range from -1 to -10°C (Fig. 6). This result confirms the earlier inference that organic matter causes an additional effect on the contents of unfrozen pore moisture [Ershov *et al.*, 1987; Cheverev, 2004].

CONCLUSIONS

The suggested method for estimating the amount of pore water that can remain liquid in freezing soils consists in measurements of water activity (potential) with subsequent thermodynamic calculations that convert the activity values to the pore water-ice equilibrium temperature. The method has demonstrated high performance and good agreement with the results of direct contact measurements (within 0.05°C) and NMR spectroscopy, at both warm (about -1°C) and cold (down to -15°C) negative temperatures in the latter case.

The pore moisture behavior was studied in terms of its sensitivity to particle-size distribution, clay mineralogy, specific surface area, and salinity. The specific surface area is a key control of the pore moisture composition, judging by its correlation with the amount of liquid pore water in the analyzed soil samples at temperatures below -5°C .

The potential method is applicable to saline and peat-bearing soils, in which predicting unfrozen water contents by other methods may be problematic.

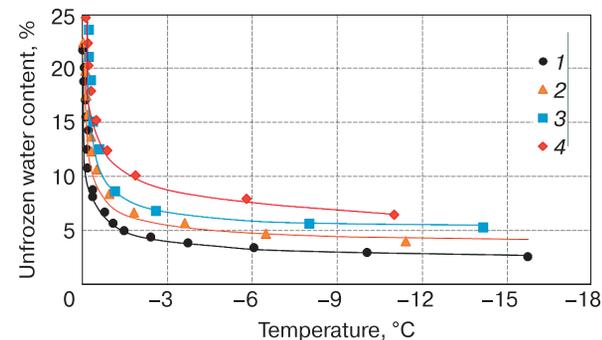


Fig. 6. Temperature-dependent unfrozen water content in soils with different contents of organic matter (I_r): 0.4 % in clay silt-4 (1), 2.7 % in clay silt-5 (2), 3.1 % in clay silt-2 (3), 6.2 % in clay silt-3 (4).

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