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FROZENING OF SOIL SOLUTIONS AS A FACTOR OF THE CHANGING PROPERTIES OF SOILS, THEIR GENESIS AND FERTILITY

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Abstract: *It is shown that the winterizing of soil solutions leads to increase in their concentration, ionic force, a mass fraction of sodium and potassium that in total with increase in solubility of gases leads to destruction of a mineral part of soils, aluminosilicates and can influence destruction of construction objects. This process is followed by increase in contents water-soluble K, Ca, Mg, Fe and is shown by change of character of infrared ranges and derivatogramm of soils. The maintenance of cations in solutions at their winterizing is caused by solubility of rainfall which is (in mg/l): for Fe(OH)2 at 2 °C - 4,5·10-5; Fe (OH)3 - 2·10-8; for KCl - 34,2; K2SO4 - 7,4; for Na2SO4 - 52,9; for MgCl2 - 54,6; MgSO4 - 18; MgCO3·H2O - 0,13. When freezing point to destruction of the soil absorbing complex also the data of infrared spectroscopy and a derivatografiya obtained by us. Freezing of soil solutions divides them into 2 fractions: freezing and nonfreezing at the accepted negative temperature and time of her action. In nonfreezing fraction of soil solution resistance is lower, it is more than contents of ions. It allows to say about more intensive destruction of soils under the influence of this fraction. In not frozen part of soil solutions, in comparison with frozen, the ratio of cations changes, however, in connection with existence in soil solutions of humic substances, complexes and associates, regularity of change differ from established for a kriolitozona in general.*

Key words: *freezing of solutions, cryogenesis, ion mobility in soils, potassium, calcium, magnesium, iron.*

Introduction

When the soil solutions freeze, their freezing out takes place. The frozen part of the solution is less mineralized, the unfrozen part contains large concentrations of elements. Theoretically, this leads to the destruction of the mineral part of the soil under the influence of the greater ionic strength of the solutions. However, it is not clear how the state of organic compounds changes. In different soils, this process must have its own features. The ratio of ions in solutions should also vary.

The freezing point of the solution depends on the pH, the humus content, the ionic strength of the solution, and the presence of surface active substances in it. Thus, different microzones of soils freeze in different time, which determines migration processes. An increase in the concentration of salts and the ionic strength of the solution leads to a decrease in the freezing point and an increase in the boiling point of the soil solutions. An increase in the content of humic substances in the soil solution leads to evaporation of water at lower temperatures and to freezing at higher temperatures. The change in the composition of soil solutions during their freezing is estimated in this study.

Objects and methods

The object of the research was the taiga cryogenic soil [12], sod-podzolic soils [5, 9] and for comparison - a sample of arable layer of ordinary chernozem [3,4].

The method of the research consisted of evaluating the water-soluble and motile compounds of Ca, Mg, K, Fe, the resistance in the soil solution of frozen and unfrozen samples at $-1^{0}C$, in evaluating the infrared spectra [6], and derivatograms of original samples and samples after 5-fold freezing.

Results and discussion

In our studies in 6 series of experiments, the changes in the ion composition of soil solutions of the taiga-forest zone and permafrost-taiga soils during their freezing were estimated [12, 14]. The following Tab 1. shows the data obtained in experiment No. 1.

As it can be seen from the presented data, when the solutions are frozen out, the content of potassium increases, but the iron content and resistance vary for light and heavier soils unequally. Sokolov I.A. pointed out the changes in the composition of soil solutions during freezing for light and clay soils [15]. However, in the studied soils, during freezing in non-hardened solutions the resistance decreases and the content of iron increases significantly [12, 14].

The data in Tab. 2 shows that, the frozen and unfrozen solutions differ in iron content and in resistance. In unfrozen solutions, the resistance is generally lower, which is due to their greater electrical conductivity and greater concentration of salts. However, for the humus horizons, the pattern is reversed. In unfrozen solutions, there is also a large concentration of iron. At the same time, no such pattern is observed for humus samples.

Freezing of the soil, due to an increase in the ionic strength of the solution reacting with the solid phase, leads to the destruction of aluminosilicates and the increase of desorption of iron from the solid phase of the soils into the solution. Thus, according to the data obtained, when composting at +20° C and during freezing of the cryogenic-taiga soil at -15° C for 1 day, desorption of Fe in mg-eq/100 g, using desorbent 0.05M HCl, was 2.5 and 3.5 meq/100 g respectively; at desorption 0.1M HCl - 3.5 and 4.5; when iron is displaced by 0.2M HCl - 4.5 and 4.7 mg-eq/100 g of soils.

As can be seen from the presented data, soil freezing significantly increased the mobility of iron in the permafrost-taiga soil. At the same time, the content of the most mobile forms of iron compounds greatly increased. This is illustrated for the cryogenic-taiga soils of the Magadan Region (experiment No. 2) by the data of the Tab. 3.

In accordance to the laws of physical chemistry, when the solutions are frozen, the precipitating solid phase consists of a pure solvent. In this case, the presence of a soluble substance lowers the freezing point, and the more concentrated the solution is, lower freezing point is. However, these patterns should differ depending on the granulometric and chemical composition of the soils and the chemical composition of the waters.

Experiment No. 3 estimated the effect of freezing water on the composition of water extract from sod-podzolic soils, which is presented in the Tab. 4.

As can be seen from the presented data, the content of potassium is greater in the unfrozen solutions than in the frozen ones in 3 cases out of 5, calcium in 5 cases out of 5, iron in 3 cases out of 4, magnesium in 5 cases out of 5. The use of non-parametric criteria of difference shows the validity of the changes.

Table 1.

The content of Fe, K in the frozen and unfrozen fractions of soil solutions of cryogenic-taiga soils of Yakutia (sections 1, 2, 3), mg/l

Soils	The frozen solution		The unfrozen solution		Resistance, Ohm/cm	
	Fe, mg/l	K, mg/l	Fe, mg/l	K, mg/l	1 (frozen solution)	2 (unfrozen solution)
light clay, sandy loam	1,8±0,7	2,6±0,4	2,8±0,7	7,9±1,7	16,0±1,1	19,8±1,7
medium loam	0,25±0,09	2,7±0,4	0,09±0,04	8,7±1,6	42,4±3,2	26,7±3,8

Table 2.

Determination of resistance in frozen and unfrozen samples of soil solutions from the cryogenic-taiga soils of Yakutia

Profile	Horizon, depth, cm	Resistance, The frozen solution	Fe, mg/l	K_2O, mg/l	Resistance, The unfrozen solution	Fe, mg/l	K_2O, mg/l
1	A_0 0-2	41,4±2,2	0,2	2,0	149,3±4,3	0,3	7,0
	A 3-12	52,2±1,9	0,4	5,0	8,7±0,1	0,1	6,0
	Bm 13-68	38,9±0,6	-	3,0	19,8±1,1	-	5,0
	BC_{CA} >68	53,4±2,9	-	2,0	30,2±1,3	-	7,0
2	A_0 0-2	24,2±2,4	0,4	2,0	38,7±3,5	0,1	8,0
	A 3-27	36,1±1,4	0,01	2,0	24,7±0,7	0,03	14,0
	Bm 28-62	42,5±3,2	-	4,0	32,3±1,0	0,01	18,0
	$BC_{(CA)}$ >62	50,5±2,9	-	2,0	-	0,02	5,0
3	A_0 0-3	14,0±0,1	0,05	1,0	18,6±0,3	1,0	4,0
	A 4-21	22,2±0,5	0,6	2,0	27,8±0,5	2,0	6,0
	ABm 22-30	12,9±0,4	0,01	2,0	23,7±0,4	3,4	24,0
	Bm >30	8,8±0,2	0,7	2,0	7,7±0,1	0,7	4,0
4	A_0 0-3	18,4±0,1	8,2	2,0	23,3±0,8	1,1	8,0
	A 4-20	13,4±0,4	1,8	1,0	22,1±0,9	2,0	3,0
	Bm 20-66	21,2±0,4	5,6	5,0	18,6±0,3	3,0	10,0
5	A_0 0-4	11,6±0,2	5,2	5,0	10,5±0,1	7,6	8,0
	A 4-20	16,1±0,4	0,5	5,0	14,0±0,1	4,3	12,0
	Bm 20-50	17,8±1,3	2,0	2,0	28,2±0,7	1,9	4,0
	BC >50	20,0±0,6	1,4	2,0	23,4±0,5	1,7	4,0
average value	$\bar{x}$	27,1±6,3	1,4±0,6	2,7±0,3	22,2±2,0	1,5± 0,4	8,3±1,2
	A_0A	25,0±4,8	1,9±1,0	3,0±0,5	6,4±15,6	2,1± 0,9	7,5±0,7
	BmBC	28,7±4,6		2,5±0,4	20,0±2,5		8,9±2,3

Table 3.

Effect of freezing of permafrost-taiga soil on displacement of iron by varying concentrations of HCl (mg-eq/100 g)

Variant	Displacement HCl (0,05-0,2M)			
	0,05	0,10	0,15	0,20
60% ПВ (1)	0,46	1,73	3,28	4,43
freezing at a -15° (2)	3,90	4,24	4,43	4,58
2/1	9,7	2,50	1,30	1,00

Table 4.

The effect of freezing water extracts from soils on their chemical composition, mg/l

Horizon	The composition of the frozen solution				The composition of the unfrozen solution			
	K	Ca	Fe	Mg	K	Ca	Fe	Mg
sod-podzolic medium loamy well-cultivated								
Ап	0,4	0,07	0,02	0,5	7,3	6,5	1,9	9,8
Bg	1,4	0,8	0,05	3,2	12,7	7,9	0,3	9,5
BCg	2,3	0,2	0,05	2,7	-	1,2	0,1	4,7
sod-podzolic middle-loamy Michurinsky garden								
Ап	16,9	0,06	0,0	0,7	137,3	0,5	0,0	4,1
A_2	6,7	0,1	0,06	1,7	14,5	0,6	0,0	3,6
$\overline{O}$	5,5±3,1	0,25±0,14	0,04±0,01	1,8±0,5	40,1±32,5	3,3±1,6	0,5±0,3	6,3±1,4

In the experiment No. 4, the effect of freeze-drying of water extract on its chemical composition for Moscow soils was evaluated. According to the data obtained, the content of potassium in frozen water was 6.2 ± 0.5 mg/l, in the un-frozen - 9.2 ± 1.4 mg / l.

Experiment No. 5 estimated the influence of freezing on the composition of soil solutions (P: H2O = 1: 2) for arable and sub-plow horizons of sod-podzolic soils. The obtained data are given in Tab. 5.

There are more K, Ca, Fe, Mg and the ratio (K + Mg)/Ca in the non-frozen solution than in the frozen of the arable horizons. The opposite trend is observed for the ratio (K + Mg)/Ca in subsurface horizons (which requires further research).

In the 6th experiment, the soils were frozen 5 times. After each freezing, an aliquot of frozen and unfrozen solutions was taken for analysis. In a wide correlation soil solution (500:5), sampling of 10 ml did not significantly change the ratio of the elements.

Table 5.

The content of cations in frozen and unfrozen samples soil solutions (1: 2), mg/l

The condition of the solution	K	Ca	Fe	Mg	(K+Mg)/Ca
1 - The frozen solution	4,7±2,5	0,2±0,1	0,04±0,01	1,8±0,4	32,5
2 - The unfrozen solution	42,8±28,5	3,2±1,4	0,38±0,3	7,1±1,3	15,6
2/1	9,1	16,0	9,5	3,9	0,5
arable horizon					
The frozen solution	8,6±8,3	0,1±0,01	0,01±0,01	0,6±0,1	131,4
The unfrozen solution	72,1±65,5	0,3±0,25	1,0±0,9	6,9±2,9	316,0
horizons A_2, B, Bг					
The frozen solution	3,5±1,7	0,4±0,2	0,05±0,01	2,4±0,5	14,7
The unfrozen solution	13,6±0,9	3,2±2,4	0,2±0,1	5,9±2,2	6,1

The data obtained are shown in Tab. 6. With increasing the multiplicity of freezing, the content of iron in the solution increases, which is due to the destruction of the mineral part of the soils. In the unfrozen part of the solution the concentration of Ca and Fe is higher. In well-humified soils, freezing affects more the increase in the mobility of iron than in weakly humified soils.

However, the change in the chemical composition of soil solutions during the freezing of soils is due to the simultaneous occurrence of several processes. The displacement of iron from the solid phase of soils is due to the kinetics of the process, and when the time of interaction of soils with water is longer, desorption is higher. The displacement of iron from the soil is due to the depositing capacity of the soils, and when each successive fraction is displaced, more firmly formed bound pass into the solution, and the concentration in the equilibrated solution will be lower. The displacement of iron from the soil is due to the destruction of the mineral part of the soil during freezing and with the increase in the ionic strength of the unfrozen residue water. In this case, the concentration of iron in solutions with repeated freezing of the soil-to-solution system increases. From our point of view, the last factor plays a significant role.

The characteristics of infrared spectra of soils are given in the Tab. 7.

Table 6.

Composition of frozen and unfrozen waters with 5-fold freezing soil, mg/l

Variant (the composition of the ice)	good humus soil		Poor soil humus	
	Fe	Ca	Fe	Ca
1-2 freezing	0,13±0,01	49,6±8,9	0,21±0,02	16,3±0,01
3	0,18	58,3	0,46	25,7
4-5 - freezing	0,23±0,02	58,3±0,1	0,31±0,02	15,9±0,1
the remainder of the unfrozen water	0,27±0,02	58,5	0,25	27,5

Table 7.

Change in infrared spectra of soils during their freezing

Variant	T% at λ cm $^{-1}$						
	1630	1406	1033	770	690	$\frac{1630}{1033}$	$\frac{1630}{1406}$
chernozem 1	0,7	2,2	0,28	3,4	3,7	2,5	0,3
cover loam 2	1,7	3,0	0,23	2,7	4,2	7,4	0,6
chernozem frozen 3	2,7	5,7	0,79	7,4	8,2	3,4	0,5
cover loam frozen 4	2,6	5,6	2,70	7,4	8,9	1,0	0,5

As noted above, soil freezing has significantly changed the nature of their infrared spectra. The transmission coefficient T% was increased in the region of 1630 cm^{-1}, 1400 and in other regions of the spectrum. In chernozem during freezing, the amount of T% changed from 10.3 to 16.4 and in the cover loam - from 16.4 to 22.2.

The character of the derivatograms of soils has also changed. According to the obtained data, the value of TG% in chernozem during freezing changed from -4.1% to -14.7%, DTA C^0 - from -29.0 to -10.8; in the clay loam mantle, respectively, TG from -7.3% to -7.6; DTA, C^0 - from -4,4 to -1,3.

From our point of view, the effect of freezing on the composition of soils and soil solutions depends on soil moisture, strength of water bond, pore size, intensity of electric fields at different distances from the sorption centers of the solid phase of soils.

According to the published data [1, 2, 10], when the Yakut soils are freezing in the unfrozen solution, the content of ferrous iron increases to 30-40 mg/l, Ca, Mg, K, Na, chlorides, sulfates. The direction of the change during the freezing of the chemical composition of the waters proceeded according to the scheme HCO3-> SO42-> Cl-, i.e. at lower temperatures, the proportion of chlorides and sulfates increases in the non-freezing waters, which is due to the solubility products of possible precipitation [13].

According to Anisimova N.P. [1], when the temperature decreases, firstly carbonates crystallize, then sodium and magnesium sulphates at -3.5° to -8° C, and calcium sulphates at -17 °. In the unfrozen solutions, the proportion of sodium and magnesium increases. The part of sodium carbonate (hydrogen carbonate) sometimes reaches 10 g/l. However, the authors indicate that when the water of different degrees of mineralization and chemical composition is frozen, the properties of the remaining unfrozen liquid phase change irregularly.

According to our data [12], this properties depend substantially on the content of organic matter in soils. When the organic horizons freeze in the unfrozen part of the solution, the content of water-soluble organic substances increases, but they, due to complex formation, can reduce the ionic strength of the solution and increase the resistivity. Thus, according to the data obtained, in the unfrozen solutions of the humus and arable horizons of the cryogenic-taiga soils, the resistance was 36.4 ± 15.0 ohm/m, and in the frozen soils - 25.0 ± 4.8. At the same time, in the lower horizons these values were 20.0 ± 2.5 and 28.7 ± 4.6 respectively.

The changes that occur will also differ for soils of different granulometric composition [7, 8, 11, 12, 15]. In fine-grained soils, even at -10° C, some amount of water remains in the film form. However, surface films have a lower solubility than free water. This ability differs depending on the charge of density of the sorption sites of the SAC. Increase in the freezing of the ionic strength of the remaining unfrozen water, an increase in the concentration of H^+, CO_2, O_2, and methane in waters at low temperatures leads to the destruction of aluminosilicates. The SiO_2 content in the cold permafrost waters of Yakutia varies from 10 to 25 mg/l, while in river waters this concentration does not exceed 10 g/l (according to the chemistry guide, the O_2 content in mg/100 ml in water at 0° C is equal to 4,9, and at 20° C - 3,1, H_2 - 2,1 and 1,8 respectively, CO_2 - 171 and 87,8, methane - 5,6 and 3,3.

It is pointed out that the increase in the concentration of SiO_2 in solutions during the freezing period is due to cryogenic concentration and to the solution from the soils due to the carbon dioxide released during the crystallization of water [1]. The content of cations in solutions during their freezing is also due to the solubility of precipitates, which, for example, is equal to (in mg/l): for Fe(OH)2 at 2° C, 4.5 × 10-5; Fe(OH)3 - 2 · 10-8; for KCl - 34,2; K2SO4 - 7,4; for Na2SO4 - 52,9; for MgCl2 - 54,6; MgSO4 - 18; MgCO3·H2O - 0,13.

The destruction of the soil-absorbing complex upon freezing is indicated by the infrared spectroscopy and derivatography obtained by us.

Conclusion

Thus, the freezing of soil solutions divides them into 2 fractions: freezing and non-freezing at the assumed negative temperature and the time of its action. In the nonfreezing fraction of the soil solution, the resistance is lower, the content of K, Fe, Ca, Mg is greater, which allows us to conclude that there is more intensive soil degradation under the influence of this fraction. In the unfrozen part of soil solutions, compared with the frozen, the ratio of cations changes, however, due to the presence of humic substances, complexes and associates in soil solutions, the regularities of the changes differ from those established for cryolithozone.

When the soil freezes, the soil solutions begin to freeze, increasing their concentration. This leads to the destruction of the mineral part of the soil, similar to the phenomena of halmyrolysis in the dry steppe regions. This process is accompanied by the destruction of aluminosilicates and can affect the destruction of building objects.

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ВЫМОРАЖИВАНИЕ ПОЧВЕННЫХ РАСТВОРОВ, КАК ФАКТОР ИЗМЕНЕНИЯ СВОЙСТВ ПОЧВ, ИХ ГЕНЕЗИСА И ПЛОДОРОДИЯ

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Аннотация: *Показано, что вымораживание почвенных растворов приводит к увеличению их концентрации, ионной силы, массовой доли натрия и калия, что в совокупности с повышением растворимости газов приводит к разрушению минеральной части почв, алюмосиликатов и может влиять на разрушение строительных объектов.. Этот процесс сопровождается увеличением содержания водорастворимых K, Ca, Mg, Fe и проявляется изменением характера инфракрасных спектров и дериватограмм почв. Содержание катионов в растворах при их вымораживании обусловлено растворимостью осадков, кото-рая составляет (в мг/л): для Fe(OH)2 при 2°С - 4,5·10-5; Fe(OH)3 - 2·10-8; для KCl - 34,2; K2SO4 - 7,4; для Na2SO4 - 52,9; для MgCl2 - 54,6; MgSO4 - 18; MgCO3·H2O - 0,13. На разрушение почвенно-поглощающего комплекса при замерзании указывают и полученные нами данные инфракрасной спектроскопии и дериватографии. Замораживание почвенных растворов разделяет их на 2 фракции: замерзающую и незамерзающую при принятой отрицательной температуре и времени ее действия. В незамерзающей фракции почвенного раствора ниже сопротивление, больше содержание ионов. Это позволяет говорить о более интенсивном разрушении почв под влиянием этой фракции. В незамерзшей части почвенных растворов, по сравнению с замерзшей, изменяется соотношение катионов, однако, в связи с наличием в почвенных растворах гумусовых веществ, комплексов и ассоциатов, закономерности изменения отличаются от установленных для криолитозоны в целом.*

Ключевые слова: *вымораживание растворов, криогенез, подвижность ионов в почвах, калий, кальций, магний, железо.*