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THERMODYNAMIC AVAILABILITY OF PLANT NUTRITION FROM SOIL DEPENDING ON CHANGES IN WEATHER FACTORS IN THE DAILY CYCLE

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> *Soil is a form of existence of dispersed systems.*
> O.E. Fersman

Abstract. *The weather is one of the determining factors in crop productivity. The purpose of this publication is to experimentally confirm and highlight the mechanism of the emergence of the dynamics of pore solution's chemical composition and its thermodynamic accessibility to plants during the interaction of black soil with thermodynamic weather factors in the daily cycle. It has been established that the dynamics of availability should be sought precisely in the daily cycle of soil interaction with the environment. The basis of experimental laboratory research was the thermodynamic hydrophysical method. Samples of typical light loamy black soil of undisturbed structure from the Obukhiv district of the Kyiv region were studied. The studies have found that the emergence of the dynamics of thermodynamic accessibility of the pore solution and its chemical composition is ensured by subordinate processes that occur in the soil under the influence of cyclic environmental factors – temperature, atmospheric pressure, and moisture saturation. During the laboratory experiments, reproducible dynamics of the chemical composition of the pore solution were obtained in the daily range of changes in the specified factors. It is likely that the formation of such dynamics in three cycles of desorption – sorption is provided by all five categories of soil absorption capacity. The chemical composition of the pore solution is functionally related to the heterogeneity parameter of soil environment, which is determined by the thermodynamic potential of moisture. Among the components of the chemical composition, the dynamics of the content of nitrate ions (NO_3^-), as one of the most important biogenic compounds, deserves an increased attention. The unique dynamics of NO_3^- content consists in its increase as the heterogeneity (desorption) of the soil (soil moisture) increases, approximately to the values of field capacity. This is explained by the specific behavior of these ions, which have a negative adsorption capacity (physical absorption capacity), between the two surfaces: solid particles-liquid and liquid-air, namely their concentration near the surface of separation in contact with the atmosphere. For structured soil with the presence of trapped air in macropores, nitrate ions are protected from leaching by the flow of moisture and are released into the pore solution in a volley when the macropores open, which is important for the conditions of nitrogen nutrition of plants. The conducted research outlines a whole section of thermodynamic research of soils with undisturbed structure, the implementation of which will result in parametric models for ensuring the production process of plants.*

Keywords: *thermodynamic system of soil, thermodynamic weather factors, heterogeneity, hysteresis, dynamics of moisture availability, dynamics of pore solution's chemical composition, nitrates*

Relevance of the research. The soil fertility is understood as the property of soil to satisfy the needs of plants for the nutritional components necessary for the production process [1]. Despite the existing of its various forms and types, the concept of fertility remains unspecified due to the consideration of soil as a container with nutrients, which can be controlled by adding or consuming nutrients, in accordance with the agricultural law of return [2].

However, the sacred phenomenon of fertility has a much more complex nature. In particular, the productivity of the same soil can vary significantly from year to year, although according to agrochemical indicators, the nutrient content in it remains practically unchanged. This difference is believed to be due to the weather conditions of each year. However, the real mechanism of the influence of weather conditions on productivity is not considered in this case. According to chemists' calculations, the gross reserves of biogenic elements in a 20 cm layer of typical black soils will be enough for obtaining a wheat yield of 3 t/ha during 60–150 years regarding nitrogen, during 85–250 years regarding phosphorus, and during 530–870 years regarding potassium [3]. But this can be only under the condition of their full mobilization. It is obvious that weather conditions affect the availability of nutrients from the soil and the optimality of their provision for the production process. At the same time, they affect both the transpiration capacity of the plants and the availability of nutrients from the soil, from those the plants choose the most optimal in space and time for their own production process. After all, it is an axiom that plants have followed the path of adapting and harmonizing their production cycle with the functional cyclical dynamics of the interaction of the soil, as a heterogeneous system, with the cyclicity of external weather disturbances. At the same time, attention should be paid to the predominantly daily cyclical nature of the production process of plants, and therefore the dynamics of the availability of nutrition from the soil to them, as adaptive systems, should be sought precisely in the daily functional cycle of soil condition.

In a heterogeneous system of soil, the thermodynamic moisture potential is an indicator of dynamics status [4]. After all, the most plant nutrients are obtained from the pore solution, the availability of which is determined by the value of the moisture potential. Agrochemists also pay attention to the thermodynamic nature of the biogenic elements availability for plants [5].

ecently, agrochemists have also started paying increasing attention to determining the content of readily available forms of biogenic elements: available forms of nitrogen (N), mobile potassium (K), and mobile phosphorus (P) [6].

However, it is not entirely correct to determine such availability only by agrochemical methods. After all, according to K.K. Gedroits [7], the absorption capacity of the soil is divided into five categories: mechanical, physical, physicochemical, chemical, and biological, which differ in their strength of stabilization of the components of soils' thermodynamic system and the degree of conservatism or dynamism for the each of indicator categories. By considering only the level of chemical absorption capacity, which to a greater extent characterizes the gross content of elements, we effectively exclude the participation of available nutritional components of other categories of absorption capacity. And the nature of these different categories and their intertransitions are determined by the heterogeneity of the four-phase soil system, where the fourth phase, in addition to solid particles, liquid and gas, is an alive matter [8]. However, when conducting agrochemical analyses, this heterogeneous soil structure, which depends on moisture content and other factors, is completely ignored: the soil is dried, ground, sieved, and treated with certain chemicals, after which the resulting solution is analyzed [9]. In due time, V.I. Vernadsky has very critical opinion regarding the analysis of "air-dry" soils, devoid of moisture, gases, and organic matter, believing that such soils do not exist in nature [10]. Insisting on the need to study soils in their natural state, Vernadsky focused on the complete lack of knowledge of soil solutions, which, in his opinion, represent the "substrate of life", an extremely complex and dynamic system of equilibrium. Supporting the life and enabling terrestrial vegetation to exist, soil solutions, as V.I. Vernadsky pointed out, are obviously "the main element of the biosphere mechanism" [11]. Therefore, agrochemical indicators, although they are the most conservative, do not fully characterize the availability of nutrients from the soil. Above we draw attention to the predominantly daily cycle of the bioproduction process. Therefore, the basis for the dynamics of the indicators, which are the least stabilized in the soil's absorption capacity of biogenic elements, should be sought precisely in the daily cycle of the dynamics of nutritional components stabilization. And, first of all, it is necessary to establish the cause and possible mechanism of the emergence of the daily dynamics of the availability of biogenic elements in natural pore solutions as a result of the interaction of all categories of soil absorption capacity as a integral system. After all, plants, as adaptive systems, react sensitively by concentrating fast-growing root hairs precisely in the direction of horizons where nutrition is most accessible to them [12].

Plants have mechanisms, which vary subject to the intensity for providing their own production process with nutrients – from the slowest chemical leaching from crystalline rocks, e.g., as performed by lichens, to the most intense thermodynamic availability based on the dynamics of the potential pore solution in the soil. The latter mechanism can provide the highest intensity of the production process, which, e.g., is required by steppe cereal ecosystems. After all, the vegetation season of steppe forbs is quite short requiring a high intensity of the production process to form biomass and reproductive organs of grasses during the short vegetation season, in which the decisive role is assigned to moisture reserves in the Steppe soils.

We consider it appropriate to first study this specific intensive mechanism for ensuring the availability of nutrients for agricultural crops for the most productive soils from the black soils' variety. After all, the preservation of these soils is a priority task for Ukraine, where the largest area of black soils is located. And it is in Ukraine, as the successor of one of the most ancient agricultural civilizations – Trypillia, where the conditions are created and the highest motivation is present for revealing the sacred phenomenon of fertility, and accordingly, the ways of preserving and effectively managing the productive function of the national heritage of Ukraine – black soils.

Therefore, it is in Ukraine, where there is the highest motivation to reveal the mechanism of the influence of weather cyclicity on ensuring the dynamics of the availability of nutrients from black soils, which is an element of the strategy of conscious preservation and management of the productive function of this national heritage, which is being actualized by modern global climate changes. Accordingly, the very mechanism of the emergence of the dynamics of availability of nutrients from the soil for plants should be sought in the daily cycle of soil-environment interaction when considering the soil as a complete thermodynamic system, in which a dynamic equilibrium of the chemical composition of natural pore solutions arises in the heterogeneous structure of soil framework.

The purpose of the conducted research is to experimentally confirm and highlight the probable mechanism of the emergence of the dynamics of pore solution’s chemical composition and the availability of plant nutrition components from black soils, as an integral heterogeneous thermodynamic system of natural composition, in interaction with weather factors of the external environment, which ensures its productive function.

Materials and research methods. The basis of this scientific research is thermodynamic methods of laboratory and field experimental studies of the natural soils and their regimes, a systematic analysis of functional parameters of soils based on the proposed dynamic functional model in interaction with the external environment [13]. This dynamic model is based on the principles of synergetics, which consider the soil as a thermodynamically non-equilibrium system and a dissipative active kinetic environment, in which self-stabilization and self-organization processes are constantly present, ensuring their evolution in accordance with the cyclicity of external weather conditions [13]. It is the permanent thermodynamic disequilibrium of the soil that provides local and periodically increasing thermodynamic availability of nutritional components for plants, taking into account local phase transitions of matter. Research was conducted for over thirty years on various types of soils belonging to the sites in the drainage and irrigation ones. The most large-scaled agro-landscape studies were conducted in the Forest-Steppe zone in the Obukhiv district of the Kyiv region at the experimental agro-ecological polygon during 1989–2005, where typical light loamy black soils of varying degrees of washout are spreaded and a soil conservation system of agriculture with contour-ameliorative organization of the territory was implemented [14].

It was for these soils that in-depth laboratory studies of the dynamics of availability and the dynamics of the chemical composition of pore solutions were conducted under the conditions of targeted management of soil heterogeneity. Chemical analyses of pore solutions were carried out in the certified hydrochemical laboratory of the Geological Faculty of Taras Shevchenko National University of Kyiv under the leadership of PhD in Chemical Sciences T.V. Gerbunova.

Research results and their discussion. The first stage in achieving the goal of the study was to consider the regularities of the specific structure of a real dispersed soil system. When considering the structure, the traditional assessment of soil structure for agrophysics, which is based on the principle of reductionism, i.e. the assessment of soil fragments, into which it breaks down when its integrity is violated, was abandoned. After all, the plants, climatic factors, and moisture interact with the soil as an integral dispersed thermodynamic system, where many microprocesses of transformations of matter, energy, and information occur, and those processes are characterized by the structure of the pore space. At the same time, its heterogeneity is decisive, and it is characterized by the surface of the solid-liquid and liquid-air interfaces, as well as the biomembranes of organisms. And it is the structure of the soil’s pore space that determines the dynamics of interface surfaces when moisture saturation changes. To characterize the pore space, a new physical model was created in the form of a corrugated equivalent of capillary [15]. This model takes into account the irregularity of the intersection of imaginary capillaries, which is characterized by the well-known model of the Jamin capillary [16]. Another, also well-known, model of the so-called equivalent capillary of A.V. Lykov integrally takes into account the combination of imaginary capillaries of all sizes [16]. The new model of the corrugated equivalent capillary combines the benefits of both of these physical models of soil pore space and thereby acquires a new quality. It is used to substantiate the existence of air bubbles trapped by liquid membranes in the pore space of the soil. The main condition for the equilibrium existence of this air is the equality of the radii of curvature of the liquid membrane from the outside, in contact with the atmosphere (r_a), and inside this bubble of trapped air (r_{ta}), i.e. the equilibrium condition $r_a = r_{ta}$. Since the real dispersed soil system can be characterized, according to the Jamin model, by two characteristic dimensions r_{min} and r_{max}, in the model of a corrugated equivalent capillary, a segment is determined, where the condition $r_{min} \leq r_a \leq r_{max}$ is fulfilled, which is the justification for a certain group of pores, where air trapped by liquid membranes exists in an equilibrium state. It is the presence of this air that is the main factor in the occurrence of capillary hysteresis in the soil. The famous scientist O.O. Rode drew attention to this unique phenomenon back in the previous century and emphasized that, despite the fact that in the thermodynamic interpretation of soil-hydrological phenomena, hysteresis is quite deliberately not taken into account, it is actually a phenomenon of extreme importance not only in theoretical terms, but also in solving quite practical problems [15]. Thus, capillary hysteresis is one of the fundamental properties of soil, which is directly related to its other fundamental property – heterogeneity [18].

Thermodynamic potential dynamics. The use of the physical model of a corrugated equivalent of capillary allowed to create a “Method for Determining the Structure of the Pore Space of Soils (Dispersed Media)” [19], which became an applied aspect of the use of the hysteresis phenomenon. The patented utility model is based on the study of the capillary hysteresis loop obtained in a special mode: desorption from full capacity as quickly as possible when there is practically no trapped air in the soil, and sorption as slowly as possible when equilibrium is established in the soil in the expansion of pores with trapped air. The difference in moisture saturation between the fast desorption and slow sorption branches for fixed values of capillary potential characterizes the moving average value of the total volume of trapped air in the group of pores, where the equilibrium condition $r_{min} \leq r_a \leq r_{max}$ is satisfied. The graph aggregates points with different values of capillary potential (P_i and different volumes of trapped air $V_{ta} = f(P_i)$ is called a structural characteristic of the soil pore space). In fact, the curve, graphically plotted as the difference in moisture content between the branches of the hysteresis loop, represents a differential curve of the distribution of pore space by radii. As the pore radii are related to the Jurin’s functional dependence on the capillary potential: $P \approx -0{,}15/r$ or $r \approx -0{,}15/P$ [16]. Air trapping in pore expansions increases the overall heterogeneity by the amount of the total internal surface area of the bubbles. Therefore, it is necessary to distinguish between the area of the liquid-air surface interface in contact with the soil atmosphere, which was called extra-heterogeneity (external) [20], and the area of the liquid-air surface interface in the trapped air bubbles themselves, which was called intra-heterogeneity (internal). It is the intra-heterogeneity that most actively responds to the changes in external thermodynamic conditions, because air separated from the atmosphere by liquid membranes reacts sensitively to the changes in external thermodynamic conditions – temperature (T^oC), atmospheric pressure (P_{atm}), and moisture saturation (θ) – by changing gas pressure and moisture saturation of the pore’s body. In this case, a change in gas pressure in the bubble leads to the displacement of the liquid, or its entry into the pore’s body, depending on the direction and combination of directions of change in external thermodynamic parameters. The cooperativity of such microprocesses in the pore space of the soil leads to the redistribution of moisture in it and a change in the thermodynamic state of the soil at the level of the macroparameter of the system of unsaturated soil, and, accordingly, to a change in the availability of moisture for plants. The presence of such a dynamics of capillary potential has been experimentally studied under the changes in temperature [20], humidity, and gas pressure in the range, which corresponds to the daily cycle of their variability. It has been found that a rapid change in any external parameter causes a self-oscillating process of capillary potential dynamics in the soil [20].

Therefore, the combination of two fundamental properties – the heterogeneity and hysteresis – ensures the dynamics of pore solution availability during soil interaction with changing external environmental conditions.

Naturally, such processes develop in the time and space of the soil environment, to which plants and plant communities and biota in general, have been adapted. Therefore, the overall response of the thermodynamic state of moisture to changes in external conditions depends not only on the absolute amplitude of changes in thermodynamic parameters, but also on the speed of their changes [15]. And it is the daily cycle that provides the highest speeds, and, accordingly, the highest amplitude of the reaction of the soil thermodynamic system to external changes, which coincides with the daily bioproduction cycle of plants. Therefore, it is the hysteresis of the soil that provides the dynamics of stabilization of the pore solution, within the capillary hysteresis loop, when interacting with the daily variability of external thermodynamic (weather) parameters.

Analysis of soil structure through the structure of its pore space based on the thermodynamic methods allows us to differentially consider the spatial continuum of pore space, quantitatively characterize the dynamics of soil heterogeneity, and also identify specific local subordinate (internal) processes of the microgradient structure of the soil environment, which ensure local transportation and phase transitions of matter.

Chemical composition dynamics. One of the most important issues is the assessment of the influence of the daily cyclicity of weather factors on the chemical composition of the pore solution, since both its thermodynamic availability and its chemical composition are the results of the same internal (subordinate) soil processes. In particular, the reaction of trapped air bubbles to the cyclical variability of external thermodynamic environmental conditions leads, in addition to intra-pore moisture redistribution, to the emergence of gas saturation dynamics of the pore solution, which has local nature around the bubbles and provides gas concentration gradients in the liquid of around the pores with trapped air. The carbon dioxide (CO_2), which has the highest solubility in the pore solution among atmospheric gases, deserves special attention in these processes. But the main thing is that, when it dissociates, it increases the concentration of hydrogen ions, that is, it lowers the pH. In fact, trapped air becomes a local source of carbonic acid in the soil environment [20]. In turn, radial acidity gradients become a factor in phase transitions of matter, primarily for compounds that cement soil particles. In particular, the dissolution of these compounds, which have predominantly carbonate composition, releases cemented soil particles, which can enable their relative movement under the action of external forces. It is likely that this mechanism ensures the self-development of the soil in the direction of its decompression by increasing the volume of elementary pores and transforming them into structural macropores.

The influence of capillary potential on the dynamics of the chemical composition of the pore solution for a typical light loamy black soils, which is shown in Fig. 1, has been experimentally confirmed. The experimental setup was as follows: a cylindrical soil sample of undisturbed structure with a diameter of 12 cm and a height of 10 cm, located in a plastic cutting ring and waterproofed from above and below with paraffin-bitumen caps, was equipped with two ceramic probes of control tensiometers on the side surface of the soil cylinder and a central working probe, through which the moisture saturation of the soil sample was changed according to the hydrophysical tests methodology [21]. The experimental methodology provides for the sampling of 10 ml portion-wise microsamples of pore solution through a central working ceramic probe during the desorption process of a soil sample, which is saturated to full moisture capacity. The decrease in soil moisture saturation during the sampling was equal to the 1–2,5 % of the volume. The extraction of pore solution in the radial space of the sample actually simulated the extraction of solution from the soil by plants' roots. Semi-microhydrochemical standard analyses was performed on the selected samples to determine the main macrocomponents Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}, NO_3^{-}, and pH when diluting the sample to the volume required for the analyses. The results of the determinations are shown in Fig. 1, where the concentration of each macrocomponent, presented in mg.eq./l, and pH are functionally related to the capillary potential expressed in absolute values (|P|), kPa, at which the samples were taken. Thus, it has been shown that there is a dynamic change in the chemical composition of the pore solution as the soil desorption progresses, which may be associated with a decrease in the radii of curvature of the liquid-air interface in a heterogeneous soil system, that is, in fact, with an increase in its heterogeneity. Three desorption cycles were carried out and after each cycle the soil monolith was saturated with distilled water through the central working ceramic probe.

According to the results of chemical analysis of pore solution samples, a certain reproducible regular dynamics of the chemical composition components content is visible, although the

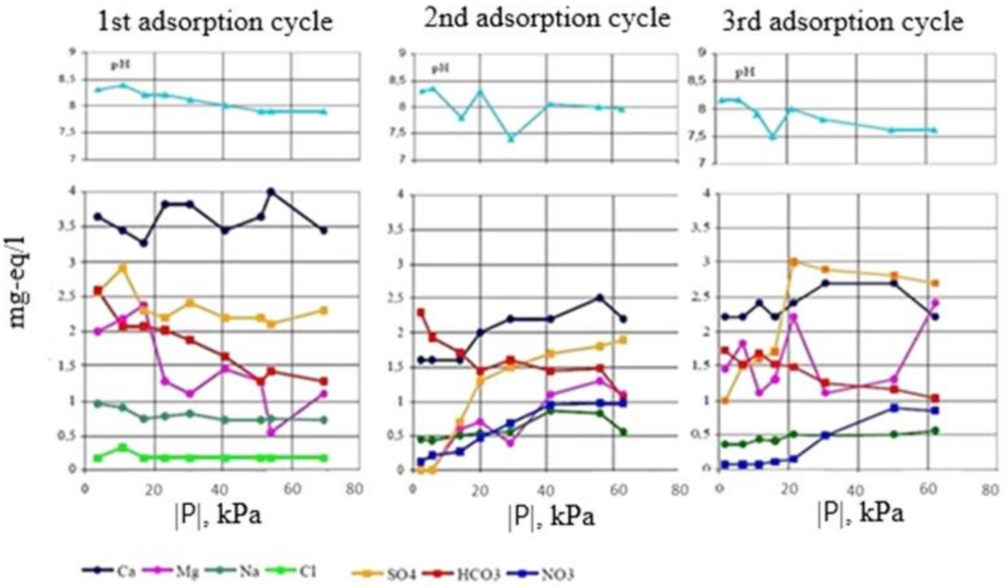

Fig. 1. Dynamics of the chemical composition of the pore solution for a typical light loamy black soil, interval 0,0–0,1 m (placore)

small volume of samples reduces the accuracy of their determination, which sometimes violates the monotony of the obtained dependences. In particular, the following regularities are noteworthy:

– the acidity of the pore solution tends to increase by almost an order of magnitude (a decrease in pH of 1) in each of the three desorption cycles;

– the content of hydrocarbons (HCO_3^-) naturally decreases as desorption (decrease in soil moisture) occurs in all three cycles;

– the content of sulfates (SO_4^-) decreased in the first cycle, however, in repeated cycles there is a clear tendency towards an increase in their content;

– chlorine ions (Cl^-), which have a negative adsorption capacity and can only be found in solution without a replenishment source, were recorded only in the first desorption cycle, and were no longer detected in repeated cycles;

– unfortunately, nitrate ions (NO_3^-) were not determined in the first cycle, however, in repeated cycles, a clear tendency towards an increase in their content in the solution as desorption proceeds is observed;

– the dynamics of the content of Ca^{2+}, Mg^{2+} and Na^+ cations have common features: at the first stage, their content decreases from the highest absolute values, but during repeated desorption cycles, a tendency towards an increase in their content is recorded as the soil is desorbed.

The obtained patterns were reproduced on other soil samples, so their trend has important consequences. In particular, the increase in nitrate content as desorption proceeds can be explained by the fact that nitrate ions have a negative adsorption capacity, which is a manifestation of the physical absorption capacity of the soil [22], therefore, in unsaturated soil they gravitate towards the surface of the liquid-air interface. That is, they concentrate directly below the surface of the liquid-air interface, acquiring the ability to slide and flow along this surface when a moisture potential gradient appears. It is likely that this mechanism of pulling nitrates to the roots operates during pore solution extraction. Under the conditions of air compression, nitrate ions concentrate near the inner surface of this bubble (intra-heterogeneity) and when it opens or a plant roots penetrates it, a volley of these ions occurs, which is a source of one of the most important biogenic elements for plants – nitrogen.

This is the way how we see the experimentally found mechanism of increasing the content of nitrate ions in the pore solution due to their volley ejection during the opening of pores with trapped air during the soil drying process, which directly affects the availability for plants of the nitrogen from the pore solution. The reproducibility of this extremely important pattern is experimentally confirmed by the results of tests of a typical black soil's sample from the depth interval of 0,20–0,30 m of the same soil profile on the plateau (Obukhiv district, Kyiv region). Table 1 contains the absolute values of the capillary potential |P|, kPa, at which samples of the pore solution were taken, and the corresponding values of the nitrate ion content (mg-eq/l) for the II and III desorption cycles for two samples of typical black soil taken from two depth intervals. Figure 2 presents the graphs of the dynamics of the nitrate ions content in the drained pore solution and a graph of the water retention curve of sample No. 1 in the second desorption cycle with the designation of the points of micro-sampling of the pore solution on this curve (see Table 1).

The common nature of the nitrate content dynamics during the soil desorption process is noteworthy: this is an almost monotonic increase in their content to absolute values of capillary potential of 30–45 kPa, after which a certain decrease in their content is observed. This decrease is most likely related to the nature of the pore space structure of the studied soil and gives grounds for concluding that further soil desorption will worsen the conditions for providing plants with the nitrate form of nitrogen.

In the heterogeneous environment of unsaturated soil, there is likely to be an uneven distribution of nitrate ions in the pore solution, as they are under the influence of both solid-liquid

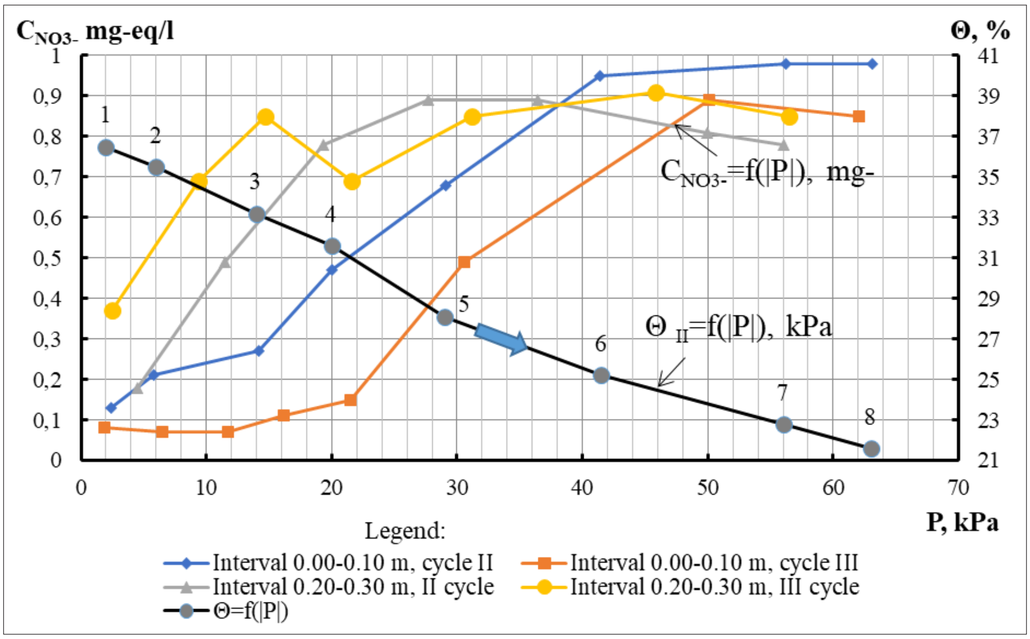

Fig. 2. Graph of repeated desorption of a sample of the typical light loam black soil (placor) from depth intervals of 0,00–0,10 m and 0,0–0,30 m with designations on the , kPa, curve of average moisture values of pore solution sampling and the curves of the dynamics of the nitrate nitrogen content in the drained solution over two desorption cycles , mg-eq/l

1. Nitrate nitrogen (NO_3^-) content (mg-eq/l) in drained pore solution depending on absolute values of capillary potential (|P|, kPa) for typical black soil samples from two depth intervals on the second and third desorption cycles

№	**Sample 1, interval 0,00–0,10 m**				**Sample 2, interval 0,20–0,30 m**			
	2nd cycle		**3rd cycle**		**2nd cycle**		**3rd cycle**	
	|P|, kPa	**$C_{NO_3^-}$ mg-eq/l**	**|P|, kPa**	**$C_{NO_3^-}$ mg-eq/l**	**|P|, kPa**	**$C_{NO_3^-}$ mg-eq/l**	**|P|, kPa**	**$C_{NO_3^-}$ mg-eq/l**
1	2,4	0,13	1,9	0,08	4,5	0,18	2,5	0,37
2	5,8	0,21	6,5	0,07	11,5	0,49	9,4	0,69
3	14,2	0,27	11,7	0,07	19,3	0,78	14,7	0,85
4	20,0	0,47	16,2	0,11	27,7	0,89	21,6	0,69
5	29,1	0,68	21,5	0,15	36,4	0,89	31,2	0,85
6	41,4	0,95	30,6	0,49	49,9	0,81	45,8	0,91
7	56,2	0,98	50,1	0,89	56,0	0,78	56,5	0,85
8	63,1	0,98	62,1	0,85	–	–	–	–

and liquid-air interfaces. Therefore, these ions, "repelling" from solid particles, gravitate to the surface of the liquid-air interface, due to negative adsorption capacity, therefore, these ions will experience the least the influence of the solid soil skeleton in the most powerful zones of capillary moisture, which are usually observed in the form of joint cuffs at the contact of dispersed soil particles or in water-filled pores. Therefore, it is possible to assume that the distribution of nitrate ions is extremely uneven in the heterogeneous soil environment and may have a network structure, also taking into account the intra-heterogeneity of macropores with trapped air and the presence of a constant source of nitrification of organic matter in the soil. It is these macropores that play a role of a storage, a reserve of nitrate ions, preventing their migration and leaching by the free pore solution.

An important point is the interpretation of the dynamics of the cation content in the pore solution, in particular their almost monotonic decrease in the first desorption cycle and increase in repeated desorption cycles.

Conclusions. The influence of weather thermodynamic factors in the daily cycle, namely temperature, atmospheric pressure, and precipitation, on the emergence of the dynamics of thermodynamic availability for plants of soils' pore solution and the dynamics of its chemical composition has been experimentally confirmed. The general formula for the influence of weather looks like the following: the dynamics of weather factors – the dynamics of soil heterogeneity – the dynamics of moisture potential and its chemical composition, which determines the dynamics of nutrient availability.

The dynamics of the soil pore solution's chemical composition is determined by the dynamics of heterogeneity (soil moisture), which occurs under the influence of external thermodynamic disturbances and leads to the destabilization of all categories of soil absorption capacity.

The amplitude of the soil heterogeneity dynamics under the influence of weather is determined by the rate of variability of thermodynamic factors, and their greatest influence on the degree of soil heterogeneity is provided by daily fluctuations in weather factors.

The different distribution of ions – components of nutrition in the pore solution – between the two interfaces of solid particles – liquid and liquid-air – is significantly different from their distribution in the free solution, which is due to the property of different adsorption capacity (physical absorption capacity), which leads to their uneven spatial distribution and a certain selection in the structure of the soil pore space.

A unique phenomenon of an increase in the nitrate content (NO_3^-) in the pore solution as the heterogeneity (desorption) of the soil increases, which is determined by the structure of the pore space, in particular the presence of structural macropores with trapped air, has been experimentally found. This phenomenon is of a great importance for the conditions of nitrogen nutrition of plants and requires further studies.

Without providing ready-made management solutions for regulating the nature of fertility, the conducted studies outline the direction of thermodynamic microgradient studies of soils of undisturbed structure based on the miniaturization of sensors and the priority of *in-situ* and *on-line* real-time studies, which will allow combining in parametric models the cyclical nature of external weather factors with the cyclical dynamics of the plant production process.

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ТЕРМОДИНАМІЧНА ДОСТУПНІСТЬ ЖИВЛЕННЯ РОСЛИН З ҐРУНТУ ЗАЛЕЖНО ВІД ЗМІНИ ФАКТОРІВ ПОГОДИ В ДОБОВОМУ ЦИКЛІ

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> *Ґрунт – це форма існування дисперсних систем.*
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Анотація. *Погода є одним із визначальних чинників продуктивності сільськогосподарських культур. Метою публікації є експериментальне підтвердження і висвітлення механізму виникнення динаміки хімічного складу порового розчину та його термодинамічної доступності для рослин при взаємодії чорноземного ґрунту з термодинамічними факторами погоди в добовому циклі. Встановлено, що динаміку доступності слід шукати саме в добовому циклі взаємодії ґрунту з довкіллям. Основою експериментальних лабораторних досліджень був термодинамічний гідрофізичний метод. Досліджували зразки чорнозему типового легкосуглинкового непорушеної структури з Обухівського району Київської області. Дослідженнями встановлено, що виникнення динаміки термодинамічної доступності порового розчину і його хімічного складу забезпечують субординаційні процеси, що виникають у ґрунті за впливу на нього циклічних факторів довкілля – температури, атмосферного тиску і вологонасичення. У лабораторних експериментах отримана відтворювана динаміка хімічного складу порового розчину в добовому діапазоні змін вказаних факторів. Вірогідно формування такої динаміки у трьох циклах десорбції – сорбції, забезпечують усі п’ять категорій вбирної здатності ґрунту. Хімічний склад порового розчину функціонально пов’язується з параметром гетерогенності ґрунтового середовища, яку визначає термодинамічний потенціал вологи. Серед компонентів хімічного складу найбільшої уваги заслуговує динаміка вмісту іонів нітратів (*NO_3^-*), як однієї з найважливіших біогенних сполук. Унікальна динаміка вмісту *NO_3^-* полягає у його зростанні по мірі зростання гетерогенності (десорбції) ґрунту(вологості ґрунту) орієнтовно до значень НВ. Це пояснюється особливою поведінкою цих іонів, що мають від’ємну адсорбційну здатність (фізична вбирна здатність), між двома поверхнями розділу тверді частки-рідина та рідина-повітря,а саме їх концентрацією біля поверхні розділу на контакті з атмосферою. Для оструктуреного ґрунту із наявністю затиснутого повітря у макропорах нітрат-іони захищені від вимивання потоком вологи і залпово викидаються у поровий розчин при відкритті макропор, що має важливе значення для умов азотного живлення рослин. Проведені дослідження окреслюють цілий напрямок термодинамічних досліджень ґрунтів непорушеної структури результатом реалізації якого стануть параметричні моделі забезпечення продукційного процесу рослин.*

Ключові слова: *термодинамічна система ґрунту, термодинамічні фактори погоди, гетерогенність, гістерезисність, динаміка доступності вологи, динаміка хімічного складу порового розчину, нітрати*