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CONCEPT OF INVOLVING GASES IN THE FORMATION OF THERMODYNAMIC AVAILABILITY OF PLANT NUTRIENTS AND THE COURSE OF SOIL PROCESSES

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> "Soil without gases is not soil, soil chemistry cannot be known – even in its general features – by studying only the solid and liquid components of the soil"
> V.I. Vernadsky [1]

Abstract. *The important role of gases in the planetary energy-mass exchange of the lithosphere with the atmosphere is determined, and attention is focused on the multifaceted mechanisms of gas exchange, especially under non-isothermal soil conditions. The conceptual principles of involving gases in ensuring the thermodynamic availability of plant nutrition, which emphasize the role of gases in a heterogeneous soil system, which is characterized by the presence of trapped air bubbles, are based on experimental data. Trapped soil air bubbles in the soil environment play the role of a distributed energy source when interacting with the thermodynamic parameters of the environment – temperature, atmospheric pressure and soil moisture content. The reaction of the soil capillary potential to a daily dynamics of external thermodynamic parameters has the nature of a self-oscillating process with a significant amplitude of the thermodynamic availability of the pore solution for plants.*

This turns the trapped air bubbles into centers of thermodynamic disequilibrium (CTD), acid centers of a certain strength (AC) and ecotone centers of soil biota. Thermodynamic accessibility is determined by the dynamics of soil heterogeneity, i.e. its energy saturation with surface types of energy, as well as by increasing matter mobility and intertransitions of different categories of soil absorption capacity. The functional parameters of the soil are determined by the gas composition of the soil atmosphere, where a special role belongs to carbon dioxide (CO_2), as the main factor in maintaining soil homeostasis. Emphasis is placed on the fact that under natural conditions of soil functioning, the composition of the smallest bubbles is enriched with oxygen and nitrogen, and most importantly, the size of these bubbles becomes close to nanoradii, which gives them abnormal properties.

Using the example of nanotechnologies with various gases, the possibility of targeted control of soil processes to increase the productivity and quality of plant products and ameliorative improvement of soils has been proven. The conclusion about the extremely high potential of integrating nanobubble technologies into ameliorative agriculture when using modern drip irrigation technologies has been made.

Keywords: *thermodynamic soil system, soil processes, soil gases, trapped air, nanobubbles, soil energetics, thermodynamic accessibility*

Relevance of the research. The Earth's epigeosphere is characterized by the transformation of huge flows of energy and matter, where a special role belongs to the pedosphere, as the lithospheric shell bordering the atmosphere, which actually regulates planetary energy and mass exchange with the environment and space. The patterns of pedosphere development are perhaps the most complex among all the Earth's geospheres. After all, all four phases interact and interpenetrate in it: solid matter – gases – moisture and living matter. Moreover, the role of living matter in the transformation of energy and mass exchange flows of the epigeosphere is constantly growing. V.I. Vernadsky drew attention to the biogenic structure of the modern atmosphere [2], which is changing its composition quite rapidly. And now significant anthropogenic emissions

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of greenhouse gases cause a greenhouse effect, which leads to global climate change towards warming and aridization [3].

Analysis of previous research and publications. The most significant evolutionary changes in properties occur in the pedosphere, as a regulator of the interaction of the lithosphere with the atmosphere, in which the decisive role belongs to atmospheric and soil gases. However, the role of these gases in the evolution of the pedosphere properties has not been fully studied yet. In recent years, the mechanism of emissions of greenhouse gases such as carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), carbon monoxide (CO), hydrogen (H_2) and other minor atmospheric gases have been intensively studied [4]. However, the role of each gas in soil functioning and in living organisms lives has not been fully studied yet due to the extreme complexity of the heterogeneous soil system and the multifaceted functional purpose of gases.

It should be mentioned the imperfection of modern methods for studying the gas regime of soils [5]. And the current state of studying this problem is primarily due to the extreme complexity and multifaceted ways of moving gases in a heterogeneous four-phase environment of a highly organized soil system, which is also complicated by the cyclic non-isothermality of soil regimes. The most complete analysis of such mechanisms of cyclic migration of matter is considered in the theory of drying of various materials [6], where the mechanisms of moisture thermal diffusion, relative thermal diffusion of gases in a non-isothermal pore space, thermal sliding of gases, in the presence of a temperature gradient and many other specific mechanisms migration of substances in a heterogeneous environment are considered.

In particular, it has been proven [6] that due to the relative thermal diffusion of gases in soil pore space in the presence of a temperature gradient, water vapor with a molecular weight of $M_{H2O} = 18$ and carbon dioxide $M_{CO2} = 44$, compared to the average molecular weight of atmospheric air $M_{atm} = 29$, can move in opposite directions. Probably, one of such mechanisms is the enrichment of the soil atmosphere with CO_2 during non-isothermal evaporation of moisture from the soil. In mathematical models of gas migration, those prevail where the driving force of movement is the diffusion mechanism, i.e. movement along concentration gradients. However, such models are unsuitable for a heterogeneous soil environment.

Using the example of the thermal movement of moisture in the vapor state, it has been experimentally proven that the established actual flow of vaporous moisture in the soil, moving after the heat flow that occurs in the pore space of the soil due to the thermal sliding of gases [7], exceeds diffusion in intensity and can be provided only by the convective flow of soil air. Therefore, in the non-isothermal regime of the soil environment, the convective mechanism of gas movement in the pore space prevails.

The movement of water vapor under the influence of a temperature gradient generates circulatory (dissipative) structures where the capillary flow of moisture compensates for vaporous losses in certain areas of evaporation, which, in turn, causes a compensatory flow of liquid and convective transport of dissolved substances and change in their concentration in the zone of predominant moisture evaporation [7]. Such circulatory movements of moisture and gases in different phase states are typical for soil, which generally indicates the inconsistency of diffusion models of gas movement in soils and emphasizes the extreme complexity of mass transfer in the soil environment and its insufficient study.

The purpose of the publication is to form the conceptual principles of involving gases in ensuring the thermodynamic availability of plant nutrition from the soil and the transformation (dissipation) of energy in soil processes through the significant dynamics of heterogeneity, i.e. the variability of the surface area of the liquid-gas interface, as well as to substantiate the possibility of controlling the intensity of these processes by changing the gas composition of the soil atmosphere.

Materials and methods of research. The methodology of soil research, where soil is a non-equilibrium thermodynamic system, provides for the use of mainly thermodynamic hydrophysical field and laboratory research methods that are integrative for determining the parameters of the current thermodynamic state of a heterogeneous system of unsaturated soil. When using these methods [10], it was possible to differentiate the pore space of the soil by its fundamental property – hysteresis, i.e. the ambiguity of the relationship between capillary potential and soil moisture content.

Using the created "Method for determining the structure of soil pore space (dispersed media)" [8], it was possible to divide the total heterogeneity, i.e. the surface area of the liquid-gas interface, into extraheterogeneity (external), or the interface surface area when capillary moisture contacts with soil atmosphere, and intraheterogeneity (internal) – the contact area of the solution with the inner surface of trapped air bubbles. It is intraheterogeneity that turned out to be the most dynamic state parameter that ensures the dynamics of surface energy in unsaturated soil, i.e. its energy buffering: the storage of surface energy at the surface of the liquid-gas interface when air is trapped and its slow release as this area decreases due to the opening of the bubbles of intraheterogeneity. This phenomenon of hysteresis is used by soil biota and plants in their own production process to minimize their own energy consumption. The dynamic model of soil functioning and development in interaction with the environment [9], formulated using a systems approach, became the methodological basis for studying the role of gases in soils.

Research results and their discussion. Modern ideas about the gas regime of soils are imperfect. In particular, it is believed that the main mechanism of gas exchange is carried out by the processes of "soil respiration", where the processes of soil biota metabolism prevail. It has been already mentioned that there are other purely physical mechanisms of movement and selection of gases of the soil atmosphere [6, 7]. The dominance of purely agronomic views on "soil respiration" does not aim to consider the mechanisms of gas transformation and their role in the functional parameters of soil processes. And only considering the soil as a non-equilibrium thermodynamic system in interaction with the environment highlighted the extraordinary role of the gas component in the life of the soil and ensuring its productive function (fertility).

It has been experimentally established [10, 11] the emergence of subordinate (internal) energy-consuming processes of redistribution of matter with its phase transitions occurring in the soil, which transforms the soil environment into a microgradient structure with pulsating movements of energy and mass exchange in the environment of macropores with trapped air. These translational movements of a certain intensity (energy consumption) determine the level of soil homeostasis, which ensures the reproduction of the structural organization and basic properties of the soil environment [10], and it is the soil air bubbles, separated from the atmosphere by liquid membranes in the expansions of the pore space play the role of an energy source in the soil, responding to the variable cyclic external thermodynamic parameters – temperature, atmospheric pressure and moisture content.

For a better understanding of the dynamics of the trapped air content, a physical model of the soil pore space was created in the form of a corrugated equivalent capillary, which considers in detail the conditions for the existence of trapped air in the extensions of the soil pore space [11]. In particular, the condition for the equilibrium of a trapped air bubble is the equality of the curvature radii of the liquid membrane both from the outside, when it contacts with the atmosphere, and inside, which limits the inner surface of the trapped air $r_a = r_{зп}$. Such an equilibrium is possible in the range of pore sizes where де $r_{min} < r_{ta} < r_{max}$, where where r_{min} and r_{max} are the typical pore sizes determined by the sphere of the most inscribed radius in the pore body and r_{min} is the radius of the sphere inscribed in the necks of this pore.

The ratio of these typical pore sizes $n = \frac{r_{max}}{r_{min}}$ is an important characteristic that is determined in the laboratory diagnostics system by the amplitude of the capillary hysteresis loop [6, 11]. The threshold size of structural macroporosity is determined by the value $n > 2$ and the excess gas pressure that can be created in a bubble of trapped air $P_{надл} = 0{,}15\frac{r_{max} - r_{min}}{r_{max} \cdot r_{min}}$ depends on this ratio. That is, the greater this difference, the higher the excess pressure can be created in the bubble. That is why the largest structural soil macropores are very important in agronomy. In turn, under the action of excess pressure, the diffusion of gases that make up this bubble begins through liquid membranes to the soil atmosphere according to their solubility in the pore solution. Table 1 shows the comparative solubility of some gases.

Among the atmospheric gases, the solubility of oxygen (O_2) is 24,4 times lower compared to carbon dioxide (CO_2), and nitrogen is 46,6 times lower. Therefore, in bubbles of trapped air, when the excess preasure (P_{excess}) occurs, the gas composition is enriched in oxygen and nitrogen, according to their solubility in the pore solution.

The content of CO_2 in the soil atmosphere is increased, compared to the open atmosphere, approximately by 3 %, although in anaerobic

1. Solubility of some gases in water when T=25 °C, mol L^{-1} atm^{-1} [12]

Ammonia (NH_3)	Sulfur dioxide (SO_2)	Carbon dioxide (CO_2)	Methane (CH_4)	Oxygen (O_2)	Nitrogen (N_2)
57,0	1,25	0,0308	0,00129	0,00126	0,000661

conditions of some soils it can increase by 20 % or more. The main thing is that carbon dioxide dissociates in the pore solution forming carbonic acid H_2CO_3. Due to this, the bubbles of trapped air become acid centers of carbonic acid, forming a radial acidity gradient of the pore solution in the unsaturated soil and disrupting the carbonate equilibrium of the soil cement. It should be noted that carbon dioxide, in addition to the environmentally negative effect of its emission for the atmosphere, plays an extremely important role in soil functioning binding carbon and calcium in it, as well as ensuring the dynamics of thermodynamic availability of nutrients for plants from all categories of soil absorption capacity.

Soil energetics. Capturing soil air into the structure of the soil matrix and the including gases together with moisture into the components of the thermodynamic system of soil functioning as a working medium is of extremely importance in the conversion (dissipation) of the external solar energy flow, which generally determines soil energetics and its dynamics. An integral parameter of soil energy saturation is the thermodynamic moisture potential [9, 11]. The dynamics of soil capillary potential under the influence of the dynamics of variability of external thermodynamic parameters was experimentally investigated: temperature, atmospheric pressure and moisture content. In particular, a thermal pulse in the real range of daily temperature variability of an isolated soil sample at constant moisture content ($\theta = \text{const}$) causes a self-oscillating process of changing the capillary potential of the soil sampl. Initially, synchronously with heating, the capillary potential increases (decreases in absolute value), and with the onset of cooling it rapidly decreases to a minimum, and begins to slowly increase to the initial values [10]. Deviations of the capillary potential values in both directions from the initial values reach 20–40 kPa, and the total amplitude reaches 30–60 kPa, which is a fairly significant fluctuation in the thermodynamic availability of plant nutrition in the daily cycle.

The behavior of gases in the physical model of the pore space in the form of a corrugated equivalent capillary allow us to understand the processes of emerging the self-oscillating mode of the dynamics of the capillary potential [11]. With the onset of heating, the volume of trapped air in the soil expands, squeezing moisture out of the pore body. Having the effect of moistening this process leads to the closure of larger pores with liquid membranes and an increase in the values of the capillary potential. This is also facilitated by a decrease in the surface tension of the solution with increasing temperature. At the same time, the equilibrium conditions of the trapped air are disrupted in the smallest pores and it is compressed, increasing the intensity of the dissolution of gases in these bubbles, or small bubbles may be carried away by the convective flow of the pore solution to larger pores.

The increase in the capillary potential stops when these two opposite processes become equal in intensity. With the beginning of cooling, the minimum values of the current capillary potential are observed in the soil taking into account the dissolution of gases in the smallest pores, with the subsequent process of gas release from the pore solution. In this case, capillary meniscus forces cause tensile forces in the soil and slow restoration of the initial values of the capillary potential in the soil sample.

The saturation of the smallest bubbles of the trapped air with the least soluble oxygen (O_2), nitrogen (N_2) and their dissolution in the pore solution under excess pressure leads to the question – whether plants absorb them from the pore solution in the environment of the smallest pores? Perhaps this is one of the mechanisms of absorption of atmospheric nitrogen (N_2), which requires targeted further research. In particular, when having the values $P = -60$ kPa, the radius of the bubbles is $r \approx 2{,}5 \cdot 10^{-6}$, or 2500 nm, and when they are compressed, their size decreases by an order of magnitude. In this case, it is important that the smallest bubbles with a size of $1 \cdot 10^{-6} \div 1 \cdot 10^{-9}$, i.e. micro- and nano-radii, acquire anomalous properties.

The study of nanobubbles is a new aspect of science in the area of nanotechnology. In 1950, the Einstein-Plesset theory was proposed to predict the lifetime of bubbles, and in 1959, the American physicist Richard Feynman presented this concept, which demonstrated great potential for application in medicine, cosmetics, chemical technology, polymers, treatment and health care, and many other areas [13]. However, the rapid development of nanobubble technology began only in the third millennium. Nanobubbles with a size of $1 \cdot 10^{-6} \div 1 \cdot 10^{-9}$ м can occur naturally, in particular, the mechanism of nanobubbles in water on a hydrophobic surface is described [14].

There are plenty of such hydrophobic surfaces in soils, they are mainly films of organic substances on mineral particles. However, for industrial use, nanobubble generators have been invented that use different principles – cavitation, electrolysis, nanoporous membranes, ultrasound, and others. The importance of nanobubbles is based on their anomalous properties that distinguish them from other bubbles: they are electrochemically active, non-floating and non-toxic, stable and can remain in the aquatic environment for a rather long time, acquire a zeta potential, due to which they have the properties of colloids to involve ions into a double electric layer, and such involvement occurs on both surfaces of the bubble, which ensures the delivery of necessary elements to any organ in organisms.

Nanobubbles can be formed from various gases – oxygen, nitrogen, carbon dioxide, hydrogen, ozone and others, which have different effects on the purposefully controlled system. Among the multifaceted applications of nanobubble technologies, one should focus on their use in the agrosphere. There is already a lot of data on the positive impact of nanobubbles on yield, quality of grown products, water retention and other soil properties, in particular their structuring, mobilization of hard-to-reach biogens due to an increase in the number and selection of microbiota in the rhizosphere of plant roots, as well as other aspects of crop production [15–18]. The main element of the technology for using nanobubbles, mainly of oxygen (O_2) composition, was the technology of introducing nanobubbles into irrigation water supplied to plants by means of drip irrigation.

However, among the existing published data, the use of nanotechnologies in crop production has certain shortcomings, and most importantly, there is the lack of systematic application of nanobubble technologies. They show insufficient professionalism, experiments are conducted mainly in closed soil, and there is no interpretation of the effect of nanobubbles on the soil from the standpoint of soil science, agrophysics and land reclamation. In particular, it is observed an increase in soil moisture and water-holding soil capacity, but the impact of using nanotechnologies on the capillary soil properties is not yet considered, which may be of great importance for hydrotechnical land reclamation. Moreover, the impact of various gases on soils, which may become an element of land reclamation technologies in the future, is not considered either.

The study of using nanotechnologies in land reclamation agriculture is planned in the scientific program of the Institute of Water Problems and Land Reclamation in the next five-year period of 2026–2030.

Conclusions. The functioning of the soil as a thermodynamic system highlighted the extremely important role of the gas phase in the soil life, the transformation of energy and matter in it, which, ultimately, ensures its productivity.

An important role in these processes belongs to the bubbles of soil air trapped in the expansions of pores, as a form (mechanism) of involving gases into the heterogeneous soil environment. These bubbles become a source of thermodynamic disequilibrium (source of energy), acid centers and centers of ecotones of soil biota in the soil, which transform the soil into a microgradient dissipative structure with cyclic pulsating radial movements of energy and mass exchange with phase transitions of matter. Due to these processes, soil homeostasis is maintained and the reproduction of the basic properties and its structural organization is ensured.

Among the gases of the soil atmosphere, carbon dioxide (CO_2) plays an important role in soil functioning, so its content can be equated to one of the fertility parameters.

The technical capabilities of introducing gases with irrigation water by means of drip irrigation, including in the form of nanobubbles, will allow for more targeted control of soil regimes and their reclamation effect on the soil.

It is time to integrate nanobubble technologies into the practice of reclamation agriculture due to their extraordinary prospects in increasing the productivity and quality of plant products, improving the microbiological state of the soil and, perhaps most importantly, their environmental friendliness. The use of nanobubbles of various gas compositions will significantly expand the possibilities of reclamation technologies.

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КОНЦЕПЦІЯ УЧАСТІ ГАЗІВ У ФОРМУВАННІ ТЕРМОДИНАМІЧНОЇ ДОСТУПНОСТІ ЕЛЕМЕНТІВ ЖИВЛЕННЯ РОСЛИН ТА ПЕРЕБІГУ ҐРУНТОВИХ ПРОЦЕСІВ

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«Ґрунт, взятий без газів, не є ґрунтом, хімія ґрунтів не може бути пізнана –
навіть у своїх загальних рисах – вивченням тільки
твердих і рідких складових частин ґрунту»
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Анотація. *Визначено важливу роль газів у планетарному енергомасообміні літосфери з атмосферою, акцентована увага на багатогранних механізмах газообміну, особливо за неізотермічних умов ґрунту. Концептуальні засади участі газів у забезпеченні термодинамічної доступності живлення рослин базуються на експериментальних даних, де акцентована роль газів у гетерогенній системі ґрунтів, для яких характерна наявність бульбашок затиснутого повітря. Адже бульбашки затиснутого ґрунтового повітря у ґрунтовому середовищі відіграють роль розподіленого джерела енергії при взаємодії з термодинамічними параметрами довкілля – температурою, атмосферним тиском та вологовмістом ґрунту. Реакція капілярного потенціалу ґрунту на переважно добову динаміку зовнішніх термодинамічних параметрів має характер автоколивального процесу із значною амплітудою термодинамічної доступності для рослин порового розчину. Це перетворює бульбашки затиснутого повітря у центри термодинамічної нерівноважності (ЦТН), кислотні центри певної сили (КЦ) та центри екотонів ґрунтової біоти. Термодинамічна доступність визначається динамікою гетерогенності ґрунту, тобто його енергонасиченості поверхневими видами енергії, а також підвищенням мобільності речовини і взаємопереходів різних категорій вбирної здатності ґрунтів. Функціональні параметри ґрунту визначає газовий склад ґрунтової атмосфери, де особлива роль належить діоксиду вуглецю (CO_2), як головного чинника підтримання гомеостазу ґрунту. Акцентована увага на тому, що в природних умовах функціонування ґрунту відбувається збагачення складу найдрібніших бульбашок на кисень і нітроген, а найголовніше, розмір цих бульбашок наближається до нанорадіусів, що надає їх аномальних властивостей. На прикладі нанотехнологій з різними газами доведена можливість цілеспрямованого управління ґрунтовими процесами з метою підвищення продуктивності і якості рослинної продукції та меліоративного покращення ґрунтів. Зроблений висновок про надзвичайно високий потенціал інтегрування нанобульбашкових технологій у меліоративне землеробство з використанням сучасних технологій краплинного зрошення.*

Ключові слова: *термодинамічна система ґрунту, ґрунтові процеси, ґрунтові гази, затиснуте повітря, нанобульбашки, енергетика ґрунту, термодинамічна доступність*