Energy-Entropic Analysis Of Agroforesolandscapes Soils

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Annotation

Soil samples were taken at the Novaya Panika test site (Frolovsky district, Volgograd region). Dark chestnut soils are represented by varieties of dark loamy and medium loamy on loess-like loams, and light loamy on deluvial loams, represented by sandy deposits. The ratio of the coarse fraction to the fine fraction did not reveal sharp fluctuations in changes in the structure. Differences in indicators occur at such small levels (thousandths and tens of thousandths) that this only indicates an even greater detail of thermodynamic units. The general indicator of a variety of light loamy, medium loamy, heavy loamy dark chestnut soil, destruction associated with erosion, deflation, various types of anthropogenic influences or the synthesis of neoplasms, revealed an entropy indicator (Π_s) and energy (Π_G) (Π_H) equal to 0,5 units. The results of the thermodynamic approach to assessing the intensity of soil formation considered in this work show the broad possibilities of thermodynamic methods. Using the approaches of different scientists in the article on the basis of our data on the granulometric composition and gross chemical composition to the energy of soils, taking into account the entropy and energy components, revealed the importance of the dispersion of matter in their energy intensity. The greatest potential of residual energy is present in the silty fraction of loam varieties of the subtype of dark chestnut soils.

Keywords. Agroforestry landscape, agroforestry, thermodynamic approach, dark chestnut soils, enthalpy, Gibss energy, entropy

Introduction

To solve the problem of assessing the effectiveness of agroforestry and protective afforestation, it is proposed to use a thermodynamic approach based on studying the directions of non-equilibrium processes and patterns of energy transformations in natural systems. Agroforestry landscapes can be represented as thermodynamic systems in the form of a set of subsystems (stand of forest belts, soil, agrocenosis, the surface layer of the atmosphere) that can interact energetically with each other and exchange matter. The agroforestry system has a large number of components, with their characteristic properties, which, when optimized, must be compared, balanced, brought to a common objective weighted average denominator. Such a generalizing criterion assumes the thermodynamic characteristics of research objects with the definition of entropy, based on objective physical laws.

When applying the provisions of thermodynamics to agroforestry systems, the peculiarities of their organization should be taken into account. In this regard, the following provisions are highlighted:

- agroforestry systems are open to matter and energy flows;
- processes in agroforestry systems are irreversible;
- agroforestry systems are far from equilibrium;
- agroforestry landscapes are heterophase and structured.

Modern active management of agroforestry landscapes is impossible without knowledge of the theoretical foundations of energy and nonequilibrium thermodynamics, functioning and development of agroforestry systems.

A thermodynamic system is a macroscopic body or a group of bodies that are characterized by processes accompanying the transition of heat to other types of energy and processes.

The methodological substantiation of the energy-entropic analysis of soils appeared thanks to the fundamental works of V.R. Volobuev [3], V.A. Kovda [5], Rozanov [7], A.G. Nazarov [6], as well as in the work of Zhang Z., Cheng X., A fully coupled THM model based on a non-equilibrium [8]. The relevance of this line of research lies in the possibility of using ideas about the energy contained in the soil, about the thermodynamic properties of soils and subjects, in particular, the enthalpy of the literal component, Gibbs free energy and entropy for assessing the bioenergetic potential of soils.

Of the available works on the energetics of soils, the most studied are the organic components of chestnut soils [2]. There is much less work on the energy of the mineral part, in particular, dark chestnut. Thermodynamic components are widely used in soil thermodynamics:

- internal energy U;
- ecthalpy (heat content, heat function) H;
- Gibb Free Energy G;
- entropy S.

Entropy is a physical quantity, a measure of disorder in the soil system; the larger the value, the greater the chaos in the system, the less reactionary it is. Entropy is the bound energy arriving at 1° C. The sum of the amount of heat that is needed to bring it to a given state from a crystalline state at absolute zero.

With regard to the Gibbs free energy, it should be borne in mind that the negative value of ΔG shows the energetic advantage of the process about its potential. The positive value of ΔG in the soil indicates, unambiguously, the impossibility of the dynamics of the process.

Thus, the use of the Gibbs potential G and the conclusion of the entropy S as thermodynamic potentials in the study of processes in the mineral part of soils is promising.

Materials and research methods

The method of thermodynamic calculations for soils includes:

– data analysis of the complete particle size distribution with the determination of the weight contribution of each fraction;

– description according to literature data of quantitative, mineralogical analysis of soil;

– determination of the values of the content of humus and plant residues;

– calculation of these standard values of free energy (-ΔG°), enthalpy (-ΔH°) and entropy (S°) of each fraction of soil particles.

The granulometric composition of soils is determined by a generally accepted method. To determine the mineralogical composition of the soil, calculations are used based on the results of chemical analysis of soils and the determination of minerals in the soil. This method is called submodal [1]. According to the formula $Mк = \frac{Po}{Mo}$, where Mк – molecular amount of oxide, Mo – molecular weight of oxide, Po – oxide content in weight percent. Then we multiply the mole fraction by the value of the thermodynamic constant. The sum of the values ΔG, ΔH, S, which revealed the oxide of minerals, gives the general picture for soils. The values of thermodynamic constants found in soil are given in numerous chemical and geochemical works and reference books. The application of these data for the characterization of soil minerals follows from the additive thermodynamic potentials, by simple summation of the potentials, obtaining the value of the potentials of complex mineral systems, taking into account their molecular amount.

The values of the thermodynamic constants of substances are given in reference books for standard conditions T= 298,15°K (25°C), P= 1kg/cm² [5].

Soil samples were taken at the Novaya Panika test site (Frolovsky district, Volgograd region). Dark chestnut soils are represented by varieties of dark loamy and medium loamy on loess-like loams, and light loamy on deluvial loams, represented by sandy deposits.

Discussion results

The data on the granulometric composition are given in Table 1. According to the data obtained, the soil is characterized as medium loamy: the content of physical clay in its 0 - 40 cm varies 61,1 – 61,8%, the predominance of the fraction along the entire profile is silt, medium and fine dust, such Thus, this soil is defined as silty-medium-fine-dusty loamy.

Table 1 - Granulometric composition of dark chestnut medium loamy soils (landfill "New Panic")

Depth	Gig. Humidity, %	Fraction size, mm							Name of soils
		1-0,25	0,25-0,05	0,05-0,01	0,01-0,005	0,005-0,001	<0,001	Phys. clay	
0-20	2,04	9,27	13,10	16,52	1,60	20,56	38,95	61,11	Light clay
20-40	3,60	6,03	21,63	10,58	12,32	23,15	26,29	61,76	Light clay
40-60	2,04	7,86	38,52	9,68	12,32	17,92	13,70	43,94	Medium loam
60-80	1,51	7,34	22,9	2,92	15,41	23,15	28,28	66,84	Light clay

80-100	2,53	10,62	18,5	7,30	13,47	19,49	30,62	63,58	Light clay
100-120	1,50	11,08	20,06	1,36	9,89	24,72	32,89	67,5	Light clay
120-140	2,55	6,99	29,29	6,83	13,47	24,80	18,62	56,89	Heavy loam

To determine the thermodynamic characteristics of dark chestnut soils, it is necessary to describe the mineral part as a sum of oxides [1]. Mineralogical analysis data are taken from the work of AD Voronin [4] with co-authors. Analysis data showed that with a decrease in the size of fractions of mechanical elements, the variety of secondary minerals increases: the content of quartz decreases and the amount of feldspars, micas, and heavy metals increases.

Medium sand (0,5 – 0,25 mm) in dark chestnut soils is 98% quartz and 2% feldspars. The difference in the dark chestnut light loamy soil of the 0-24 cm horizon is a higher content of chalcedony.

The content of heavy minerals is slightly higher in medium dust, where it is about 5% in dark chestnut soil (both in heavy loamy and light loamy), and about 2–3% in solonetz. In fine dust, their amount drops to 2% in the upper horizons of the dark chestnut soil. The most significant influence on the physical and physicochemical properties of soils and their fertility is exerted by the mud fraction (<0,001 mm). The nature of this influence largely depends on the composition and content of minerals included in the clay fraction.

The mineralogical and chemical composition of fractions of mechanical elements and soils in general allows us to conclude that the process of soil formation in dark chestnut soils leads not only to the movement of readily soluble salts, sulfates, and carbonates in their profile and the partial movement of the finest colloidal particles (mainly montmorillonite) , and is also accompanied by physical and chemical weathering of the aluminosilicate part, leading both to its decomposition to primary oxides, their leaching into the illuvial horizons, followed by the formation of secondary minerals there, and to the formation of secondary minerals according to the scheme feldspars-mica-hydromica-montmorillonite.

The quantitative characteristics of minerals, according to the above procedure, were expressed in volume and weight fractions (or percent), which, taking into account the grams - the molecular weight of the M_o mineral and its relative weight contribution (P_o) in the total mineral mixture, was converted into a dimensionless value - $M_к$ molecular amount of oxides.

Finding the molar amounts of minerals in each granulometric and mineralogical fractions ended the stage of systematizing the initial data. Standard thermodynamic ($-\Delta G$, $-\Delta H$, ΔS) were taken from the reference book [5], and then the energy-entropic values of each grain size fraction, genetic horizon and soil as a whole were determined using the above method (Table 2). The total energy assessment consisted of differential (at the level of oxides) and integral at (level of the horizon) and the entire soil.

For a correct interpretation of the results of the assessment of dark chestnut soils, it should be borne in mind that the thermodynamic values used ($-\Delta G$, $-\Delta H$, ΔS) do not express any absolute values reflecting the "reserves" of accumulated energy in the soil. These values are relative, reflecting the residual fraction of energy that is stored in the soil of a specific material mineralochemical property.

Table 2 - Thermodynamic characteristics of dark-chestnut medium-loamy soil (polygon "New Panika").

ΔH^0_{298},	ΔG^0_{298},	ΔS^0_{298},	Depth	Fraction size
kJ/mol	kJ/mol	J/mol·deg	cm	mm
-1387,26	-1303,15	63,83	0 – 20	<0,001
-1387,68	-1303,66	63,71	20 – 40	
-1389,75	-1305,5	63,6	40 – 60	
-1395,83	-1311,12	63,63	60 – 80	
-1439,7	-1350,47	68,51	0 – 20	0,001-0,005
-1440,99	-1351,52	68,55	20 – 40	
-1446,04	-1356,35	68,70	40 – 60	
-1438,82	-1349,33	68,49	60 – 80	
-1459,7	-1369,26	69,30	0 – 20	0,005-0,01
-1461,51	-1371,01	69,36	20 – 40	
-1463,97	-1373,35	69, 52	40 – 60	
-1454,78	-1364,77	68,89	60 – 80	
-1464,85	-1374,4	69,50	0 – 20	0,01-0,05
-1470,69	-1380,18	69,65	20 – 40	
-1471,15	-1381,18	69,92	40 – 60	
-1478,46	-1388,21	69,32	60 – 80	
-1500,72	-1410,59	69,60	0 – 20	0,05-0,25
-1501,33	-1411,28	69,55	20 – 40	
-1499,33	-1409,39	69,41	40 – 60	
-1503,42	-1413,24	69,57	60 – 80	
-1510,96	-1420,63	69,67	0 – 20	0,25-0,5
-1508,11	-1417,97	69,57	20 – 40	
-1509,06	-1418,86	69,55	40 – 60	
-1511,88	-1421,51	69,72	60 – 80	

The higher the entropy of a polymorphic compound, the relatively less reactive it is. Entropy is the bound energy per 1^o, it is equal to the sum of the amount of heat that must be imparted to the system to bring it into a given state from the crystalline state at absolute zero.

Thermodynamic functions (($-\Delta G$, $-\Delta H$, ΔS) due to additivity are combined by the equation of relative abundance taking into account the most important physical classes of particles (sandy, silty and physical clay) [3].

$H=\sum(-H)>0.1+\sum(-H)\ 0.1\text{-}0.01+\sum(-H)<0.01$

$(-G)= \sum(-G)>0.1+\sum(-G)0.1\text{-}0.01\sum(-G)<0.01$

S= ∑S>0.1+∑S 0.1-.0.01+∑S<0.01.
For example, given (table 3).

Table 3 - The sum of three fractions of medium loamy dark chestnut soil (0-80 cm).

Particle size mm.	ΔH^0_{298}, kJ/mol	ΔG^0_{298}, kJ/mol	ΔS^0_{298}, j/mol deg
Silty (<0,001)	-5560,53	-5223,44	254,80
Dusty (0,001-0,05)	-17490,68	-16410,05	828,72
Sand (0,05-05)	-12044,89	-11323,47	556,63

Data on the summation of thermodynamic values for fractions of mechanical elements of different particle size distribution are given (table 4). Particularly distinguished are medium and fine sand fractions (0,25 – 0,5 mm; 0,05 – 0,25 mm) and coarse dust (0,005 – 0,01 mm). The thermodynamic function of enthalpy in light loamy soil in these fractions varies from -7405,52 to -7561,49 kJ/mol; in medium loamy from -5885,15 to -6040,0 kJ/mol; heavy loamy from -5857,64 to -6032,07 kJ/mol. Gibbs energy in light loamy from -6957,17 to -7094,41 kJ/mol; in medium loamy from -5523,97 to -5678,96; in heavy loam from -5497,98 to -5671,67.

Table 4 - The sum of three fractions of medium loamy dark chestnut soil (0-80cm).

Particle size mm	$\Delta H^0_{298,}$ kJ/mol	$\Delta G^0_{298,}$ kJ/mol	$\Delta S^0_{298,}$ kJ/mol · deg
<0,001	-5560,53	-5223,44	254,80
0,001-0,005	-5765,55	-5407,68	274,25
0,005-0,01	-5839,97	-5478,4	277,08
0,01-0,05	-5885,15	-5523,97	277,39
0,05-0,25	-6004,89	-5644,5	278,12
0,25-0,5	-6040,00	-5678,96	278,51

Entropy in light loamy soil from 347,96 J/mol deg. up to 348,3 J/mol deg; in medium loamy from 277,39 J/mol deg. up to 278,5 J/mol deg. Analysis of thermodynamic characteristics by fractions showed that the energy indicators with increasing depth in light loamy soil are potentially high compared to the overlying layers. It is worth noting the sand fraction, its values are also high. The potential of dark chestnut soils in energy units, can be traced.

The sum of the three fractions makes it possible for us to calculate the entropy index (Π_s) and energy (Π_G), (Π_H) indicators determine the thermodynamic trend towards destruction associated with erosion, deflation, various types of anthropogenic influences or the synthesis of neoplasms in the soil layers

$(\Pi_s)=\frac{\sum S>0.1}{\sum S<0.01}$; $\Pi_G=\frac{(-G)>0.1}{(-G)<0.01}$; $(\Pi_H)=\frac{(-H)>0.1}{(-H)<0.01}$

Other thermodynamic indicators express the relative energy-entropic contribution of three groups of dispersion to the total energy consumption of the natural system (table 5).

Table 5 - Indicators for the thermodynamic orientation of dark chestnut soils.

Light loamy:	Medium loamy	Heavy loamy

$(П_s)=\frac{348,30}{661,09}$ = 0,526865	$(П_s)=\frac{278,51}{529,05}$ = 0,526429	$(П_s)=\frac{278,40}{528,74}$ = 0,526541
$П_{G}=\frac{7109,36}{13346,65}$ = 0,53267	$П_{G}=\frac{5678,96}{10631,12}$ = 0,534183	$П_{G}=\frac{5671,67}{10592,94}$ = 0,53542
$(П_H)=\frac{7561,49}{14273,03}$ = 0,529775	$(П_H)=\frac{6040,00}{11326,08}$ = 0,533283	$(П_H)=\frac{6032,07}{11286,93}$ = 0,53443

In table 5, the ratio of the coarse fraction to the fine fraction did not reveal sharp fluctuations in the changes in indicators. The differences in them occur at such small levels (thousandths and tens of thousandths) that this only indicates an even greater detail of the thermodynamic units. The general indicator of a variety of light loamy, medium loamy, heavy loamy dark chestnut soil, destructive associated with erosion, deflation, various types of anthropogenic influences or the synthesis of neoplasms, revealed the entropy indicator ($П_s$) and energy ($П_G$) and ($П_H$) equal to 0,5 units.

Conclusion

The results of the thermodynamic approach to assessing the intensity of soil formation, considered in this work, show the wide possibilities of thermodynamic methods. Using the approaches of different scientists [1-4, 6-10].

Based on our data on the granulometric composition and gross chemical composition to the energy of soils, taking into account the entropy and energy components, the essential of the dispersion of a substance in their energy intensity is revealed. Since the greatest potential of residual energy is present in the silty fraction of varieties of loam of the subtype of dark chestnut soils.

Entropy and energy indices, which determine thermodynamic destruction and neoplasms, did not reveal sharp changes in these indices.

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