

STUDY OF THERMODYNAMIC FUNCTIONS OF SOIL ORGANIC MATTER IN THE COURSE OF ITS DECOMPOSITION

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Abstract

The thermodynamic functions of southern taiga forest litter samples were determined by means of DSC. It was found that more thermostable compounds (at least in the interval 50–150°C) with higher absolute values of the Gibbs function for intermolecular structures are formed in the course of forest litter decomposition. The data obtained indicate the spontaneous nature of the processes relating to the transformation of organic matter in soil.

Keywords: forest litter, soil organic matter, thermodynamic functions

Introduction

Classical thermodynamics deals mainly with closed systems that do not exchange matter with their surroundings. The behaviour of such systems may readily be predicted via the second law of thermodynamics, according to which spontaneous processes can occur unless appropriate state functions approach extremal values.

However, most natural systems, such as soil, are open and exchange matter with their environment, so that the state functions do not reach extreme values. This is why the existence of open systems and especially organisms was for many decades considered to contradict the laws of classical thermodynamics (thermostatic) and non-equilibrium thermodynamics based on kinetic approaches appeared. Despite many theoretical advantages of the new thermodynamics, it has certain problems when dealing with real biological systems because of the great number of variables to be measured in order to obtain the parameters of the kinetic equations.

In recent years, it has been found [2] that the hierarchical structure of natural systems allows the study of separate quasi-closed subsystems on the basis of classical thermodynamics. Such hierarchical systems consist of a number of structures of higher hierarchies ($j+1, j+2, \dots, j+n$) which originate from structures of lower hierarchies (j), and series of hierarchical structures (selected on the basis of their formation energies) correspond to the series of the mean lifetimes (relaxation times) of these structures [3]. This relationship gave a possibility to elaborate the principles of hier-

archical thermodynamics [4], which combines the principles of classical thermodynamics and the macrokinetics of relatively slow quasi-equilibrium processes. The most important postulate of this new theory for the purpose of our research is that when supermolecular structures are formed, the specific values (per unit of volume or mass) of the Gibbs function of the intermolecular interactions approaches a minimum. This means that, in the case of organisms, the latter accumulate energy-intensive chemical substances that have higher absolute values of the Gibbs function for the formation of supermolecular structures (structural stabilization).

The purpose of the present study was to estimate the changes in the Gibbs function for supermolecular structures in the course of the transformation of plant debris on the surface of forest soils in the south taiga zone by means of differential scanning calorimetry (DSC). DSC is the main tool with which to measure the thermal properties of substances, and is widely used in biophysics and biochemistry in studies of phase and structure transitions resulting from the heating of cells and substances that give rise to exo- or endothermic effects. In soil science, this method is mostly applied for the analysis of exothermal effects in the temperature range 300–500°C, in which the oxidation of structural components takes place [8]. Interesting regularities in a lower temperature interval (100–200°C) may also be observed by means of DSC.

Objects and methods

Forest litter samples were collected in the Central Forest State Biosphere Reserve (Russia).

The structure and thickness of the forest litter in the area under study generally correlates with the degree of overmoistening of the soils: in well-drained soils (such as dystric cambisol), the forest litter is 4–5 cm thick and consists only of layers L and F; soils with impeded drainage (stagnic podzoluvisol) are covered by forest litter 12–15 cm thick and consisting of layers L, F and H. In lowland peat soil (terric histosol), however, the forest litter is rather thin (3–5 cm), due to the specific vegetation and the high activity of the soil mesofauna in the upper horizons.

The subhorizons of the forest litter (L, F and H) represent the stages of transformation of plant tissues from relatively fresh (subhorizon L) to rather decomposed (subhorizon H) material.

The changes accompanying the decomposition process were also studied on samples of *Picea abies* needles after 1 and 2 years of decomposition in the field.

The organic samples were air-dried, ground and sieved through a 0.25 mm mesh. 25 mg of each sample was dried in vacuum (0.01 atm) to constant mass and sealed in a special aluminium container. The thermal characteristics were measured with a differential scanning microcalorimeter (DSM-2M, Russia).

Values of the Gibbs function were calculated by using the following equation:

$$\Delta G = \frac{\Delta H}{T_m} (T_o - T_m) = -\Delta S \Delta T$$

where ΔH is the enthalpy change, T_0 is a standard temperature (298 K), T_m is a maximum temperature of a peak, and ΔS is the entropy change.

Results and discussion

Figure 1 presents changes in heat capacity in the temperature range 50–250°C. It follows from the curves that heat is consumed in the interval 50–170°C. The area under the peak is ΔH . A second peak may be found for some samples, in the interval 180–220°. Intensive heat liberation occurs in consequence of the oxidation of organic matter. We consider the first peak to be caused by changes in the intermolecular bonding of some polymer carbohydrates.

Thermodynamic functions (ΔG and ΔS) calculated according to the above equation are given in Table 1. It follows from the tabulated data that, while the decomposition proceeds, the ΔG values become more negative and the ΔS values become more positive, due to changes in ΔH and T_{max} .

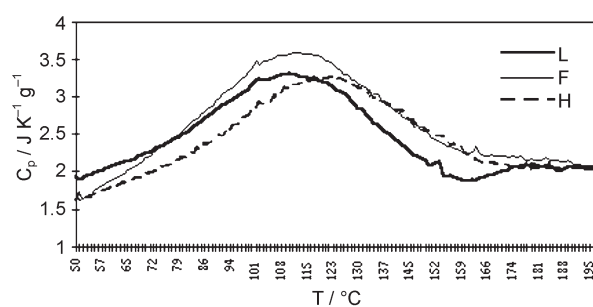


Fig. 1 Relationship between specific heat capacity and temperature for the organic horizons of stagnic podzoluvisol

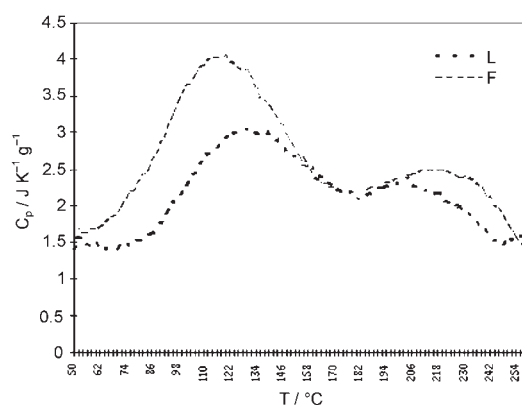


Fig. 2 Relationship between specific heat capacity and temperature for the organic horizons of dystric cambisol

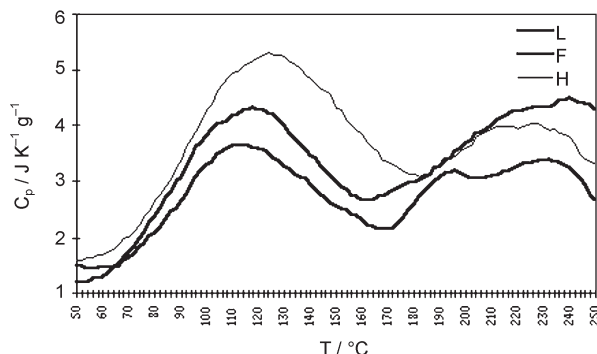


Fig. 3 Relationship between specific heat capacity and temperature for the organic horizons of terric histosol

Table 1 Some thermodynamic characteristics of the samples under study

Soil	Horizon	$\Delta H/$ $J g^{-1}$	$T_m/^\circ C$	$\Delta G/$ $J g^{-1}$	$\Delta T/^\circ C$	$\Delta S/$ $J g^{-1} K^{-1}$
Dystric cambisol	L	100	120	-24.10	95	0.25
	F	120	114	-27.50	89	0.31
Lowland peat soil (terrific histodol)	L	104	110	-23.00	85	0.27
	F	122	114	-28.00	89	0.31
	H	179	124	-44.60	99	0.45
Stagnic podzoluvisol	L	81	110	-17.98	85	0.21
	F	94	113	-21.43	88	0.24
	H	87	122	-27.36	97	0.28
Dystric podzoluvisol	L	122	110	-27.07	85	0.32
	F	131	114	-30.12	89	0.34
	H	87	120	-33.03	95	0.35
	Initial	98	104	-20.50	79	0.26
<i>Picea abies</i> needles	After 14 months of decomposition in the field	141	106	-30.10	81	0.37
	After 23 months of incubation in the field	148	108	-32.20	83	0.39

Increases in the absolute values of the Gibbs function mean that the changes in the structure of the organic matter in the course of its decomposition and the formation of humic substances are spontaneous in nature.

The data obtained are in good accordance with the above-mentioned theory of Gladyshev: in the course of biological evolution, organisms accumulate energy-rich chemical substances that have more negative values of the Gibbs function for the formation of supermolecular structures (structural stabilization) and higher positive val-

ues of the Gibbs function for molecular structures due to the relative accumulation of energy-rich compounds (characterized by higher values of the heat of combustion). Since we do not have our own data on the heat of combustion, this must be assessed on the basis of data published earlier. According to Utkin [10], some chemical compounds present in plant material have the following heats of combustion (kJ g^{-1}):

Monosugars	15.48
Disugars	16.53
Cellulose	17.57
Peptides	20.92
Lignin	26.36

It is well known [1] that, in the course of decomposition of organic matter in soils, water-soluble compounds (such as sugars and disugars) are leached out and mineralised almost completely within several months, and after several years the lignin content is increased 2-fold due to the faster mineralization of celluloses. The chemical energy content (expressed as ΔG^{ch}) therefore increases in the course of decomposition, due to the accumulation of energy-rich lignin compounds. This is in good agreement with the results of Aliev (cited from [6]), who showed that the humification of alfalfa roots led to an increase in the heat of combustion by $3.5\text{--}4 \text{ J g}^{-1}$ as compared with that for fresh roots.

One of the main advantages of the thermodynamic approach is the possibility to predict the development of a process or a system (to which the laws of thermodynamics may be applied) on the basis of the macroscopic properties of the system, without examination of the mechanisms of the process itself. However, these mechanisms may be the essence of the study in many cases. For example, changes in the thermodynamic functions were detected in our experiments, but the processes responsible for these changes remain uncertain. On the one hand, the temperatures of the peaks (Figs 1–3) lay within the interval that corresponds to hygroscopic water. On the other hand, the mass of the samples was lower by 10–15% after vacuum-drying, which corresponds to the contents of hygroscopic moisture in these samples (determined as the mass loss at 105°C).

Similar regularities were found by Orlov *et al.* [7], who studied humic acids and humates by means of thermal analysis. They explained the low-temperature endothermic effects in terms of the loss of hygroscopic water ($85\text{--}90^\circ\text{C}$) and the early stages of humate decomposition (132°C and higher) because of the rupturing of aliphatic chains.

There is no reason to suppose that these endothermic effects are related to the depolymerization of celluloses (the latter account for at least half of the mass of the samples studied), since it has been shown that this process occurs only when the sample is heated to 250°C [5].

To reveal the possible nature of the observed endothermic effects, the following experiment was carried out. 54 mg of layer H of lowland peat soil was heated to 114°C without vacuum-drying. Intensive heat consumption took place at 105°C . After heating for 5 min at 114°C , the mass of the sample was decreased by 9 mg. Then

(after cooling), the sample was heated to 154°C, which led to a 1.3 mg mass loss. The sample was next heated to 200°C (with a mass loss of 0.7 mg) and to 220°C (with practically no mass loss). It should be noted that the peak temperatures in the second and subsequent heating were the same. After removal of the hygroscopic water, therefore, heating of the sample caused structural changes associated with heat consumption. Since the effects took place after cooling and subsequent heating of the sample, this indicates that these structural changes are kinetically reversible. However, much further research remains to be done to reveal the exact nature of these structural changes.

Thus, it may be stated that in the course of organic matter decomposition the residue becomes more thermostable (the absolute values of the Gibbs function increase). This may be one of the reasons why the intensity of organic matter mineralization decreases in the range of samples (L, F and H) for which the degree of decomposition increases [9]. However, as shown above, the chemical energy content increases in the same range in consequence of the relative enrichment in lignin and cellulose content.

The decrease in the Gibbs function values for the intermolecular structures indicates the spontaneous nature of organic matter transformation in soils (or humification in the broad sense of this word).

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