

## SOIL CHEMISTRY

# Transformation of Low-Molecular Nitrogen-Containing Compounds in Soil

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**Abstract**—A simple model is proposed to show the decomposition of low-molecular organic compounds in soil. The model permits us to estimate the rate of oxidation of different carbon atoms in amino acid molecules, the share of their use by microorganisms for anabolism, and the inclusion in humus, as well as the number of cycles oriented to microorganism renewal in the soil during the vegetation period. At initial stages of soil evolution, passive mechanisms (natural selection of heavily decomposed high-molecular components of plant residues) play an essential role in accumulation of humus substances. In the course of soil evolution, active mechanisms assume ever greater importance (inclusion of low-molecular labile N-containing compounds). Changes in the mechanisms may be considered as an additional factor in the microorganism strategy to be adopted for succession in the ecosystem and as one of the indicators of soil transition from an inert to a bioinert system.

### INTRODUCTION

Organic matter of soil is essentially responsible for sustainability of the balance of many nutrients and, in particular, carbon on the earth. The soil contains  $1.39 \times 10^{18}$ – $1.48 \times 10^{18}$  g of carbon, which corresponds to two-thirds of the whole carbon store in terrestrial ecosystems [13, 51, 52, 54]. It exceeds that of living phytomass by 2–3 times [53] and is twice as much as the total carbon content in the atmosphere [43]. Presently, the content and many properties of inert soil components, which comprise 90–95% of the total mass of organic soil substances, are adequately characterized. However, functioning and transformation of soil organic matter is substantially determined by labile compounds—individual low-molecular organic compounds. The role of these substances in humus formation has not been adequately investigated because of their low concentration in soil and rapid transformation.

In the present work, the behavior of low-molecular organic N-containing compounds is characterized, and their role in the formation and renewal of humus is considered.

### MINERALIZATION

In natural ecosystems, the primary reserve of nitrogen in soils is produced and then replenished mainly through immobilization of atmospheric nitrogen by free-living, associated, and symbiotic microorganisms. It makes up 10–70 kg/ha per year in mature soils [7, 24, 39]. In primitive soils, the fixation of molecular nitrogen is considerably lower owing to the lack of available energy sources. Nitrogen-fixing bacteria transform molecular nitrogen first to amino acids and then to high-molecular compounds (proteins) or, through the stage of nucleic bases, to RNA and DNA. After the bacteria die off, these high-molecular com-

pounds are decomposed enzymatically to organic oligomers and monomers—amino acid chains and amino acids, nucleotides and nucleic bases, respectively. Part of these monomers come to the soil directly and undergo transformation characteristic to the given type of compounds and to the particular soil conditions. A comprehensive assessment of the reserves and supply of various nitrogen-containing components in soils is given in a number of papers [5, 6, 9, 18, 20, 22].

The sequence and one possible scheme of the decomposition processes of N-containing compounds are considered in Fig. 1. The whole diversity of the natural N-containing compounds can be combined into several large groups according to the chemical characteristics of their monomers. Protein compounds and nucleic acids are attributed to the first two groups. A special group is distinguished for humic substances, because these biopolymers are characterized by irregular structure and high diversity of their constituent monomers. Humus nitrogen is represented by four major forms [58]: (1) nitrogen of the ammonium anion, (2) nitrogen of amino acids and aminosugars (hydrolyzable by 6 N HCl), (3) nitrogen directly bound to aromatic nuclei (nonhydrolyzable by 6 N HCl), and (4) nitrogen of heterocycles (nonhydrolyzable by 6 N HCl). The presence of at least the second and fourth forms shows the possible genetic relations of humic substances with protein compounds and nucleic acids. The next two groups are represented by nitrogen-containing compounds—chlorophyll and chitin—with lower molecular mass.

After entering the soil, the high-molecular compounds mentioned above are decomposed enzymatically to their corresponding monomers: protein compounds, to amino acids, and RNA and DNA, to nucleotides and nucleic bases. During decomposition of

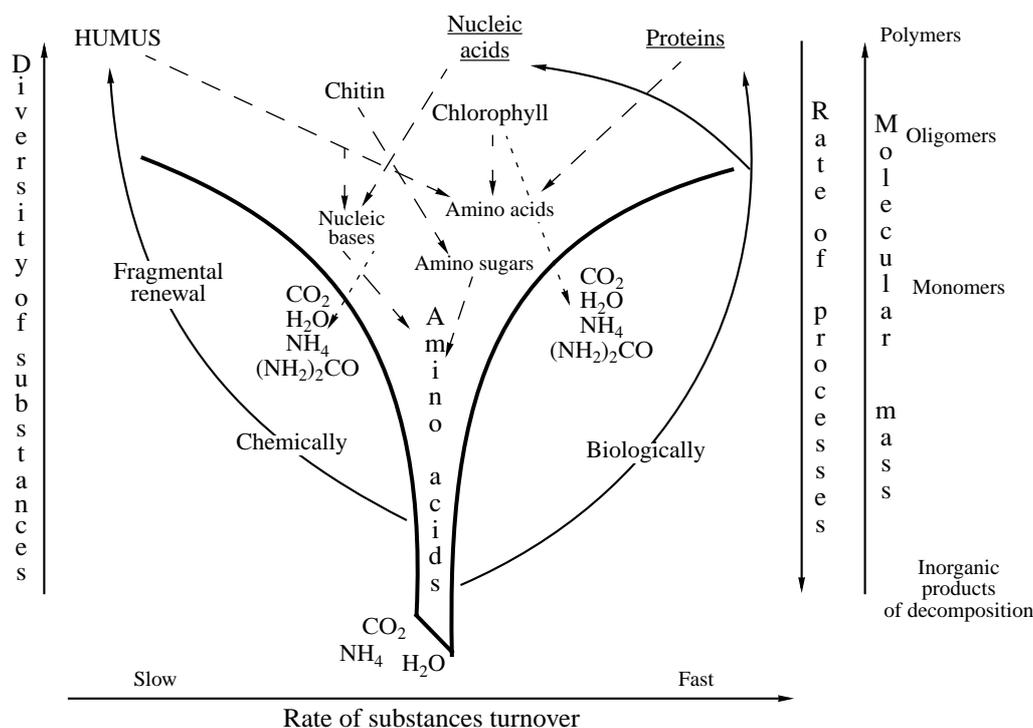


Fig. 1. Scheme of transformation of organic N-containing compounds in soil.

humic substances, the residues of amino acids and some amount of nucleic bases are eliminated from them [16]. In the cells of microorganisms, nucleic bases are transformed primarily to amino acids: pyrimidineous, to  $\beta$ -alanine [34, 35], and purineous, to glycine during anaerobic decomposition and to urea during an aerobic one [34]. (It should be mentioned, however, that at the decomposition of both nucleic bases and other nitrogen-containing organic compounds, the ammonia groups are sequentially eliminated, and besides  $\beta$ -alanine and glycine, the final organic product of decomposition of nucleic bases is urea [34, 35].) Chlorophyll is also decomposed through protoporphyrine to glycine [34]. Similar to other amino sugars, *D*-glucosamine produced from chitin brings its amino group through transamination to glutamine [35].

Hence, during decomposition, all natural organic N-containing compounds pass through the stage of amino acids independently of the type of nitrogen binding in the initial compound, molecular mass, and chemical and physical properties. All the diversity of N-containing compounds is reduced to several amino acids (glycine, alanine, and glutamine) with the amine as the final form of organic-bound nitrogen before its complete mineralization. According to Knyazev (personal communication, 1989), this sequence of natural destruction of organic N-containing compounds in soils is named "amino acid funnel" (Fig. 1). At the final stage of mineralization, about half of the amino acid carbon is enzymatically oxidized to carbon dioxide, and about one-third of the carbon and a major part of the nitrogen is

utilized in anabolism of microorganisms, while a small part of the nitrogen and carbon of amino acids is involved chemically in humus, at sites of previously eliminated less stable fragments [15, 23, 30, 46, 57].

As was shown earlier, amino acids play a key role in the transformation of organic N-containing compounds in soils, which is why we shall consider mainly this class of compounds, taking into account that at the same time amino acids are intermediate metabolites of other N-containing substances.

The lower part of the scheme (Fig. 1), which describes the transformation of low-molecular N-containing components in soil, can be simplified as a model (Fig. 2). Immediately after a low-molecular organic compound (A) comes into the soil, some part of it (H) is chemically included in humic substances. In the conditions of homogeneous media that occur in the absence of high local accumulations of microorganisms in the decomposed material, the rate of the direct chemical incorporation of an individual compound considerably exceeds that of its microbiological destruction [38, 56]. The fragments incorporated in humus (Ah), as well as the ones remaining in the soil solution (Af), are microbiologically utilized (Bf + Bh = Bio) at different rates (g, a). As a result, a part of compound (Y) is utilized in anabolism, while another one (1-Y) is oxidized to CO<sub>2</sub>. Then the microorganisms continue either to consume new portions of entering compounds or to die off accompanied by CO<sub>2</sub> production at the rate b. A more exhaustive description of this model is given in [46].

The present model was described parametrically in the laboratory for several low-molecular organic compounds (alanine, glycine, glucose, urea), labeled with  $^{14}\text{C}$  at different sites of the molecule in different soils: soddy-podzolic with different humus content [46] and sierozem with various levels of salinization [15]. The parameters obtained characterize the ratio and rates in the model (Fig. 2) and schemes of decomposition of low-molecular organic compounds (Fig. 1) in the soils studied:

(1) The initial chemical incorporation of the second carbon atom of amino acids into humus makes up 25–35% of the inflow amount. For the carbon of a carboxylic group, the incorporation does not exceed 10–15%. Possible chemical reactions of incorporation of amino acid molecules into humus molecules were described earlier [12, 49, 60]. A considerable part of the compounds incorporated (one-fourth to one-third) is microbiologically eliminated from humus molecules during the first weeks.

(2) The remaining part of the initial compound is utilized by microorganisms, with 35–50% of the carbon atoms used in anabolism (economic coefficient), while the other part is oxidized to  $\text{CO}_2$  in the first cycle. The consumption rate of low-molecular organic compounds by soil microorganisms is measured in hours (1–2 h [46]).<sup>1</sup>

(3) The rate of eliminated and exoenzymatic oxidation of carbon from the carboxylic group to  $\text{CO}_2$  is considerably higher, and the share of microbiological utilization for anabolism is lower compared to other, initially less oxidized, carbon atoms of amino acids [46]. The rate and the share of microbiological use of carbon from the carboxylic group of amino acids are comparable to the corresponding parameters of urea carbon, because in both cases there is no storage of energy in the form of ATP during oxidation to  $\text{CO}_2$ .

The high rate of exoenzymatic oxidation of the carboxy group of amino acids and, probably, of other low-molecular carboxy acids is, possibly, an evolutionary adaptation of the soil ecosystem to the high inflow of organic acids formed from carbon-containing compounds. Practically every atom of organic-bound carbon entering the soil passes through the stage of the strongly acidic carboxy group on its oxidation to  $\text{CO}_2$ . By this mechanism, a lot of  $\text{H}^+$  ions arise in the absence of their compensation with bases. In this connection, nonalkaline ways of neutralization have to be developed in the course of the evolution; one of them could be decarboxylation. By the suggestion of Kozlovskii (personal communication, 1994), the evolutionary step of the emergence of a decarboxylation mechanism could have occurred in the Carboniferous period (360–286 million years ago) during the most expressed shortage of calcium and other cations. The mechanisms and schemes of decarboxylation, as well as deamination of amino acids in soils, were described in more detail ear-

<sup>1</sup> Here and after the constants of decomposition and biochemical cycle rates are characteristic for optimal laboratory conditions.

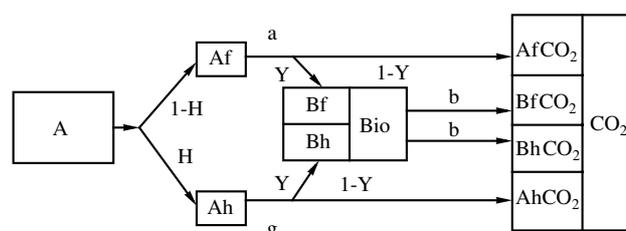


Fig. 2. Scheme of decomposition of low-molecular organic compounds entering the soil (comments in the text).

lier [47, 56]. The rate of decomposition of different parts of the molecule of one compound is correlated with the degree of oxidation of the corresponding carbon atom. So, the most oxidized carbon atom of a carboxylic group is characterized by the highest rate of elimination compared to other atoms in the organic molecule. Hence, it is more valid to evaluate the general rate of decomposition of organic residues in soil with account for the average-weighted oxidation of compounds, calculated similarly to the oxidation degree of humic substances [18], but not only by the content of individual compounds (lignin, cellulose, etc.).

Amino acid carbon incorporated in the microbial biomass participates in the intracellular biochemical cycles. The half-renewal time of carbon in soil microorganisms makes up 1–5 days [21, 46]. These results are in good correlation with the data on the change of 20–40 generations of microorganisms (bacteria) during a vegetation period [2, 3, 21, 22].

The period of half-renewal of newly incorporated carbon in humus makes up tens to hundreds of days [46]. For more stable humic fragments, this period is known to be from tens to hundreds of years, depending on the humus fraction, the character of its binding with the mineral part of the soil, the soil horizon, etc. [30, 31, 32, 36, 37].

The rates of the fluxes mentioned, calculated from the parametrization of the model, reflect the so-called “effective mineralization time” (Effektive Mineralisierungszeit) [44], or, more correctly, the “biologically effective time” (biologisch wirksame Zeit) [41]. This time corresponds to the highest microbiological activity, determined under optimal laboratory conditions (25–28°C, 60% of maximum water content). It should be mentioned that the biologically effective time in this sense is not similar to the period of biological activity (PBA) [8, 19]. For field conditions, the effective mineralization time is calculated as the product of the reduction function (Reduktionsfunktion) for each of the essential or accounted factors. Hence, for the conditions of the southern taiga (soddy-podzolic loamy soil), during one vegetation period (5 months), 25–30 days of the “effective mineralization time” is “stored” (computation by the CANDY (CARBON AND NITROGEN DYNAMICS) model [41] is shown in [40]). This means that in field conditions transformation rates for the compounds will be about 5 times lower than the rates

for the optimal laboratory conditions shown above. From the approximate rate of amino acid decomposition in soil in a natural environment [29, 46] and their average concentration in soil [25], and under the assumption that the amounts of decomposed and resynthesized compounds for long periods are roughly equal, the total amount of amino acids formed during the vegetation period can be calculated. For soddy-podzolic soil,  $T_{1/2} = 1-2$  h (corresponds to methylene group) in laboratory conditions, and  $\rightarrow T_{1/2} = 5-10$  h (average 8 h) in natural conditions. If the amino acid concentration is 10 mg/kg soil [25], then in 8 h, 5 mg/kg is produced. This yields 15 mg/kg per day and 2.25 g/kg in 5 months (one vegetation season). Thus, 3000 kg/ha of amino acids are produced and decomposed by microorganisms during one vegetation season (in a 10-cm soil layer).

This means that in soddy-podzolic soil during a year no less than 500 kg/ha of nitrogen passes through the stage of amino acids. For chernozemic soils with a higher amino acid concentration [25, 33] and longer biologically active period, the amount of nitrogen passing through the stage of amino acids should be even higher. In cultivated intensively fertilized soils, the total amount of organic nitrogen, which is included in the biomass and, correspondingly, passes the stage of amino acids, might be considerably higher. Panikov *et al.* [22] have shown that during a year more than 2000 kg/ha of nitrogen passes through the biomass stage. However the nitrogen amount mentioned should not exist in the soil all at once and be available during the whole vegetation period. In natural ecosystems, a relatively small pool of nitrogen (15–50 kg/ha) most likely is subjected to several (10–30) complete cycles of the turnover. It roughly corresponds to the number of cycles of microorganisms calculated above and to the values most frequently found in the literature—20–40 for the vegetation season [2–4, 10, 21, 22]. Thus, the share of organic nitrogen, which is mineralized and eliminated from the turnover of organic compounds, makes up several percent of the total amount involved in the cycle. Alternatively, an inexplicably high amount of available organic nitrogen is found in the soil during one vegetation season. Such a practically closed recycling of organic nitrogen in natural ecosystems provides a repeated use of the relatively small amount of its available forms and reduces to a minimum its losses in mineral forms.

The calculations shown confirm the fact that the role of a substance in an ecosystem is determined not only by its concentration, but also by the rate of its transformation and turnover [Fokin, personal communication, (1989)]. Thus, amino acids play one of the key roles owing to the high rate of recycling, despite their low concentration in the soil.

## HUMIFICATION

Amino acids not only are the most probable intermediate stage of decomposition of nitrogen-containing

organic compounds in soil, but play a specific role in the renewal of humic substances. In Fig. 1, the incorporation of amino acids in humic substances is shown. The ratio of pools and fluxes of nitrogen-containing compounds in Fig. 1 may vary depending on the localization of the processes (in particular horizons or layers and cutans or the bulk mass, the occurrence inside or outside microorganism cells, etc.), as well as the C/N ratio in the decomposing material.

From the results of short-term experiments on the interactions of labeled amino acids with soil sterilized by  $\text{HgNO}_3$  [14] or by steam [15], the conclusion was made that the inclusion of amino acid carbon in humic acids occurs chemically, without preliminary microbial transformation. Similar conclusions were made by Ziechmann [59]. In nonsterile soil, where microbial decomposition mainly takes place, the share of chemical inclusion in humus is lower than in the laboratory experiments carried out by us. Chemical inclusion is conditioned by the presence of two active functional groups (particularly, the amino group [49, 57]), which allow their direct binding with humus [12, 49, 60]. Such chemical inclusion of low-molecular compounds explains mechanisms of fragmental renewal of humus molecules [26] at the temporal or local excess of low-molecular compounds in the soil (during the period of active decomposition of litter in the rhizosphere area).

The results of experiments on determination of shares of nitrogen and carbon incorporation from amino acids (alanine, glycine) and pyrimidine bases (uracile) into the fractions of humic substances of the soil during a year of composting in natural conditions permitted us to calculate the annual shares of renewal of humus molecules (table) [30]. Calculations of renewal shares were made not only from the concentration of low-molecular compounds in soil, but also from their total amount synthesized during the vegetation period by microorganisms (see above). A more detailed calculation method was described earlier [14, 30]. Data on the mean residence time (mrt) of carbon in humic fractions averaged from the literature (2nd graph: age—mrt), determined by the radiocarbon method [32, 37], are given for comparison. In the 3rd graph, the corresponding shares of annual renewal are shown (it is assumed that the share of a year-to-year renewal corresponds to the reverse value of the mean resident time). Despite some assumptions made during the calculations of renewal of humus fractions in soddy-podzolic soil [14, 30], the data are in good agreement with literature data on radiocarbon dating of humus in soddy-podzolic soil. From these data the following conclusions can be made:

The shares of humus renewal calculated from amino acid nitrogen characterize the general renewal of nitrogen of humus fractions, because in natural ecosystems the main part of the nitrogen initially entering the soil is represented by amino acids or passes through the stage of amino acids.

Mean residence time (mrt) and annual renewal rate ( $\text{year}^{-1}$ ) of carbon in humic substances from soddy-podzolic soil by literature data [32, 37] and calculated from data on carbon and nitrogen annual renewal rates at the expense of amino acids and nucleic bases [30]

Fraction	“Age”		Annual renewal rate ( $\text{year}^{-1}$ ) for C and N of humus fractions at the expense of				
	mrt (years)	C from all sources (from mrt)	2C-of nucleic bases	2C-of amino acids	1C-of amino acids	N-of nucleic bases	N-of amino acids
Humus as a whole	300	$3 \times 10^{-3}$	$2 \times 10^{-6}$	$5 \times 10^{-4}$	$2 \times 10^{-4}$	Not determined	
Humin	500	$2 \times 10^{-3}$	$7 \times 10^{-8}$	$2 \times 10^{-4}$	$10^{-4}$	$10^{-4}$	$7 \times 10^{-3}$
Humic acids	300	$3 \times 10^{-3}$	$10^{-7}$	$2 \times 10^{-3}$	$6 \times 10^{-4}$	$10^{-4}$	$2 \times 10^{-2}$
Fulvic acids	100	$10^{-2}$	$2 \times 10^{-6}$	$8 \times 10^{-4}$	$2 \times 10^{-4}$	Not determined	

The general rate of humus renewal by nitrogen is 2–3 times higher than that by carbon. This is explained by two reasons:

(1) The higher rate of renewal of the peripheral part of humus molecules relatively enriched in nitrogen, which gives an impression of an accelerated renewal by nitrogen compared to that by carbon of the whole humus molecule;

(2) The differences between carbon and nitrogen turnover in which a considerable part of the nitrogen continuously circulates between the pools of microorganisms and humus and mainly fulfills structural functions, not being lost from the ecosystem. Carbon is used for energy purposes (about 50% in the cycle), and after oxidation to  $\text{CO}_2$ , it is eliminated from the soil part of the turnover.

Plant and microorganism residues entering the soil contain not more than 1–5% carbon of amino acids, while 20–30% of carbon of humus is renewed at the expense of amino acids (table). Hence, during humification, the selection of amino acids occurs relative to other compounds. It is caused by their high biochemical activity, high rate of transformation, and the presence of functional groups. Thus, humification is not a purely statistical process. In mature soil, humification is accompanied by a specific selection of biochemically active compounds, which are inherent in all living organisms, although the selection mechanisms are different.

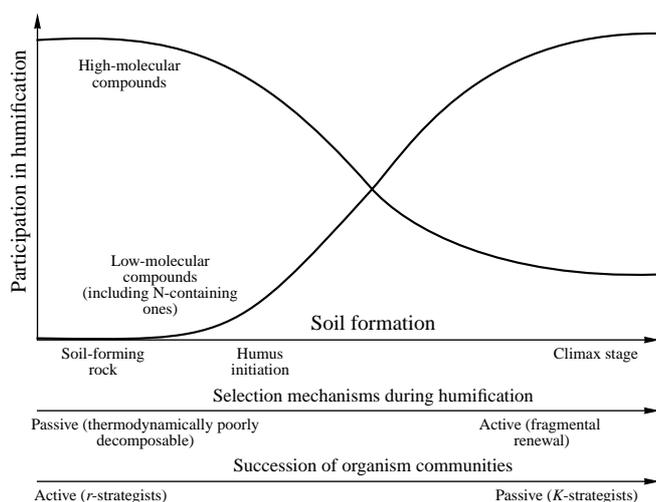
The humic acid fraction (HA) is renewed faster than the fraction of fulvic acids (FA). It should be mentioned, however, that radiocarbon dating and the isotopic ratio  $^{13}\text{C}/^{12}\text{C}$  in the humus fraction [50] often indicates the opposite. (There are data on the higher radiocarbon age of HA compared to FA in soils of the podzolic type [37].) Greater assimilation of low-molecular nitrogen-containing compounds into the HA fraction compared to the FA fraction was shown not only for soils of the podzolic type (amino acids [23], mineral nitrogen forms [48]). The discrepancy mentioned can be explained by differences in the methods applied. The radiocarbon method characterizes the rate of humus renewal only for those soils which are in a quasi-sta-

tionary state for a sufficiently long time to establish an equilibrium between the rate of disintegration of the “old”  $^{14}\text{C}$  and the rate of humus renewal by the “young”  $^{14}\text{C}$  [36]. The radiocarbon age is a mixed characteristic of both the absolute age and the rate of humus renewal until such an equilibrium is achieved. The calculation of renewal from the inclusion of  $^{14}\text{C}$ -labeled compounds in humus, on the contrary, characterizes the true renewal of the fraction (in conditions of long duration of experiments). Hence, the lower radiocarbon age of the FA fraction can be explained by the higher rate of decomposition of the newly formed molecules with an almost total absence of their intramolecular renewal [50]. At the same time, the fast renewal of the peripheral part of HA is probably combined with slow renewal of the nucleus, which is the dominant part of the molecule. This creates the appearance of an older age of the whole molecule. The conclusions given confirm the hypothesis that FA is the product of decomposition and transformation of high-molecular inert components of plant residues [1, 50]. This is partially explained by the absence of essential structural differences between FA of soils of a zonal range [9, (Orlov and Zub, 1963) cited by 18]. On the contrary, HA are practically not subjected to complete decomposition and resynthesis. They incorporate low-molecular compounds by the fragmental renewal mechanism.

The hypotheses mentioned concern functioning of HA and FA in mature soils. However, during soil formation the functioning of various compounds and their impact on humification processes may be substantially different.

#### CHANGE OF HUMIFICATION MECHANISMS IN THE COURSE OF SOIL EVOLUTION

From the aforementioned participation of low-molecular compounds in soil processes and differences in the formation of HA and FA, the probable scheme of the change in humification processes during evolution of a soil as a bioinert system is shown (Fig. 3). In the initial stages of weathering of soil-forming rock, the first inhabitants are plants (mosses and lower lichens). They possess a unique ability of having the highest



**Fig. 3.** Change of humification mechanisms during the process of soil formation.

sorption of nutrients and low-molecular compounds from biogenically poor substrates [4, 28]. As a result, during the first stages, there are practically no low-molecular compounds, including organic nitrogen-containing ones, capable of taking part in the formation of humus molecules. At the same time, the nonhumic and undeveloped substrate has a negligible buffer capacity for a negative environmental impact (the sharpest short-term variations in the number of microorganisms are peculiar to tundra soils; they diminish as one moves south [2]). This substrate is characterized by very short PBA and effective mineralization time. Therefore, in undeveloped soils, high-molecular inert plant residues are accumulated, which cannot be decomposed during the short period of microbiological activity. These components are mainly non-nitrogen or low-nitrogen polymers of a lignin and hemicellulose type. Further accumulation and transformation of these compounds result in formation of FA-type substances (FAs strongly predominate over HAs in forming and weakly developed soils). Accumulation of such partially decomposed compounds and their sorption on the free surfaces of clay minerals and condensation take place with time, which considerably lowers the rate of their migration and further decomposition. During accumulation in the soil (for example, until the soil reaches the mature state characterized by coating of clay minerals with humus films in the humus accumulative horizon), these substances act as an inert buffer system to negative and stress environmental impacts (temporary deficit of nutrients, negative water–air, temperature, redox, and acidic regimes). However, during this stage, only passive mechanisms of mitigating stress effects are manifested. The effective mineralization time increases, which provides the prolongation of microorganism activity and, in turn, gives grounds for substitution of higher plants for lower ones. From this moment, a part of the low-molecular nitrogen-containing compounds

entering the soil are included in stable high-molecular ones predominately by chemical means and enrich them with nitrogen. Humin and HA are formed (the amount of nitrogen in HA is 1.3–1.5 times higher than that in FA [18]). The enrichment of HA and FA with nitrogen continues. These high-molecular compounds function in soil according to the mechanism of fragmental renewal of molecular parts [26] and practically are not subjected to complete decomposition and renewal, in contrast to the initial plant residues and products of their transformation—mobile FA. Low-molecular compounds become important at further soil evolution in processes of humus renewal. Their role is determined by the rate of the cycles “new formation–decomposition” and “inclusion in humus–elimination,” but not by their total concentration in soil, in contrast to the inert substances. In mature soil, the key role in humus renewal belongs to low-molecular compounds (in particular, amino acids [16, 30]). Upon an increase in their concentration in local zones or in separate seasons of the year (i.e., at local or temporal excess), they are included chemically in the sites of enzymatically eliminated less stable fragments. High-molecular compounds play a secondary role in the soil formation. Upon their decomposition, mobile FAs arise, which are characterized by intramolecular transformation and slow but complete decomposition of separate molecules, though not by the processes of fragmental renewal (the analogue is given in [37]). Accounting for the stability of the molecular-mass distribution of FA, the so-called matrix renewal of humus, which is specific for each soil [26], it can be supposed that FAs are the decomposition products of those fractions or groups of humus which are characterized by a stable molecular-mass distribution or which are formed at a stable ratio between the components of the plant litter.

Hence, mature soil functions mainly through the turnover (microbiological formation, chemical incorporation into and microbiological or hydrolytic elimination from humus molecules) of low-molecular compounds. Moreover, in mature soil, a part of low-molecular N-containing compounds necessary for plants and microorganisms is stored temporally as humus molecules (mainly humin), which play the buffer role during stress situations [17, 18, 41, 55]. Thus, in mature soil, buffer mechanisms become active and are realized at the expense of fast recycling processes, and not passively, at the expense of a high amount of stored semidecomposed organic residues, as takes place in primitive or forming soils.

Thus, at the early stages of soil formation, the selection of organic compounds occurs during the domination of passive mechanisms: poorly decomposable material is stored in soil.

On the other hand, in the mature soil, active mechanisms of selection are at work: chemically and biologically active compounds with high turnover rates play a predominant role. This approach supplements the known

scheme of organism succession: at the early stages, *r*-strategists, which have the most active survival mechanisms, predominate, while in a climax ecosystem *K*-strategists prevail, which are the most thermodynamically suited to the ecosystem structure and implement "passive" survival mechanisms.

At first glance, it does not agree with the known fact of the accumulation of thermodynamically stable compounds in the course of the humification process [11, 45], especially in soils with the longest PBA [17–19]. However, this fact reflects only the result of humus formation, and not the process itself. In our opinion, in mature soil, an accumulation of initially labile nutrients occurs in nonavailable forms. The scheme advanced (Fig. 3) agrees well with and explains the internal mechanisms of kinetic humification theory developed from correlation interrelationships [19]: in soils with a long PBA, the total amount of low-molecular compounds during a year is considerably higher than in soils with a short PBA because of the higher cycling rate (synthesis–destruction). This is conditioned not only by the duration of PBA, but also by a longer biologically active time and higher concentration of low-molecular nonspecific compounds in mature soils compared to undeveloped ones. (Supposedly, the ratio of the mass of annually formed low-molecular labile compounds to the total mass of poorly decomposable high-molecular ones in soils with a long PBA is also higher.)

The more active synthesis of low-molecular nitrogen-containing compounds that have a major impact on humification and their incorporation into HA are responsible for the formation of the humate type of humus in soils with a long PBA.

The scheme advanced clearly describes the formation and evolution of the soil from an inert system into a bioinert one. This evolution is accompanied by a change in humification mechanisms: thermodynamically stable compounds accumulate in inert systems, while labile compounds, in bioinert ones, despite the necessary high energy expenses.

## CONCLUSION

The state of a soil system is the final result of the processes and only partially characterizes its functioning. The suggested hypotheses on the formation and functioning of humic substances in soils and the impact of low-molecular compounds on the formation and renewal of high-molecular compounds motivate and predetermine the strategy of studies in this field. A functionally oriented approach for studies of humic substances was advanced by Fokin [27]. Considerably greater attention should be paid to compounds with a high cycling rate—amino acids, carbonic acids, and sugars. In the determination of their impact on the total balance of compounds and on various processes of transformation and renewal of humus, calculation of the amount of synthesis of such compounds per unit time is necessary.

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