Model of CO_2-Emission by Decomposition of Low Molecular Weight Organic Substances in Soil

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Summary

A simple model of CO_2-emission by decay of low molecular weight organic substances in soil is suggested. The model includes one chemical and three biological steps. Analytical solutions of model differential equations permit the use of nonlinear regression methods for estimating parameters.

The model was verified by decomposition of ^{14}C-labelled glycine and alanine in soil. The half-life periods in soil for carbon from different positions of molecules of free aminoacids, sorbed aminoacids and soil biomass and other model parameters were calculated.

The model can be used for simple calculations of rates and half-life periods for end products of decomposition; it can also be included as a component part in general models of substance transformation in soil.

1 Introduction

The study of the transformation of individual low molecular weight organic compounds in soil is complicated by the difficulty of complete extraction and definition of initial substances and their derivates in the context of the enormous variety of soil components. At the same time, measurement of the end product of mineralization - CO_2 - is not a methodological problem, and has often been used for investigating decomposition kinetics of different soil compounds (plant residues, sugars, proteins and aminoacids, pesticides, toxic organic substances, products of incomplete combustion of fuel and many others). However the kinetics of CO_2-emission from soil is directly connected with the specific decay processes of the investigated compounds (presence, quantity and decay rates of intermediated metabolites; sorption onto clay minerals and humus; participation of chemical and biological processes in initial compound transformations; end products; toxicity of the compound and its metabolites and many others). If the transformation specifity

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CO_2 - carbondioxide formed from:
- $AfCO_2$ - carbondioxide released by microorganisms using free substance - "Af";
- $AhCO_2$ - carbondioxide released by microorganisms using sorbed substance - "Ah";
- $BfCO_2$ - carbondioxide released by dying off and decomposition of microorganisms - "Bf";
- $BhCO_2$ - carbondioxide released by dying off decomposition of microorganisms - "Bh".

The fourth stage (4) consists of the sum of two parallel processes: $BCO_2 = BfCO_2 + BhCO_2$ (CO_2 emissed by dying off and decomposition of microorganisms, formed from free and sorbed substances accordingly). The rates of $BfCO_2$ and $BhCO_2$ emission are independent, therefore this system has a simple analytical solution (GERASIMOV 1966).

Besides general CO_2-emission there are analytical solutions for each block of the scheme too, that allow to calculate the time change of each component and to make forecasts.

3 Materials and methods

For the model verification we have carried out an experiment in laboratory conditions to estimate the $^{14}CO_2$-emission by decomposition of ^{14}C-labelled aminoacids (alanine and glycine) in sod-podsolic soil. ^{14}C was in the first and second places of aminoacid molecules. The labelled aminoacids were added as a solution to premoistened soil (60% of field capacity) which was closely incubated at 28°C. During 50 days the $^{14}CO_2$ released was sorbed with 1 N NaOH that was changed periodically. To measure the ^{14}C activity of the CO_2 trapped in the NaOH, 1 ml of NaOH plus 4 ml deionized water was added to 10 ml of *C-13H scintillation cocktail. The ^{14}C activity of sorbed CO_2 was measured on a LKB betaspectrometer "Rackbeta" model 1219 with preliminary standardization. The experiment was carried out with two replicates.

4 Results and discussion

Very rapid decomposition takes place after labelled aminoacids are introduced in soil. The cumulative results of $^{14}CO_2$-emission from soil are presented as dots and triangles on fig. 2 and 3. The differences between replicates in $^{14}CO_2$-emission did not exceed 2-3%. It should be noted that the curve form of $^{14}CO_2$-emission will be determined by the aminoacid type, but by the position of ^{14}C in the molecule. The carbon of carboxyl group of both aminoacids were oxidized most rapidly and fully.

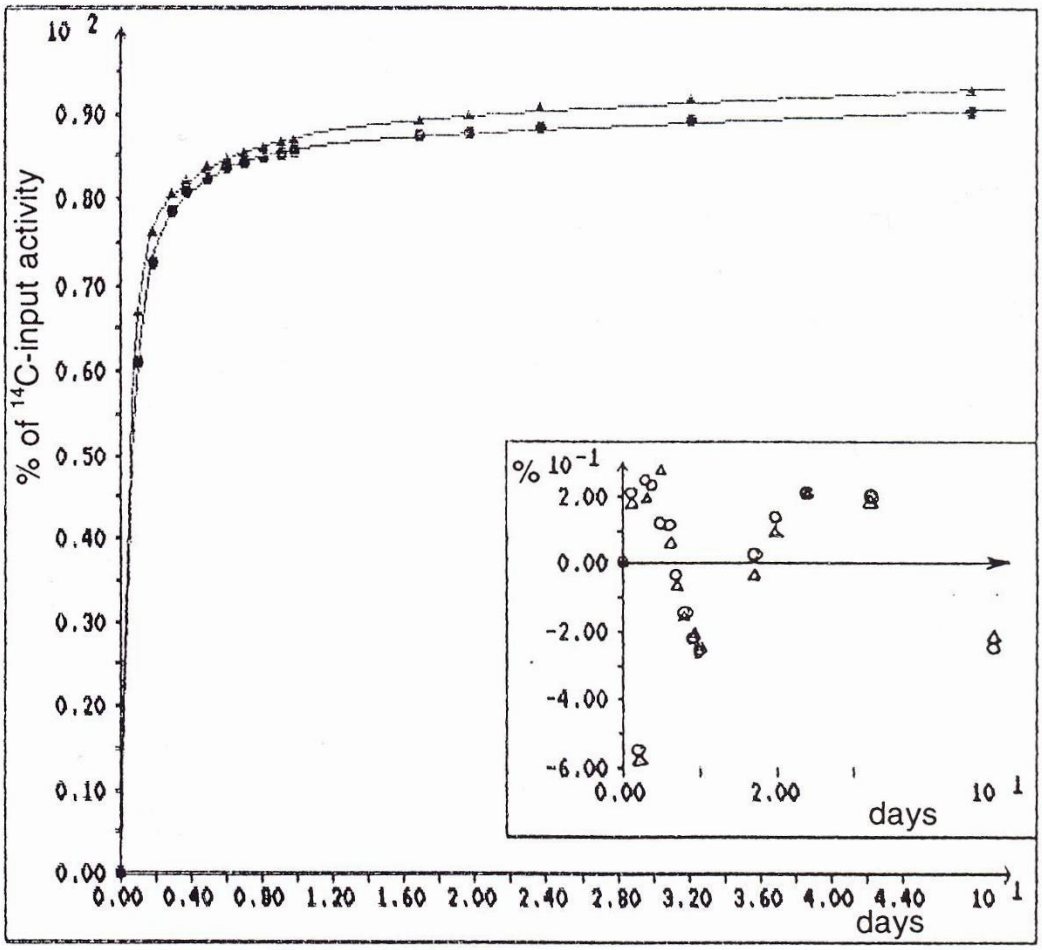

Fig. 2.: Experimental cumulative values of $^{14}CO_2$-emission by oxidizing of carbon from carboxyl group of glycine (^)and alanine (0) by decomposition in soil. Nonlinear regression was calculated in accordance with the model equation and residual between experimental and calculated values (^) and (0).

The oxidation of the methylene group carbon that is directly bound on nitrogen, proceeded at a slower rate. This is probably due to three reasons:

1. the nonshared electron pair of nitrogen resulting in binding on nitrogen and aminoacid inclusion into humus;
2. smaller initial oxidation degree of carbon from methylene group in comparison to carbon from carboxyl group;
3. greater use of carbon from the second place of aminoacid molecules in the microorganisms metabolic cycles.

According to the eq. (7) we have calculated the characteristic rate constants for initial free aminoacids and for biomass and aminoacids sorbed on humus with the methods of nonlinear regression. We have calculated the constants of "i" and "h" too. The obtained results are presented in tab. 1. On the fig 2 and 3 the curves correspond to the regression model with calculated coefficients. Special consideration must be given to the high conformity of experimental and calculated

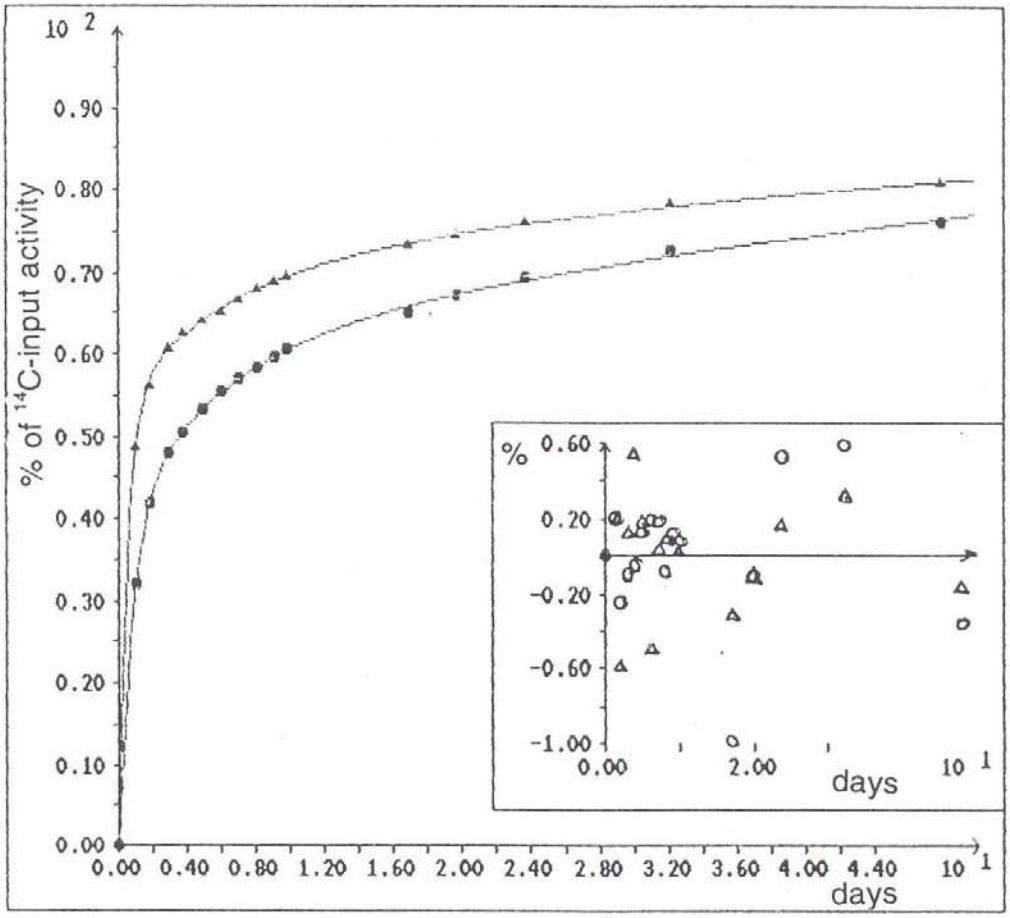

Fig. 3.: Experimental cumulative values of $^{14}CO_2$-emission by oxidizing of carbon from methylene group of glycine (^) and alanine (0) by decomposition in soil. Nonlinear regression was calculated in accordance with the model equation and residual between experimental and calculated values (^) and (0).

Constants	[1-^{14}C]		[2-^{14}C]	
	Glycine	Alanine	Glycine	Alanine
$T_{1/2}$ - Aminoacid	0.33	0.39	0.36	0.52
$T_{1/2}$ - Biomass	3.0	2.3	4.4	3.9
$T_{1/2}$ - Sorbed aminoacid	57	79	75	63
i: Part for anabolism	0.16	0.19	0.23	0.34
h: Sorbed part	0.13	0.15	0.29	0.39

Tab. 1.: Constants calculated for $^{14}CO_2$-emission model by decomposition of ^{14}C-glycine and ^{14}C-alanine by different ^{14}C-position in molecule ($T_{1/2}$ - in days).

values (in all variants r > 99.5%). The residual between experimental and calculated values for anyone point of CO_2-emission are smaller then 1% of input ^{14}C-activity (fig. 2 and 3). This fact certifies the near conformity of the suggested model to the decay processes of the investigated aminoacids.

The calculated half-life periods of the substances (aminoacids, biomass and humus included fragments) are similar to the decay rates of biomass obtained with other methods (JAWSON et al. 1989, MARUMOTO et al. 1982, NICOLARDOT et al. 1986, BONDIETTI et al. 1972). However, the decay rates of aminoacids decomposed in soil by 20°C obtained by BARAK et al. (1990) are considerably slower.

The value of coefficient "i" for methylene group of aminoacids (that microorganisms use for anabolism) corresponds with coefficients of lightly decomposed substances used by many microorganisms (LOBANOK et al. 1988, BEZBORODOV 1991). Microbiological usage of carbon from carboxyl group of aminoacids is connected with its maximal oxidation degree and, accordingly, with minimum energy that will be produced by its full oxidation to CO_2.

In accordance with the literature on aminoacid biochemistry is the fact that carbon is used from the second place of alanine compared to carbon from the second place of glycine. It is known from the microorganism's biochemistry, that after decarboxylation processes, alanine is the key substance for synthesis and pre-amination of most aminoacids.

Special consideration must be given for the greater part of carbon from both places of alanine - "h" that is included in humus in comparison to glycine. This supports results from DASHMAN & STOTZKY (1982) showing low sorption especially of glycine on clay minerals (montmorillonite and kaolinite) in comparison to other aminoacids.

The suggested model also allows calculation of the theoretical dynamic of ^{14}C-inclusion in microorganism's biomass (fig. 4): Since experimental estimation of ^{14}C-inclusion in biomass is difficult, methods describing complete extraction of microorganisms from soil without destruction of its structure, are absent. Such theoretical curves of ^{14}C-inclusion in biomass have one maximum, generated in these given conditions on the second day for carbon from second place and on the first day for carbon from the first position of aminoacid molecules after introduction to soil. The location of this maximum of inclusion in biomass of carbon from methylene and carboxyl group is 10 and 13.5% of input activity accordingly.

The obtained theoretical ^{14}C-inclusion in soil biomass is similar to the experimental curve of formation and decay of isotope-labelled microbial biomass during the decomposition of ^{14}C- and ^{15}N-labelled plant material (LADD 1981).

The maximal difference (in value) between carbon positions was observed for half-life periods of biomass. This shows that the first and the second carbon atoms

from aminoacid molecules be used by microorganisms during different time periods. The direct index of carbon use by microorganisms is the area under the corresponding curve (fig. 4) - integral of function B(t) by time. The integral differences for glycine and alanine at the same carbon positions do not exceed 10%, and for the first and second carbon places are distinguished twice and are 51 and 105%*days in average of the both aminoacids.

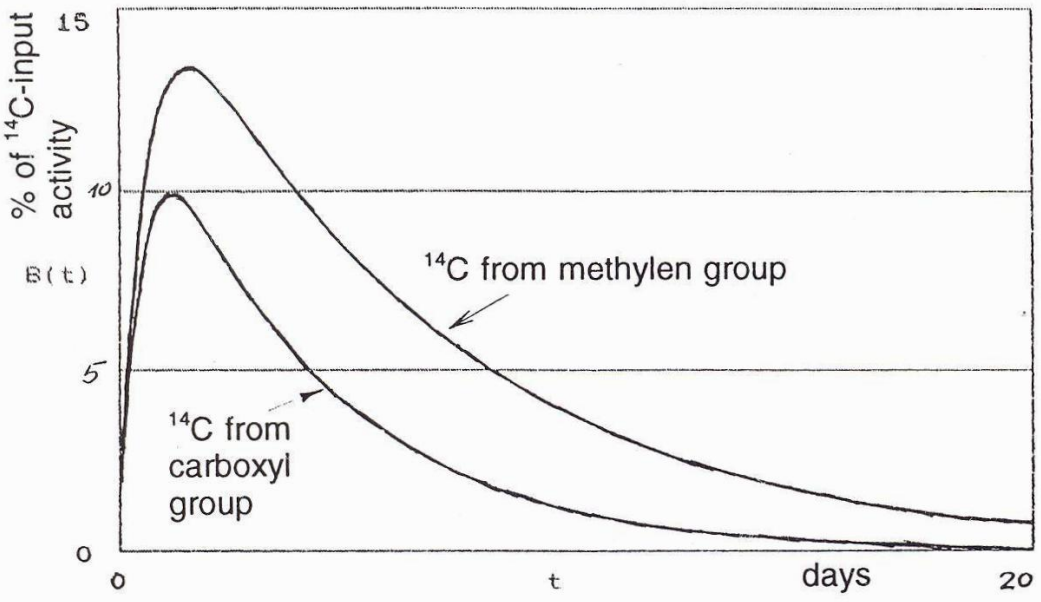

Fig 4.: Model-calculated theoretical ^{14}C-inclusions of carbon from carboxyl and methylene group of aminoacids in soil biomass.

The rate of microorganism oxidation of initial aminoacid and aminoacid sorbed on humus are equal for the different carbon positions. This confirms indirectly the similarity of the first and the last (according to the model) decay stages for carbon from both the positions.

The constant "g" for the first and the second carbon do not not differ as much as constants "a" and "b". That indirectly confirms the inclusion of both carbon atoms into humus substances (though the inclusion mechanisms are different) and, therefore, the similar decay rates.

The convenience of the suggested model is its simplicity and its algebraic solution. This allows use of nonlinear regression methods for the direct estimation of the model's parameters, making the processing of experimental data considerably easy. The nonlinear regression allows exact determination of all five model coefficients, which have a clear physical meaning.

So, the suggested model describes well the experimental curve of CO_2-emission from soil, and gives the high conformity of obtained coefficients with corresponding literary data too.

This model can be used for:

- the explanation of CO_2-emission curves from soil in its composites;
- the easy calculation of rates and half-life periods of limit stages by decomposition of free and sorbed substances, and formed biomass too;
- it can be included as a component part into general models of substance transformations in soil.

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