CARBON DYNAMICS IN SOIL RECORDED BY ^{14}C: MODEL CALCULATIONS

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Abstract: Time records of $^{14}CO_2$ from soil respiration collected in the years 1998 to 2003 on sites representing different ecosystems (mixed wood, agricultural field and grassland, southern Poland), were analysed by use of MLB model built for this purpose. The modelled turnover time (TT) is maximum 22 yr for the agriculturally cultivated soil and only 14 yr for soil under grassland and mixed forest. About 22% of an old component of 1500 yr was admixed to the agriculturally cultivated soil while it was only 12% under mixed forest. Estimated ratio of carbon content in slow and in fast decomposition boxes varies from 22 to 40 in southern Poland pointing to slow decomposing organic compounds as the major pool of carbon in soil. The lowest ratio was observed for soil of low proportion of organics content in mixed forest, and the highest for grassland of well developed soil profile. $\Delta^{14}C$ time records for not cultivated soils (under grassland and mixed forest) showed higher values than local atmospheric CO_2, moreover $^{14}CO_2$ from the mixed forest soil respiration remarkable exceeded "clean air" reference level for Central Europe.

1. INTRODUCTION

Measurement data of atmospheric CO_2 concentration and isotopic composition implemented to mathematical models became a useful tool for assessment of CO_2 fluxes circulating between major carbon reservoirs (e.g. Siegenthaler and Joose, 1992; Wigley, 1993; Kaduk and Heiman, 1994; Sarmiento *et al.*, 1995; Schimel *et al.*, 1995). Response of land biota to the increasing atmospheric CO_2 concentration as well as size of the buffering capacity is important parameters in global and regional scale modelling. Early studies of soil carbon dioxide carried out by e.g. Haas *et al.* (1983) prove variation of the ^{14}C specific activity in soil CO_2 on depth and season of the year. A diffusion model developed by Thorstenson *et al.* (1983) considers root respiration as the only source of soil CO_2. In a later work (Dörr and Münnich, 1986) seasonally varying rate of CO_2 production by root respiration and microbial decomposition of organic matter are estimated for different soil types by the ^{14}C activity. Dynamics of soil organic carbon in soil under grass- and woodland ecosystems was investigated by O'Brien (1986) and Harkness *et al.* (1986).

More advanced studies on the carbon circulation within soil and between soil and atmosphere (Parton *et al.*, 1993; Jackinson 1990; Wang *et al.*, 1994; Harrison and Bonani, 2000; Harkness *et al.*, 1986; Dörr and Münnich, 1986; Gaudinski *et al.*, 2000) confirmed complexity of decomposition processes as well as that dynamic of soil carbon dioxide cannot be described by a single turnover time. At least two components of much different age (order of tenth and hundreds / thousands yr) are required for modelling experimental records.

The paper presents results obtained in the course of a five-year study (1998-2003) conducted in southern Poland where carbon isotopic composition of soil CO_2 has been regularly measured. The results were interpreted by multilayer box model (MLB) using parameters: the turnover time (TT), CO_2 output fluxes of the boxes, and carbon content of the boxes as basic. The model results were compared with published data.

2. FORMULATION OF THE MLB MODEL

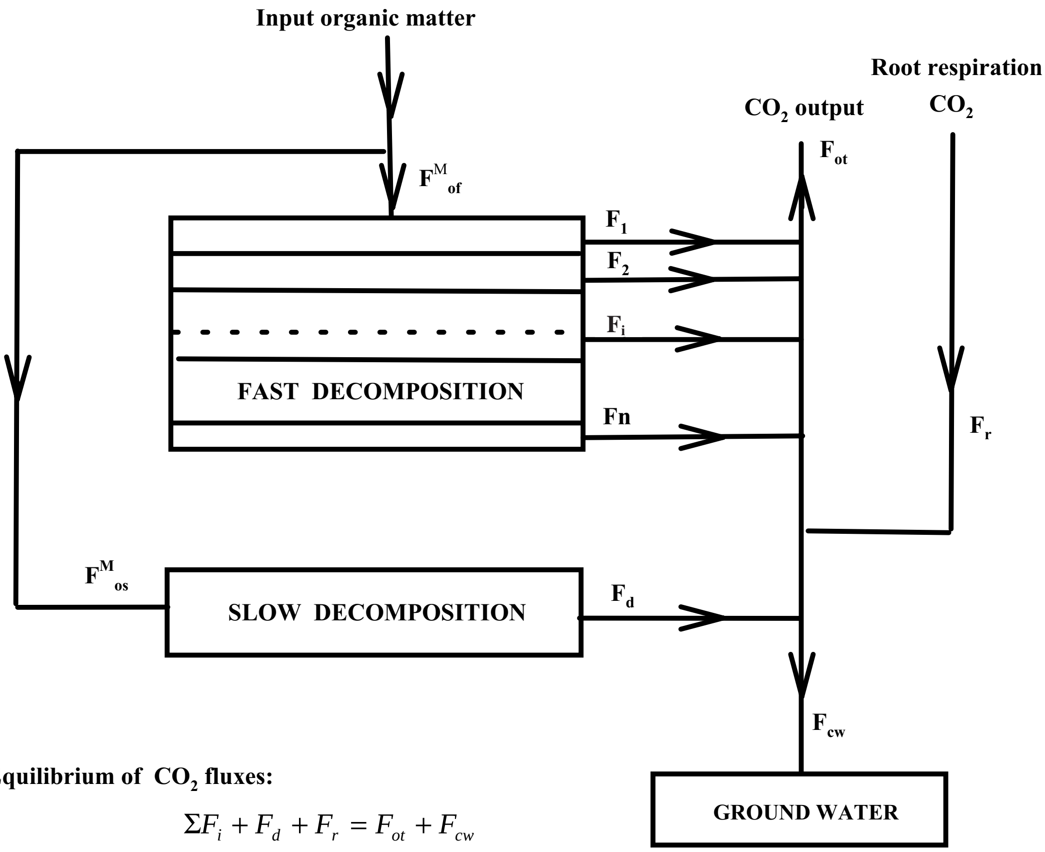
In the multilayer box model (MLB) the soil pool in which some organic matter is converted to CO_2 is divided into two sub-boxes: i) fast, and ii) slow decomposition box (**Fig.1**). Criterion for this division is time necessary for conversion of organic matter present in given box into CO_2 that finally is removed to the atmosphere. Generally accepted measure of the conversion rate is the turnover time (TT) that in case i) is of the order of tenths of years while for ii) reaches even thousands of years.

Carbon dioxide that leaves the boxes (fluxes: F_s, ΣF_i, **Fig.1**) is being mixed with CO_2 originating from root respiration of plants growing on the surface (F_r). On the other side fraction of carbon dioxide present in soil pores is dissolved by infiltrating water and transported downward (F_{cw}) partly in form of bicarbonate and carbonate recharging eventually the ground water system.

Majority of organic matter undergoing fast decomposition belongs to the box that has a layer structure containing carbon deposited in consecutive years. In the MBL model "layer" represents carbon accumulated in the box in one year, and carbon isotope composition within the layer is characteristic for the year of accumulation. Decomposition rate of carbon in the model is assumed as proportional to the mass of carbon that undergoes decomposition. This means that decomposition process of deposited carbon is constant at lest for the first some years i.e. mass of produced CO_2 per mass of carbon that can be converted to CO_2 is constant. Finally the output flux of CO_2 from the box originates from layers that were consecutively deposited for some hundreds years, however contribution of the layer to the output flux exponentially decreases with the age of the layer.

Turnover time (TT) is defined as time necessary for decomposition mass of carbon which equals to the mass present in the given box. TT can be calculated as ratio of mass of carbon not decomposed (left in the soil) to mass of carbon that was removed (decomposed) from the box. One can show that TT is proportional to reciprocal constant of decomposition rate, if this constant is small what is a usual case. Assumption of not changing with time of the constant of decomposition rate that has the same value for each layer is usually fulfilled because conditions of soil formation in given ecosystem (if not anthropogenicaly disturbed) are constant for enough long time (order of hundred years).

The output flux of the boxes (F_{ot}, **Fig. 1**) consists of CO_2 from organic matter undergoing slow decomposition (F_d), fast decomposition (ΣF_i), and that of root respira-



Equilibrium of CO_2 fluxes:

$$\Sigma F_i + F_d + F_r = F_{ot} + F_{cw}$$

Balance of corbon mass:

$$F_{of}^M + F_{os}^M + \frac{d}{dt}M_f + \frac{d}{dt}M_s = \Sigma F_i^M + F_d^M$$

Fig. 1. Schematic illustration of the MLB model and fluxes of CO_2 circulating within soil. Structure of the slow decomposition box is not shown. Upper subscripts in balance equation refer to fluxes of carbon mass that enter or leave the boxes; M_f and M_s are masses in fast and slow decomposition boxes, respectively

tion (F_r). The radiocarbon age of the first component (F_d) is usually thousand years while the carbon dioxide from root respiration (F_r) represents contemporary atmospheric ^{14}C in the investigated region. Certain fraction of soil carbon is removed to ground water system (F_{cw}) and contact with soil is broken. This F_{cw} carbon has ^{14}C specific for the place of origin considering isotopic fractionation.

Two boxes representing soil that contains certain amount of carbon are usually characterised by significantly different turnover time. Assuming equilibrium conditions and decomposition rate proportional to total mass of carbon compounds one can estimate carbon mass in a given box.

Atmospheric CO_2 and that respired from living organic matter has a ^{14}C activity strongly anthropogenically effected by nuclear bomb tests. This labelling turned out to be a very useful tracer for the investigation of the carbon cycle in the atmosphere and biosphere including soil. It can be used to estimate carbon turnover rates as well as the size of carbon inventories. The ^{14}C input function varies from year to year and with the geographical location. For our modelling we used as input function the atmospheric ^{14}C records after 1950 (Levin and Kromer, 1997; Hua *et al.*, 2003; Kuc *et al.*, 2003), before 1850 the value 100 pMC, and gradually decreasing value from 100 to 90 pMC in period 1850/1950.

3. STUDY AREA

Study area is located in southern Poland, and on places typical for the region. ^{14}C and ^{13}C in soil CO_2 were continuously recorded at least for 1 year in month intervals at the following three sampling sites (Gorczyca, 2003; Gorczyca *et al.*, 2003):

i) Mixed forest (**PZL**): The sampling site is a podsolic soil in a large mixed forest (oak, hornbeam, coniferous trees). The uppermost layer (A horizon consists of fresh leaves and roots undergoing decomposition) is approximately 15 cm deep. The next lower bleached layer (20 cm) consists of grey sand with a very small admixture of humic matter. The water table in this region is relatively shallow and some tens centimetres below ground during periods of intensive rainfall (June/August).

ii) Agricultural field (**PZO**): The soil forms the uppermost 35 cm thick (A_P horizon). The area has been cultivated with potatoes for many years and belongs to the low class of agricultural quality, fertilised in limited scale. The site is located in a small village of a hilly region on the foot of Carpathian Mountains ca. 150 km to the south-east from Kraków.

iii) Grassland (**PZT**): Turfy humus dominates in uppermost 20 cm layer (A_1 horizon). Below there is a well marked transition to a brown dusty clay (B). Colour of clay is getting more intensive to a depth of ca. 75 (C_1), then is gradual transition to grey loose sand with admixture of clay (C_2). Carbon concentration is maximal, 1.25 %, at the depth of ca.70 cm. This site is located in Kraków agglomeration, in residential quarter where dominate gardens and parks, on a grassland not cultivated at least in the last 50 years.

4. METHODS

To collect CO_2 for determination isotopic composition formed by soil respiration and decomposition of organic matter inverted–cup method in closed–system version was applied (**Fig.2**). The sampling system consists of a 40-litre metal container with cut bottom equipped with appropriate inlet/outlet connectors. Details of the sampler are described by Gorczyca (2003). The container was pressed into the soil about 10 cm preventing admixture of atmospheric gases. The gases residing under the metal container ware pumped through a molecular-sieve trap in closed circuit and CO_2 was quantitatively absorbed (**Fig.2**). An electronic control system turned on and off the diaphragm pump at pre-programmed time intervals. Collection of one sample lasted one month, while recording at least one year. The flux of the soil CO_2 is described by formula:

$$j(t) = \alpha \cdot \partial C / \partial t \tag{4.1}$$

where a is ratio of the container volume to covered area; $\partial C / \partial t$ is the time derivative of the CO_2 concentration under the inverted container. Thus the CO_2 concentration in the container rises exponentially until a saturation value. Pumping lasted only some minutes with interrup-

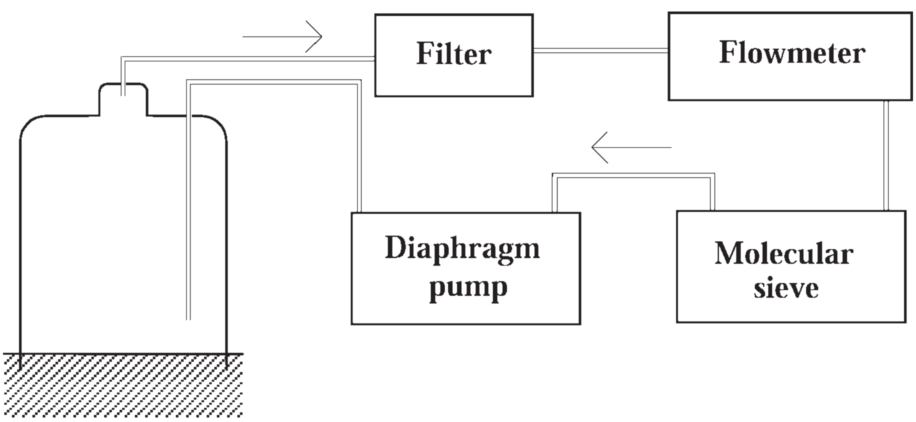


Fig. 2. *Schematic representation of sampling system used to obtain cumulative monthly samples of soil CO_2 for radiocarbon analysis*

tion intervals of about 1 hour when near-equilibrium with the saturation value became established.

Carbon dioxide adsorbed in molecular sieve was recovered quantitatively in the laboratory applying thermal desorption (ca. 3-5 litres per sample). Next benzene was synthesised to analyse ^{14}C activity in LSC spectrometer (TRI-CARB, Canberra-Packard) following standard procedure (Kuc, 1991). In small portion of CO_2 also $\delta^{13}C$ was measured and results reported on the V-PDB scale (Coplen, 1996). Radiocarbon data are reported as a deviation from the contemporary carbon standard (NBS Oxalic Acid) and expressed as pMC and $\Delta^{14}C$, following generally accepted notation (Stuiver and Polach, 1977).

$$A_{pMC} = (A_{sample} / A_{standard}) \times 100 \ \ (pMC) \qquad (4.2)$$

$$\Delta^{14}C = (A_{sample\ norm.} / A_{standard} - 1) \times 1000 \ (‰) \qquad (4.3)$$

where: A_{sample} – ^{14}C activity of the sample;
$A_{standard}$ – ^{14}C standard activity;
$A_{sample\ norm,}$ – ^{14}C activity of the sample normalised to $\delta^{13}C$ = -25 ‰.

5. SOIL DYNAMICS: RESULTS OF MODELLING

Turnover time of carbon in surface soil

The MLB model was run for data from New Zealand grassland sites (**Fig. 3**, insert) published by O'Brien and Stout (1978). The obtained turnover time (TT) is about 23 years with contribution of ca. 7% of an 4000 yr old component. Upper envelope limiting set of the measurement results compiled by Harrison and Bonani (2000) for North America (**Fig. 3**, insert) calculated by the MBL model represents also TT = 23 years with the similar contribution of an old component (7%, 4000 yr).

In the soil of a newly planted pine forest (Richter *et al.*,1995; Harrison and Bonani, 2000) organic carbon is accumulated in 1960-1990. ^{14}C measured in the surface soil steeply increased until ca 1975 and decreased afterwards corresponding to the ^{14}C bomb peak recorded in the atmosphere ca. 10 years earlier. For this type of soil TT estimated by Harrison and Bonani (2000) is 12 years (two times faster as the global average) and the old component (2300 yr) contributes in 35 %. Hence it is a relatively young soil with a higher proportion of old carbon from former ecosystem.

Turnover times calculated by the MBL are matching estimates by the other authors (Harrison and Bonani, 2000) validating the used model.

^{14}C in CO_2 of soil respiration

The carbon dioxide in the soil is produced by decomposition of organic matter and root respiration that both are temperature dependent. It leads to the well pronounced seasonal variation in temperate climate zone. Radiocarbon signature of thus CO_2 shows also a long term yearly variation.

The ^{14}C value of the soil CO_2 remarkably varies between ecosystems and depends on depth. Time records of ^{14}C in soil respired CO_2 collected at soil surface at three sampling points in southern Poland are shown in **Fig. 3**.

The $\Delta^{14}C$ records in soil CO_2 sampled in southern Poland in years 1998-2003 (**Fig.3**) have different ^{14}C levels. The averaged $\Delta^{14}C$ values of PZL are by 40 ‰ higher than

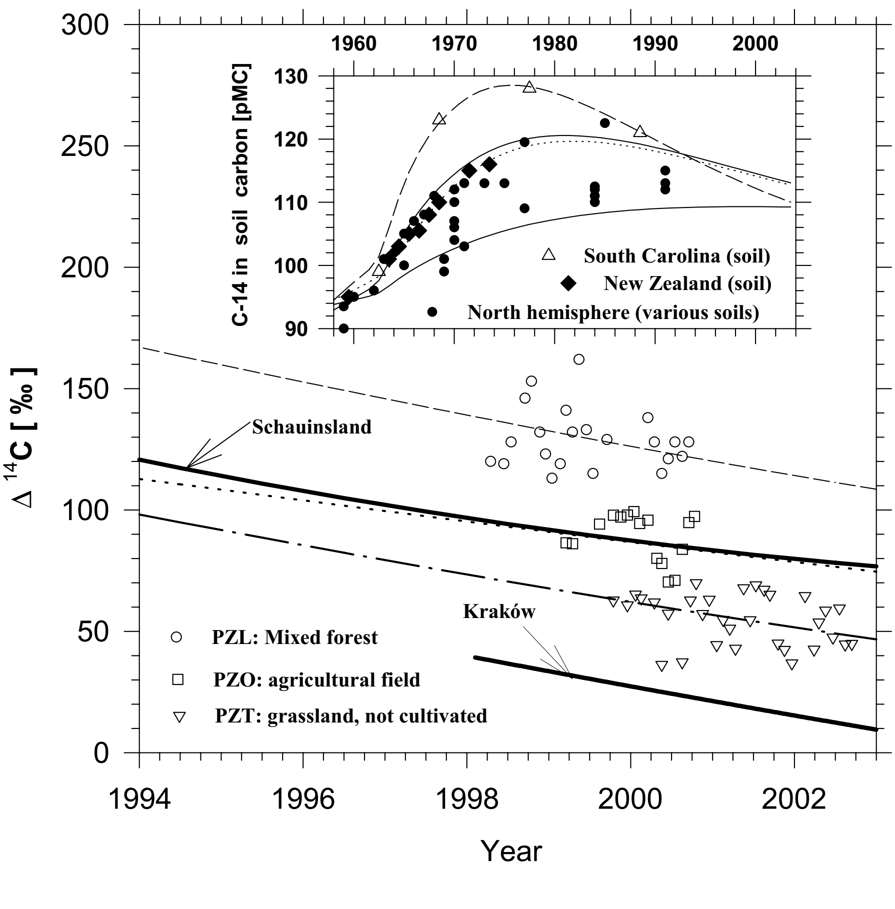


Fig. 3. *$\Delta^{14}C$ in CO_2 respired by soil, collected at the surface of southern Poland (PZT, PZL, PZO). Thin lines (solid, broken, dotted, broken-dotted) represent model calculations for the $^{14}CO_2$ records. ^{14}C in atmospheric CO_2 for Schauinsland (Levin and Kromer, 1997), and Krakow (Kuc et al., 2003) sampling points are shown as smooth curves (thick lines). In the insert radiocarbon content (pMC) in surface soil at different locations and ecosystems reported in literature (Harrison and Bonani, 2000; Richter et al., 1995.) are presented with the modelled lines*

***Table 1.** Parameters of soil in different ecosystems calculated by BML model*

Soil below	Turnover time (y)	Contribution of old component (%)	Age of old component (y)	M_{slow} / M_{fast}
Mixed wood (PZL)	14	12	1500	22
Uncultivated grass (PZT)	14	21	1350	40
Agriculture field (PZO)	22	22	1500	31

these of the Shauinsland record (Levin and Kromer, 1997) chosen as reference level and the pick to pick amplitude reaches 50 ‰ (**Fig. 3**). The relatively short record of PZO coincides with line fitting the Schauinsland data. In this case variation reaches 35 ‰. The lowest value of the $\Delta^{14}C$ record is for PZT sampling place ca. 30 ‰ below the Schauinsland reference and ca. 35 ‰ above the exponential line fitting Krakow data (**Fig.3**). However, the location of PZT explains the low $\Delta^{14}C$ values. The ^{14}C input function of the MBL model applied for this site, is the local $\Delta^{14}C$ atmospheric value (Kuc *et al.*, 2003).

The discussed MLB model was run for two "clean areas" (PZL and PZO sites - without local sources of fossil CO_2), and a polluted town area (PZT: mainly communal and traffic fossil CO_2) applying the ^{14}C input function of the Schauinsland (Levin and Kromer, 1997) and the Krakow data (Kuc *et al.*, 2003), respectively. The fitted model curves yield turnover times of 14 (PZL, PZT) and 22 (PZO) years, respectively (**Table 1**). Depleted input flux of organic matter into the fast decomposing pool in the last several years can be the reason of long TT observed at PZO site. Proportions of old component ca 12 % (1500 yr old) for PZL is relatively low indicating weak development of this pool. Low percentage of the old component at PZL can be explained by change of plant cover in the past. One can suspect the earlier primeval forest in this part was cut and original soil degraded leading to remarkable diminishing of carbon content in soil. Currently slow rebuilding is continued. The opposite situation is observed at PZT sampling point where 22 % contribution of 1350 yr old component points to well developed soil profile, not anthropogenically disturbed at least for some decades and presenting relatively large old carbon pool.

The MBL model calculation of the ratio of carbon content in the slow and fast decomposition boxes, M_{slow} / M_{fast} (**Table 1**) varies for investigated sites. The smallest value is observed for the mixed forest soil (PZL) ca . 22, the higher ratio, $M_{slow} / M_{fast} = 31$, has agricultural field, the highest observed in the region, $M_{slow} / M_{fast} = 40$, is noticed for grassland (PZT). This parameter appears to be also a good measure of soil development.

6. CONCLUSIONS

^{14}C measurement data implemented to box models are useful tool for description carbon dynamics in soil. Also exchange of carbon fluxes between atmosphere, biosphere and soil can be successfully investigated. Measurements of carbon isotopes in the soil CO_2 are required to fully understand carbon dynamics in soil.

Calculated turnover times for different types of soil in southern Poland are ranging from 14 to 22 years while contribution of old carbon (1500 yr) is from 12 to 22 %. Estimated ratio of carbon capacity of slow to fast decomposition boxes ranges from 22 to 48 indicating slow decomposing organic compounds as the major pool of carbon in soil. From the other side relatively short turnover times point to the fast decomposing organic matter as controlling soil dynamics and mainly contributing to the CO_2 flux from soil to atmosphere.

Investigations of different types of soils in southern Poland showed that calculated parameters are consistent with observations and are well matching published data for other sites also those very distanced.

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