CONCENTRATION OF RADIOCARBON IN SOIL-RESPIRED CO_2 FLUX: DATA-MODEL COMPARISON FOR THREE DIFFERENT ECOSYSTEMS IN SOUTHERN POLAND

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ABSTRACT. We report and compare the results of long-term observations (1998–2006) of monthly mean soil CO_2 fluxes and their carbon isotope composition, carried out at 3 sites with contrasting characteristics: 1) a grassland site located in the urban area of Kraków, southern Poland, which was exposed to anthropogenic impact for more than a century; 2) a mixed forest site; and 3) cultivated agricultural field site. A closed-chamber, dynamic sampling system was used to collect monthly cumulative samples of soil-respired CO_2. The CO_2 collected at the mixed forest site was enriched in ^{14}C with respect to European free-atmosphere continental $^{14}CO_2$ background (high-altitude station Jungfraujoch in Swiss Alps) by approximately 40‰, while the urban site revealed ^{14}C depletion by ~30‰ against the same reference. The $\Delta^{14}C$ values observed at the agricultural site were lying in between, clustering along the regional reference atmospheric $\Delta^{14}CO_2$ trend curve. The $\Delta^{14}C$ values of soil-respired CO_2 at the urban site turned out to be indistinguishable from the $\Delta^{14}CO_2$ values in the local atmosphere. For the estimation of mean turnover time of soil carbon for each of the monitored sites, we used a multicompartment model (MCM) accounting for input of carbon to the soil profile via deposition of fresh organic matter, as well as 3 different sources of CO_2 in the soil profile: 1) root respiration; 2) "fast"; and 3) "slow" pools of soil carbon. The estimated mean turnover time of carbon in the "fast" carbon pool was ~14 yr for both urban grassland and mixed forest sites, and ~22 yr for the cultivated agricultural field. From the observed differences in $\Delta^{14}C$ values of the measured fluxes of soil-respired CO_2, we conclude that ^{14}C content of the biogenic component in the local atmospheric CO_2 is site-specific and may differ significantly from the regional atmospheric background $\Delta^{14}CO_2$ value. Therefore, the assumption widely used in ^{14}C-based assessments of the fossil-fuel contribution local atmospheric CO_2 load, stating that ^{14}C concentration in the biogenic CO_2 component is equal to that of regional atmospheric reference value, needs to be carefully evaluated on a case-by-case basis.

INTRODUCTION

The role of the biosphere in the global carbon budget remains a vigorously debated issue (e.g. Schlesinger and Andrews 2000; Houghton 2003; Pan et al. 2011). Carbon enters terrestrial ecosystems through photosynthesis and leaves them through autotrophic and heterotrophic respiration. Although the flux of soil CO_2 into the atmosphere constitutes an important component of the global carbon cycle, its spatial and temporal variability is still not adequately characterized.

Isotopes of carbon (^{13}C, ^{14}C) proved to be useful tools in studying the dynamics of the global carbon cycle (Wang et al. 1994; Turnbull et al. 2008; Levin et al. 2010). They provide additional constraints for currently used models of the carbon cycle and help to characterize sources and sinks of carbon, both on regional and global scales (Kuc and Zimnoch 1998; Battle et al. 2000). Whereas monitoring networks for studying isotopic variability of atmospheric CO_2 are relatively well developed (Levin et al. 2003; Kuc et al. 2007), the relevant data for soil CO_2 flux are still fragmentary. While abundant literature exists on various aspects of isotope composition of pedogenic carbonates and soil organic matter and their distribution with depth (e.g. Nissenbaum and Schallinger 1974; O'Brien and Stout 1978; Cerling et al. 1991; O'Brien 1986; Balesdent et al. 1987, 1988; Wang et al. 1994; Harrison 1996; Rutberg et al. 1996), much less information is available on carbon isotope composition of soil CO_2 ($^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios), in particular with respect to the soil CO_2 flux entering the atmosphere, its variability, and dependence on site-specific parameters.

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In Europe, the first studies focusing on ^{13}C and ^{14}C composition of soil CO_2 were carried out in the 1980s in Germany (Dörr and Münnich 1980, 1987). Recently, similar studies were undertaken by Ekblad and Högberg (2000), Schüssler et al. (2000), Koarashi et al. (2002), Liu et al. (2006), and Camarda et al. (2007). Stable isotope composition of soil CO_2 (δ^{13}C, δ^{18}O) was monitored over a period of 1 yr in Switzerland by Hesterberg and Siegenthaler (1991). The concentration and ^{13}C isotope composition of soil CO_2 was investigated in several locations of southeastern Poland by Dudziak and Hałas (1996). However, a comprehensive characterization of the seasonal and interannual variability of the soil CO_2 flux and its carbon isotopic composition in this part of the European continent has not been attempted so far.

The seasonal variability of soil CO_2 flux and its carbon isotopic composition (δ^{13}C, Δ^{14}C) were investigated at several sites located in southern Poland. Preliminary results obtained for 3 sites representing typical ecosystems of central Europe (mixed forest, cultivated agricultural field, grassland) were discussed by Gorczyca et al. (2003). Here, we report the results of systematic observations of carbon isotopic composition in soil CO_2 flux performed on a grassland site located in the Kraków agglomeration, exposed to anthropogenic impact for more than 100 yr. We compare the results obtained for this site with the results obtained for 2 other sites (mixed forest and agricultural field), which are located about 40 and 150 km east of Kraków, respectively. The ^{14}C concentration in the soil CO_2 flux measured at 3 investigated sites was simulated using a multicompartment model distinguishing 2 reservoirs of soil carbon: fast-decomposing and slow-decomposing carbon pools.

CHARACTERIZATON OF THE STUDY AREA

Systematic observations of soil CO_2 flux and its carbon isotopic composition were conducted at 3 sites representing 3 ecosystems of contrasting characteristics, typical for the Polish landscape: 1) mixed forest; 2) cultivated agricultural field; and 3) urban meadow. Figure 1 shows the site locations. Soil classification according to the IUSS (2007) and general description of the soil profile at each site is presented in Table 1. Below, a detailed description of each study area is given.

Figure 1 Location of the sites where Δ^{14}C in soil-respired CO_2 was regularly measured. The sites are identified by acronyms: PZT - urban non-cultivated meadow; PZL - mixed forest; PZO - cultivated agricultural field.

Table 1 General characteristics of soils in the study areas according to IUSS (2007).

Type of ecosystem	Soil type	Surface horizon	Subsurface horizon
Mixed forest (PZL site)	Haplic Cambisol (Dystric)	Mollic horizon (0–20 cm): sandy loam (SL), brown colored when fresh, granular structure, weak acid reaction, iron concretions, gradual boundary.	Cambic horizon (20–50 cm): loamy sand (LS), gray colored when fresh, granular structure, weak acid reaction, gleyic color pattern, gradual boundary. Parent material (50–100 cm): sand (S), gray colored, gleyic color pattern.
Cultivated agricultural field (PZO site)	Leptic Cambisol (Eutric)	Mollic horizon (0–25 cm): silt (Si), gray colored when fresh, granular structure, weak acid reaction, iron concretions, gradual boundary.	Cambic horizon (25–50 cm): silt (Si), brown colored when fresh, angular blocky structure, weak acid reaction, iron concretions, gradual boundary. Parent material (50–100 cm): silt loam (SiL), brown colored.
Non-cultivated urban meadow (PZT site)	Endogleyic Cambisol	Mollic horizon (0–20 cm): silty clay loam (SiCL), gray colored when fresh, granular structure, weak acid reaction, clear boundary.	Cambic horizon (20–75 cm): silty clay loam (SiCL), brown colored when fresh, angular blocky structure, weak acid reaction, iron concretions, gleyic color pattern, gradual boundary. Parent material (75–100 cm): sand (S), gray colored, iron concretions, gleyic color pattern.

Mixed Forest (PZL Site)

The mixed forest site (20°23′E, 50°04′N, ~232 m asl) was located ~40 km east of Kraków, in the center of a large mixed forest (Niepołomice Forest), which consists of oak, hornbeam, and coniferous trees growing on Haplic Cambisol soils. The Niepołomice Forest covers an area of ~110 km^2 and is a relict of once vast forests covering the southern part of Poland. The surface horizon of the soil at the site is approximately 20 cm deep and consists of sandy loam, with ~5 cm of litter and other organic material on top. The subsurface horizon consists of loamy sand with a small admixture of humic substances. The water table at the site was relatively shallow, reaching tens of centimeters during periods of intense rainfall (June/August). Observations have been conducted at the site from April 1998 until September 2000.

Cultivated Agricultural Field (PZO Site)

The PZO site (23°15′E, 49°50′N, ~350 m asl) was located in a small village in the foothills of the Carpathians, ~150 km southeast of Kraków. The soil at the study site was cultivated for at least 100 yr. Earlier, forests dominated in the area. Over the decade preceding the measurements, mostly potatoes were grown on the site. Leptic Combisol soils are characteristic for this region. The surface horizon (0–25 cm) consists mostly of silt with high organic content. Silt dominates also in the cambic horizon (25–50 cm), with angular blocky structure, weak acid reaction, and iron concretions. Observations were conducted at the site from March 1999 until October 2000.

Urban Meadow (PZT Site)

The PZT site (19°55′E, 50°02′N, 209 m asl) was located in the Kraków agglomeration, ~300 m from the Rudawa River, passing the western outskirts of the city where it flows into the Vistula River. The site has been under anthropogenic influence for more than 100 yr. The Kraków agglomeration is occupied by approximately 1 million people. The region is also influenced by anthropogenic emissions from the industrial district of Upper Silesia, ~100 km west of Kraków. The study area, located on the floodplain of the Rudawa River, was frequently flooded in the past. There is historic evidence for the presence of marshes and wetlands in this area. At present, it is a residential area. The observation site was located on a small non-cultivated meadow. The dominating plant cover consists of perennial rye grass (*Lolium perenne*) and meadow fescue (*Festuca pratensis*). The soils at the site are of a brown alluvial type, classified as Endogleyic Cambisols. The surface horizon (0–20 cm) consists of silty clay loam of gray color when fresh, granular structure, and weak acid reaction. Beneath, in the cambic horizon (20–75 cm), silty clay loam prevails with brown color when fresh, angular blocky structure, and weak acidic reaction. Between approximately 50 and 70 cm depth, a distinct maximum of soil organic matter (SOM) content appears. Below, parent material of alluvial origin is present (sand, gray-colored iron concretions, gleyic color pattern). The water table at the site fluctuates between approximately 80 and 120 cm, depending on the water level in the neighboring Rudawa River. The observations at the site began in October 1999 and ended in July 2006. In addition to regular measurements of ^{14}C content in soil-respired CO_2, SOM was investigated at the site. Ten consecutive samples of soil were collected down to a depth of 1 m, with each sample covering approximately 10 cm of the profile. The ^{14}C and ^{13}C content was measured in the total organic carbon extracted from the soil.

MATERIALS AND METHODS

The flux of soil CO_2 and its carbon isotopic composition at the soil-atmosphere interface was monitored using the closed-chamber method (Naganawa and Kyuma 1991; Jensen et al. 1996). The adopted version of the method allowed collection of monthly cumulative samples of soil CO_2 for carbon isotope measurements. The chamber was in the form of a cylindrical, stainless steel container (volume of ~40 L), equipped with the appropriate inlet and outlet connections (Figure 2). The chamber was hammered ~10 cm into the uppermost soil layer. Monthly composite samples of soil CO_2 were collected via circulation of air located inside the chamber through the drying unit (silica gel) and the pre-evacuated stainless steel trap of 2-L volume, filled with molecular sieve (0.5 nm Pearlform, Merck). The CO_2 was quantitatively absorbed on the sieve and the air was routed back to the chamber. A dedicated electronic control system was used to switch on and off the membrane pump at preprogrammed time intervals, covering uniformly the 1-month sampling period with short pumping intervals lasting between 0.5 and 2 min. Using the closed-system design and periodic pumping, equilibrium conditions under the chamber were maintained throughout the sampling period. The system was battery operated and essentially maintenance free (Gorczyca et al. 2003).

In the laboratory, CO_2 collected in a molecular sieve was thermally extracted under a vacuum, following the procedure described by Kuc and Zimnoch (1998). After purification, the ^{14}C activity of the extracted CO_2 was measured using benzene synthesis and liquid scintillation spectrometry (Florkowski et al. 1975), while its ^{13}C content was analyzed by the dual-inlet mass spectrometry technique. The measured δ^{13}C was corrected for presence of N_2O in the analyzed CO_2 sample (Gorczyca et al. 2003). The measured $^{14}C/^{12}C$ ratios were expressed as Δ^{14}C values, defined as per mil deviations from the internationally accepted standard, normalized to $\delta^{13}C = -25‰$ (Stuiver and Polach 1977). The uncertainties of isotope analyses were approximately 0.1‰ and 5–8‰ for δ^{13}C and Δ^{14}C, respectively.

The SOM content and its carbon isotope composition was measured at the PZT site following the generally accepted AAA (acid-alkali-acid) procedure (e.g. Goh and Molloy 1978; Chichagova and Cherkinsky 1993; Pessenda et al. 1996). Soil samples (~1 kg) were dried at 60 °C to constant weight, and root fragments were removed manually. Any remaining plant debris were removed by flotation in weak HCL solution and drying to constant weight. The samples were then sieved and homogenized before applying further steps of the AAA procedure. The extracted SOM was burned to CO_2 in oxygen atmosphere (Parr acid digestion bomb, 7 bar of O_2). The obtained CO_2 gas was purified and converted for benzene for ^{14}C analysis. A portion of the gas was used to measure δ^{13}C.

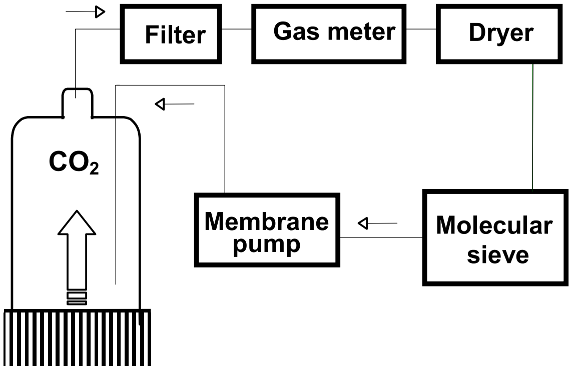

Figure 2 Experimental setup for collecting monthly composite samples of soil-respired CO_2.

MODELING OF ^{14}C CONTENT IN SOIL-RESPIRED CO_2

Distinct changes of atmospheric $^{14}CO_2$ concentration over the past several decades, induced by atmospheric nuclear bomb tests (Levin et al. 2008), provide a unique opportunity to get a deeper insight into the dynamics of the soil carbon reservoir. Knowing the atmospheric "input function" of bomb ^{14}C entering the soil carbon pool and observing the $^{14}CO_2/^{12}CO_2$ ratio of the soil-respired CO_2, it should be possible to quantify the mean turnover time of carbon in this important carbon reservoir. With this aim in mind, a multicompartment model (MCM) of carbon cycling in the soil was developed and used to interpret the ^{14}C data obtained in the framework of this study. The structure of the model is presented in Figure 3. Detailed discussion of the model is presented in Kuc (2005) where it was named *multi-layer box model* (MLB). Here, only a general outline of the model is given.

The model assumes 2 distinct pools of soil carbon: 1) the fast-decomposing (FD) pool and the 2) slow-decomposing (SD) pool. The basic factor distinguishing these 2 pools is the rate with which the soil carbon is converted to CO_2 and removed from the given compartment, forming output CO_2 flux. The FD and SD pools can be divided into an array of compartments, each representing the carbon deposited within well-defined period of time, e.g. 1 yr. The carbon present in a given compartment has a well-defined year of formation and its ^{14}C isotope composition is specific for this year. There is no exchange of carbon between the individual compartments. The number of compartments can be adjusted to specific requirements. For instance, it can be enlarged to accommodate longer periods of time. Alternatively, the deposition time for the single compartment can be also enlarged. For the purpose of this work, the FD pool was divided into N compartments, each representing annual deposition of carbon, whereas the SD pool was represented by a single compartment representing a long deposition period.

The system of closed compartments allows us to trace the "history" of individual compartments separately and, if necessary, to separately treat the output CO_2 flux from each compartment. There is no direct relationship between the location in the soil profile and the position of carbon in the given compartment. At the same depth interval in the soil profile, a mixture of carbon belonging to slow and fast carbon pools can be found.

The flux of carbon entering the soil (F_{in}) is represented by organic matter input and by CO_2 generated by root respiration (F_r). The flux of carbon entering the atmosphere (F_{out}) contains contributions from CO_2 leaving the slow and fast soil carbon pool and the CO_2 originating from root respiration. Part of the CO_2 resident in the soil is dissolving in the infiltrating water and forms the carbon flux (F_{cw}), entering groundwater system located beneath the soil profile. For typical conditions prevailing in the study areas (mean annual recharge, mean TDIC content in the infiltrating waters), the carbon flux leaving the soil profile with the infiltrating water constitutes only ~0.8% of the carbon flux entering the atmosphere. Therefore, the F_{cw} flux was not further considered by the model. Consequently, the CO_2 forming the atmospheric carbon flux in the model (F_{out}) was a weighted mean of 3 components: F_{slow}, F_{fast}, and F_r (Figure 3). The basic assumption of the MCM model was that the decomposition rate of carbon compounds in the given compartment is proportional to the total mass of carbon in this compartment:

$$\frac{d}{dt}M_{f,s} = -\beta_{f,s} \cdot M_{f,s} \tag{1}$$

where $M_{f,s}$ stands for the mass of carbon comprised in a single FD or SD compartment, respectively (kg m^{-2}), while $\beta_{f,s}$ are the decomposition constants (yr^{-1}), different for FD and SD compartments. The total CO_2 flux leaving N compartments can be expressed as a sum of partial fluxes (Kuc 2005):

$$F(t) = \sum_{n=1}^{N} F_n = \sum_{n=1}^{N} \frac{dM_n}{dt} = (1 - \exp(-\beta \cdot \Delta t)) \cdot \sum_{n=0}^{N} F^0(t - \Delta t \cdot n) \cdot \exp(-\beta \cdot \Delta t \cdot n) \tag{2}$$

where $F^0(t-\Delta t \cdot n)$ is the input flux of carbon to the given compartment at time $t-\Delta t \cdot n$ (kg m^{-2} yr^{-1}), Δt is the time interval between formation of consecutive compartments (if expressed in years then $\Delta t = 1$), and N stands for the number of compartments assumed in model calculations. Consequently, the total CO_2 flux observed at the soil-atmosphere interface is composed of carbon representing a spectrum of ages that may extend for hundreds or thousands of years. The SD compartment represents carbon that is much older than that in the FD compartment. This is realized in the model by choosing a much smaller value of β. In the applied version of the MCM model, there were 2 different values of β chosen, representing the FD and SD compartment, respectively.

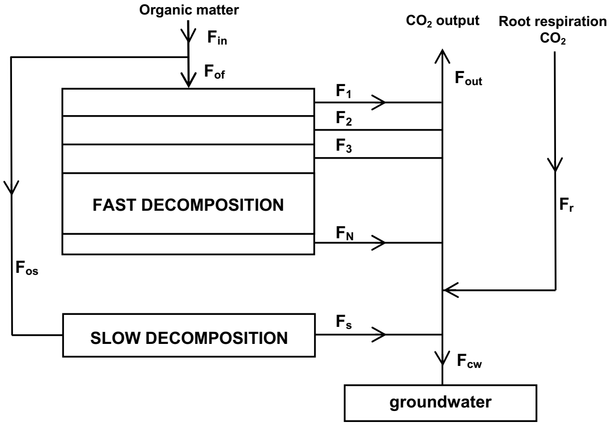

Figure 3 Block diagram of the multi-compartment model, composed of fast (FD) and slow decomposition (SD) pools, used to interpret the measured ^{14}C concentrations in soil-respired CO_2 fluxes observed at 3 investigated field sites (see text for details).

The mean turnover time (MTT) is a generally accepted measure of the conversion rate of organic carbon in the soil. It is defined as the ratio of the total carbon mass comprised in the soil carbon pool to the total flux of carbon leaving or entering this pool:

$$MTT = \frac{M}{F} \tag{4}$$

The definition of mean turnover time holds for the steady-state conditions in the soil, i.e. when both mass of carbon pool and carbon fluxes into or out of this pool are constant in time. When input and output fluxes are equal and $\Delta t = 1$, it can shown that the following relationship holds (Kuc 2005):

$$MTT = \frac{1}{1 - \exp(-\beta)} \tag{5}$$

For small values of β, Equation 5 can be simplified to:

$$MTT \cong \frac{1}{\beta} \tag{6}$$

The MCM model outlined above was used to simulate ^{14}C concentrations measured in soil-respired CO_2 collected at the investigated field sites. Assuming that each layer represents 1 yr of deposition and the time step, Δt, is equal 1 yr, the ^{14}C activity of total CO_2 flux leaving the slow or fast carbon pool can be expressed by the following equation (Kuc 2005):

$$A(t) = (1 - \exp(-\beta)) \sum_{i=1}^{\infty} A^0(t) \cdot \exp(i \cdot (\beta + \lambda)) \tag{7}$$

where $A^0(t)$ stands for ^{14}C activity of the input carbon flux and λ is the decay constant of ^{14}C. The calculated $A(t)$ function, both for fast (FD) as slow (SD) compartments yields the temporal distribution of $^{14}CO_2$ in the output CO_2 fluxes. Time intervals for which $A(t)$ is calculated depend on the ^{14}C input function that should cover a long enough period of time with respect to the exponent component in the sum appearing in Equation 7. In practice, the ^{14}C activity of atmospheric CO_2 relevant to the location of the field site where soil-respired CO_2 flux is measured is adopted as a $A^0(t)$ function.

The ^{14}C activity of CO_2 leaving the surface of the soil is a weighted mixture of ^{14}C activities of CO_2 fluxes originating in the fast decomposing carbon pool, slow decomposing carbon pool, and the CO_2 resulting from root respiration:

$$A_T(t) = (1 - S - R) \cdot A_F(t) + S \cdot A_S(t) + R \cdot A_R(t) \tag{8}$$

where S and R are contributions of SD and respiratory fluxes, respectively, and $A_S(t)$, $A_R(t)$ their ^{14}C activities. $A_F(t)$ stands for the ^{14}C activity of FD flux. In the model calculations, it was assumed that $A_R(t)$ represents the actual atmospheric ^{14}C activity, without any delay. A constant contribution of the root-respiration flux ($R = 0.1$) was assumed. In addition, the slow decomposition pool (SD) was considered as a single compartment with predefined MTT value for the CO_2 leaving this compartment (labeled T_S in Table 2 and Figure 4). Such an approach is justified by the fact that decomposition of old carbon in the soil typically provides only a small fraction of the total CO_2 flux leaving the soil-atmosphere interface. In the model calculations presented below, the ^{14}C content of the soil-respired CO_2 flux was calculated using Equations 7 and 8, with MTT, T_S, and S as fitting parameters.

RESULTS AND DISCUSSION

Variability of Radiocarbon Content in Soil-Respired CO$_2$

In areas with plant cover located in temperate climatic zones, the flux of CO$_2$ from the soil to the atmosphere is generated by decomposition of soil carbon and root respiration processes, both being temperature-dependent, leading to well-pronounced seasonal variations of the flux (e.g. Gorczyca et al. 2003). The Δ^{14}C records of soil-respired CO$_2$ collected during the years 1998–2006 in the framework of this study reveal distinct differences in the observed ^{14}C levels. The Δ^{14}C values representing the PZL site (mixed forest) are shifted by ~40‰ with respect to the regional atmospheric Δ^{14}C reference record originating from Vermunt and Jungfraujoch (Figure 4). The spread of the Δ^{14}C values measured at this site is significant and reaches ~40‰. The relatively short Δ^{14}C record for the PZO site (agricultural field) is placed on the trend line of the regional atmospheric reference Δ^{14}C curve and reveals significantly smaller amplitude of ^{14}C variations than the PZL site (~35‰). The PZT site representing the urban agglomeration is characterized by the lowest Δ^{14}C values, ~30‰ below the regional atmospheric Δ^{14}C reference level. It should be noted that the trend line of Δ^{14}C in soil-respiration CO$_2$ recorded for the PZT site is indistinguishable from the trend line of the local atmospheric Δ^{14}C available for the Kraków atmosphere (cf. Figure 4).

Apparent offsets between Δ^{14}C values of soil CO$_2$ observed at 3 investigated sites point to substantial differences in the age structure of CO$_2$ entering the soil-atmosphere interface at those sites. While some seasonal variability is expected in the observed Δ^{14}C levels due to the seasonally varying contribution of CO$_2$ originating from root respiration, which is characterized by relatively short residence time of carbon in the plant tissue, systematic offsets observed between different Δ^{14}C records in this study stem most probably from the different age structure of organic carbon in the investigated soil profiles. If this is the case, then it should be possible to pinpoint those differences via appropriate modeling.

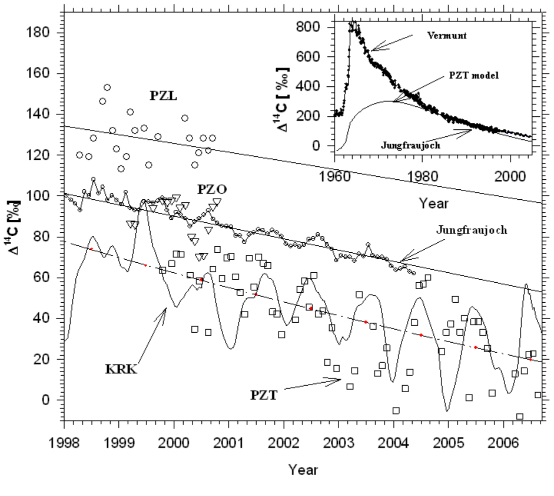

Figure 4 The Δ^{14}C records of soil-respired CO$_2$ measured at the investigated field sites: PZT - non-cultivated urban meadow (open squares); PZO - cultivated agricultural field (open triangles); PZL - mixed native forest (open large circles); KRK - Δ^{14}C in Kraków atmospheric CO$_2$ (smoothed curve). The trend lines represent the ^{14}C content in the soil-respired CO$_2$ simulated by the MCM model. As reference, atmospheric Δ^{14}CO$_2$ values for Jungfraujoch station, representing regional background, are also shown. Insert (upper right) shows the bomb ^{14}C input function since 1960 for the clean atmosphere (Vermunt, Jungfraujoch, Levin et al. 2004) and the response of the MCM model for the PZT site (see text for details).

Modeling the Δ^{14}C Values of Soil-Respired CO$_2$

The MCM model was used to simulate long-term trends of Δ^{14}C values of soil-respired CO$_2$ observed at 3 investigated filed sites. Two categories of ^{14}C input function, $A^0(t)$, were used in the calculations: (i) the input function representative for "clean" areas, far from strong CO$_2$ sources of anthropogenic origin (PZL and PZO sites); and (ii) the input function characteristic for urban area under heavy anthropogenic impact (PZT site). In the first case, the ^{14}C input function was constructed as a combined record of atmospheric $^{14}CO_2$ for Vermunt (Levin and Kromer 2004), Jungfraujoch (Levin et al. 2008), and Kasprowy Wierch (Kuc et al. 2007) sites. At the PZT site, the atmospheric $^{14}CO_2$ record available for Kraków was used (Kuc et al. 2007), extended back to the first half of the 20th century by applying the correction of 15‰ with respect to the ^{14}C input function representing the clean sites. The contribution of autotrophic respiration to the overall CO_2 flux leaving the soil-atmosphere interface was kept constant and equal to 0.1, while its $\Delta^{14}C$ value was equal to that of local atmospheric CO_2 for the given year. The mean turnover time of carbon in the fast-decomposing carbon pool (MTT), the mean turnover time of carbon in the slow-decomposing pool (T_S), and the contribution of the SD pool to the overall CO_2 flux leaving the soil surface (S) were treated as fitting parameters.

Table 2 Parameters of soil carbon pool at 3 investigated field sites, calculated by the MCM model.

Type of ecosystem	Mean turnover time of carbon in FD carbon pool, MTT (yr)	Contribution of SD carbon pool, *S* (%)	Mean turnover time of carbon in SD carbon pool, T_S (yr)
Mixed forest (PZL site)	14	12	1500
Non-cultivated urban meadow (PZT site)	14	7.5	2000
Cultivated agricultural field (PZO site)	22	12	1500

The $A_{T(t)}$ functions calculated using Equations 7 and 8 for 3 investigated sites are shown in Figure 4, while the corresponding values of the adjusted fitting parameters are summarized in Table 2. The MTT values for the fast carbon pool are 14 yr for PZL (mixed forest) and PZT (non-cultivated urban meadow) sites and 22 yr for the PZO (cultivated agricultural field) site. The significantly longer MTT value for the agricultural site can be explained by systematic removal of green plant cover every year, thus depleting the fresh organic matter input predominantly to the FD carbon pool. Mean turnover times for the FD carbon pool obtained for the mixed forest and the urban grassland sites are within the range reported for these types of ecosystems. The contribution of the SD carbon pool is ~12% for the PZL and PZO sites, with similar mean turnover times of carbon in this pool of ~1500 yr. The soils at both sites are native, undisturbed soils developed during the Holocene, and the derived parameters most probably represent natural characteristics of carbon turnover in such soils under present climatic conditions.

At the PZT site, apart from regular measurements of ^{14}C content in soil-respired CO_2, SOM was also investigated. The ^{14}C and ^{13}C content of in total organic carbon (TOC) was measured down to 1 m depth. The results are shown in Figure 5. Down to 55–60 cm depth, the ^{14}C content in TOC decreases only slightly, from ~80 pMC at the uppermost 10–15 cm of the soil profile to ~75 pMC at the depth of 55 cm. Between 55 and 75 cm, a distinct maximum of SOM content is observed, reaching ~9% at 60–65 cm depth. Across this organic-reach layer, the ^{14}C content drops from ~75 pMC at the top to ~45 pMC at the base. The $\delta^{13}C_{TOC}$ value shows the gradual increase down the profile, from approximately −27.4‰ at the top 10 cm to −26.5‰ at ~55 cm depth, coinciding with the increase of SOM content from 2–3% at the top layer to 9–10% at 55 cm depth. Below, a relatively regular reduction of $\delta^{13}C$ content is observed, also coinciding with the gradual reduction of SOM content.

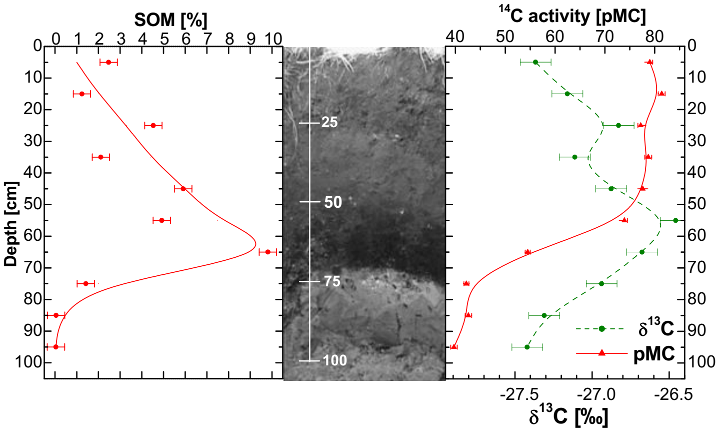

Figure 5 Depth profile of soil organic matter (SOM) and its carbon isotopic composition at the PZT site

The roughly uniform age of soil carbon down to 55 cm depth observed at the PZT site, followed by the relatively rapid decrease of this age across the organic-reach layer extending from ~75 to 55 cm depth, could be understood in light of past depositional history of this site. The organic-reach layer most probably stems from permanent existence of wetlands and/or marshes in the area from approximately 7.3–2.6 ka ago. Afterwards, frequent flooding by the nearby Rudawa River most probably led to partial homogenization of the soil profile and almost uniform ^{14}C age of the SOM. Meandering and shifts in the position of the Rudawa River in this area happened many times in the past and most probably resulted in the above-indicated changes in the deposition patterns at the investigated PZT site. The relatively high mean residence time of carbon in the slow-decomposing carbon pool, combined with the relatively low contribution of this pool in the overall soil-respired CO_2 flux recorded at the PZT site, both being estimated from the MCM modeling, can be understood in the context of peculiar characteristics of the above-described soil profile at this site.

CONCLUSIONS

Regular measurements of ^{14}C content in monthly composite samples of soil-respired CO_2 performed at 3 sites with contrasting characteristics (urban meadow, mixed forest, cultivated agricultural land) located in southern Poland revealed substantial, systematic differences in the observed Δ^{14}C values, pointing to differences in the age structure of carbon released from the soils at those sites. At the mixed forest site, the observed Δ^{14}C values were significantly higher than those representing contemporary regional atmospheric background. At the urban site with heavy anthropogenic impact, on the other hand, the ^{14}C levels measured in soil-respired CO_2 turned out to be significantly lower when compared to clean air regional atmospheric reference values. This points to a potentially significant imprint of local atmospheric CO_2 depleted in ^{14}C due to substantial contribution of fossil fuel CO_2, in the apparent age structure of CO_2 being released by soils in urban areas.

The multicompartment model (MCM) of soil carbon dynamics presented in this study appears to be a useful diagnostic tool allowing a deeper insight into the age structure of carbon released from soils. The transient bomb-^{14}C signal in the atmosphere provides in this context a unique opportunity to quantify the turnover times of carbon pools in the soils through regular observations of ^{14}C content of the soil-respired CO_2.

The results obtained in the presented study suggest that ^{14}C content of the biogenic component in local atmospheric CO_2 budgets is site-specific and may differ significantly from the regional atmospheric background $\Delta^{14}CO_2$ value. Therefore, the widely used assumption in ^{14}C-based assessments of fossil fuel contribution in local atmospheric CO_2 load, stating that the ^{14}C concentration in the biogenic CO_2 component is equal to that of the regional atmospheric reference value, needs to be carefully evaluated on a case-by-case basis.

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