Seasonal variability of the soil CO₂ flux and its isotopic composition in southern Poland

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Abstract The flux and isotopic composition of soil CO_2 has been monitored at three sites located in the southern Poland, during the time period: January 1998 – December 2000. The sites represent typical ecosystems appearing in central Europe: mixed forest, cultivated agricultural field and grassland. To monitor the flux and isotopic composition of soil CO_2, the method based on the inverted cup principle was used. The flux of soil CO_2 reveals distinct seasonal fluctuations, with maximum values up to ca. 20 mmol·m^{-2} h^{-1} during summer and around ten times lower values during winter. Also significant differences among the monitored sites were detected, the CO_2 flux being the highest for the mixed forest site and ca. two times lower for the grassland site. The ^{13}C content of the soil CO_2 flux is nearly constant throughout the year, with $\delta^{13}C$ values essentially reflecting the isotopic composition of the soil organic matter and the vegetation type. The ^{18}O content of the soil CO_2 flux shows a remarkable seasonality, with distinctly less negative $\delta^{18}O$ values recorded during summer. This seasonality is highly reduced in the CO_2 sampled from different depths of the soil. The radiocarbon content of the CO_2 flux turned out to be non-distinguishable, within the uncertainty of the measurements, from current ^{14}C levels in atmospheric carbon dioxide. However, significant reduction of the radiocarbon content was measured in the soil CO_2 sampled at 80 cm, when compared to the uppermost layer, reflecting increasing age of soil organic matter with depth.

Key words carbon-14 • carbon-13 • isotopic composition • soil CO_2 • oxygen-18

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Introduction

Isotopes of carbon (^{13}C, ^{14}C) proved to be useful tools in studying the global carbon cycle. They provide additional constraints for currently used models of the carbon cycle and help to characterise sources and sinks of carbon, both on regional and global scales [2, 18]. The concentration of ^{18}O in atmospheric CO_2 provides additional information about fluxes of this gas between the continental biosphere (soils and plant cover) and the atmosphere [4, 5, 12]. Whereas the monitoring networks for studying isotopic variability of atmospheric CO_2 are relatively well developed, the relevant data for soil CO_2 flux which constitutes an important component of the carbon cycle on continents, are still fragmentary. In Europe, this type of studies focusing on ^{13}C and ^{14}C composition of soil CO_2 were carried out in the eighties in Germany [7, 8]. Stable isotope composition of soil CO_2 ($\delta^{13}C$, $\delta^{18}O$) was monitored for the period of one year in Switzerland by Hesterberg and Siegenthaler [17]. The concentration and ^{13}C isotope composition of soil CO_2 was investigated in several locations of south-eastern Poland by Dudziak [9, 10]. However, a comprehensive characterisation of the seasonal variability of both soil CO_2 flux entering the atmosphere and its isotopic composition ($\delta^{13}C$, $\delta^{18}O$, radiocarbon content) has not been attempted so far. The paper presents the results obtained in the course of a three-year study (January 1998 – December 2000) conducted in the southern

Poland, where both the flux and full isotopic composition of soil CO_2 have been regularly measured.

Study area

The flux and isotopic composition of soil CO_2 have been monitored at three sites, which represent typical ecosystems in central Europe: mixed forest, agricultural field and cultivated grassland.

Mixed forest

The sampling site was located in the centre of a large mixed forest complex (oak, hornbeam, pine), approximately 40 km east of Kraków (20°23'E, 50°04'N). The forest grows on a podsolic type soil. The uppermost layer (litter consisting of fresh leaves and roots undergoing decomposition) is approximately 15 cm deep. The lower bleached layer (20 cm) consists of grey sand with a very small admixture of humic substances. The water table in this region was relatively shallow, reaching some tens of centimetres during the period of most intensive rainfalls (from June to August).

Grassland

The sampling site was located in a village ca. 150 km southeast from Kraków (19°56'E, 50°03'N), in a hilly region laying at the foot of the Carpathians. The brown leached soils in the region belong to lower classes according to common agricultural classification. The upper humic layer containing ca. 2.9% of humic substances extended from 0 to 25 cm depth and the lower, brown earth layer, from 25 to 50 cm. The water table was fluctuating between ca. 60 and 100 cm, depending on the season and the amount of rainfall. The meadow where the sampling unit was placed, remainded not cultivated for at least 30 years. The plant cover consisted of common grasses: perennial ryegrass (*lolium perenne*), birdsfoot trefoil (*lotus corniculatus*), meadow fescue (*festuca pratensis*) and orchad grass (*dactylis glomerata*).

Agricultural field

This site was located in the same village as the grassland site, approximately 150 m to the north. The humic layer was thicker (ca. 35 cm) due to agricultural treatment of the soil. The sampling unit was placed on a typical agricultural field where potatoes were grown during the reported time period.

Methods

To monitor the flux of soil CO_2 and its isotopic composition, the method based on inverted-cup principle was used in two different versions: (i) the closed-system version, allowing the collection of monthly cumulative samples of soil CO_2 at a given site for measurements of ^{14}C and ^{13}C content; (ii) the in-growth version which allows spot measurements

of the CO_2 flux and its isotopic composition ($\delta^{13}C$, $\delta^{18}O$). In addition, samples of soil air were collected from two depths (40 and 80 cm) to determine the resident CO_2 concentration and its carbon isotopic composition ($\delta^{13}C$, $\delta^{14}C$).

The inverted-cup method

The sampling system consisted of a large metal container (volume ca. 40 litres), with the bottom cut-off, equipped with appropriate connections. The container was placed on the soil surface, thus allowing accumulation of gases being released from the soil. To limit direct contact with free atmosphere, the container was hammered ca. 10 cm into the uppermost layer of the soil. This sampling system can be used in two different sampling modes, depending on the type of collected sample.

For the determination of soil CO_2 flux and its isotopic composition ($\delta^{13}C$, $\delta^{18}O$), the air from the container was sampled at specified time intervals using a diaphragm pump (cf. Fig. 1a). The air was pumped through a trap filled with
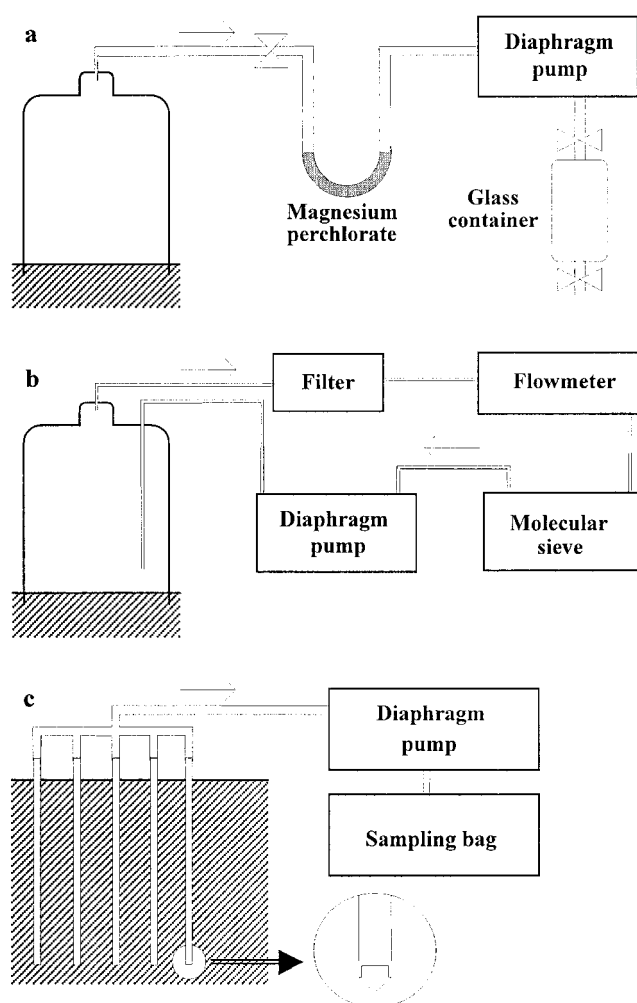

Fig. 1. Schematic representation of three different modes of sampling used to derive the flux and isotopic composition of CO_2 released from soils: a – a sampling system used for determination of the flux and isotopic composition of soil CO_2 by the in-growth method; b – a sampling system used to obtain cumulative monthly samples of soil CO_2 for radiocarbon analysis; c – a sampling system used to obtain depth profiles of soil CO_2 and its isotopic composition.

a drying agent ($Mg(ClO_4)$) into 500 ml glass flasks. The concentration of CO_2 in the collected set of samples was determined in the laboratory using the gas chromatographic method. The $\delta^{13}C$ and $\delta^{18}O$ values of the extracted CO_2 were measured by mass spectrometry and then corrected for the N_2O presence [14, 15].

To collect samples of soil CO_2 for radiocarbon analysis, the air residing under the metal container was circulated through a trap filled with molecular sieve, where CO_2 was quantitatively absorbed (Fig. 1b). A dedicated electronic control system was switching on and off the diaphragm pump at pre-programmed time intervals, covering uniformly the entire sampling period lasting approximately one month. Periods of pumping were relatively short, thus allowing near-equilibrium conditions under the container. The system was operated by a car battery, and was essentially maintenance-free, except of changing the trap with molecular sieve. In the laboratory, the collected CO_2 was extracted from molecular sieve and its ^{14}C activity was measured using a benzene synthesis and liquid scintillation spectrometry [13]. The ^{13}C content of the extracted CO_2 was analysed in a mass spectrometer.

Soil CO_2 flux

The flux of soil carbon dioxide into the atmosphere was determined with the aid of in-growth method. The CO_2 concentration was measured as a function of time, inside the inverted metal container placed on the soil surface. The flux density of the soil CO_2 was calculated using the formula:

$$(1) \qquad j_x = \frac{V \cdot \left.\frac{\partial C}{\partial t}\right|_{t=0}}{S}$$

where: V is the volume under the inverted container; S stands for the surface of the soil covered by the container; $\partial C / \partial t$ is the derivative of the CO_2 concentration under the inverted container at $t = 0$, calculated for the function describing the measured temporal evolution of the CO_2 concentration inside the container (cf. Fig. 2a).

The observed temporal evolution of the CO_2 concentration inside the inverted container can be described by the following formula:

$$(2) \qquad C(t) = \frac{A}{B} \cdot \left(1 - e^{-B \cdot t}\right) + C_0$$

where: A and B are fitting parameters and C_0 stands for atmospheric concentration of CO_2. It should be noted that the in-growth method can be used also for other trace gases being released from the soil (e.g. N_2O).

Isotopic composition of the soil CO_2 flux ($\delta^{13}C$ and $\delta^{18}O$)

The in-growth method described above was also used to obtain the isotopic composition of the soil CO_2 flux ($\delta^{13}C$, $\delta^{18}O$). Once the inverted metal container had been installed at a given site, the ^{13}C and ^{18}O content of the CO_2 under the container underwent gradual change due to mixing of atmospheric CO_2 present under the container at time $t = 0$, with the CO_2 diffusing out from the soil (cf. Fig. 2b, 2c).
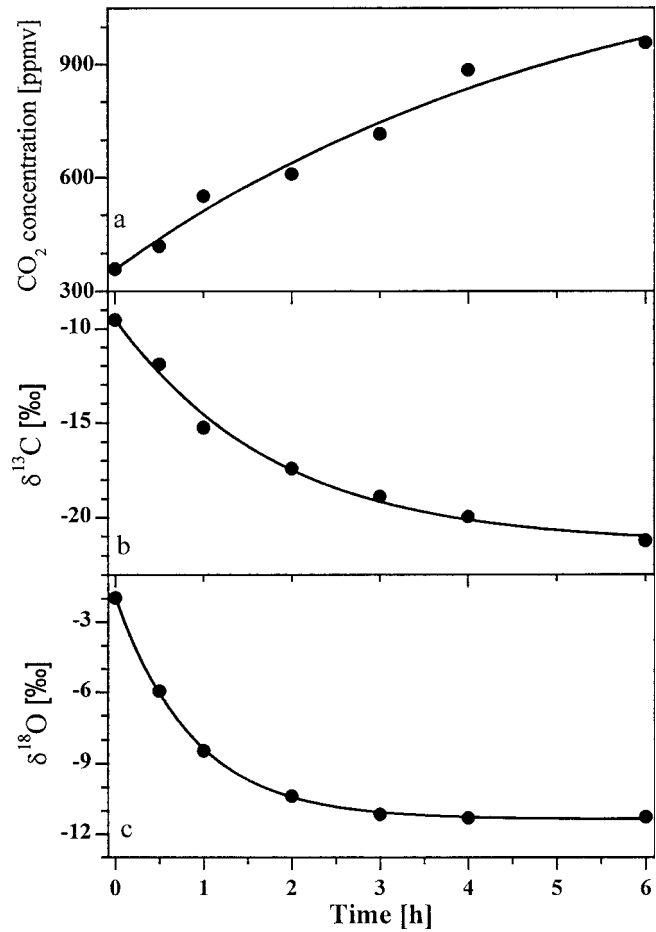

Fig. 2. The evolution of CO_2 concentration and its isotopic composition ($\delta^{13}C$, $\delta^{18}O$) under the inverted metal container as a function of time elapsed since placing the sampling container on the soil surface. The data were collected for the mixed forest site sampled in January 1999.

To the first approximation, this process can be considered as a two-component mixing. Consequently, the following mass and isotope balance equations for this process can be formulated:

$$(3) \qquad C_{mix} = C_{atm} + C_{soil}$$

$$(4) \qquad \delta_{mix} \cdot C_{mix} = \delta_{atm} \cdot C_{atm} + \delta_{soil} \cdot C_{soil}$$

where: C_{atm} and δ_{atm} – stand for concentration and isotopic composition of atmospheric CO_2; C_{mix} and δ_{mix} – represent the CO_2 measured under the inverted container and C_{soil} and δ_{soil} characterizes the CO_2 component originating from the soil. The measured isotopic composition of the mixture of two sources of CO_2 can be then calculated from eqs. (3) and (4):

$$(5) \qquad \delta_{mix} = \left(\delta_{atm} - \delta_{soil}\right)\frac{C_{atm}}{C_{mix}} + \delta_{soil}.$$

It is apparent from eq. (5) that the isotopic composition of CO_2 under the inverted container ($\delta^{13}C$, $\delta^{18}O$) is a linear function of the reciprocal of measured CO_2 concentration (cf. Fig. 3a, 3b). The extrapolation of the fitted straight line to $1/C$ gives zero yields of the $\delta^{13}C$ ($\delta^{18}O$) value of the soil CO_2.
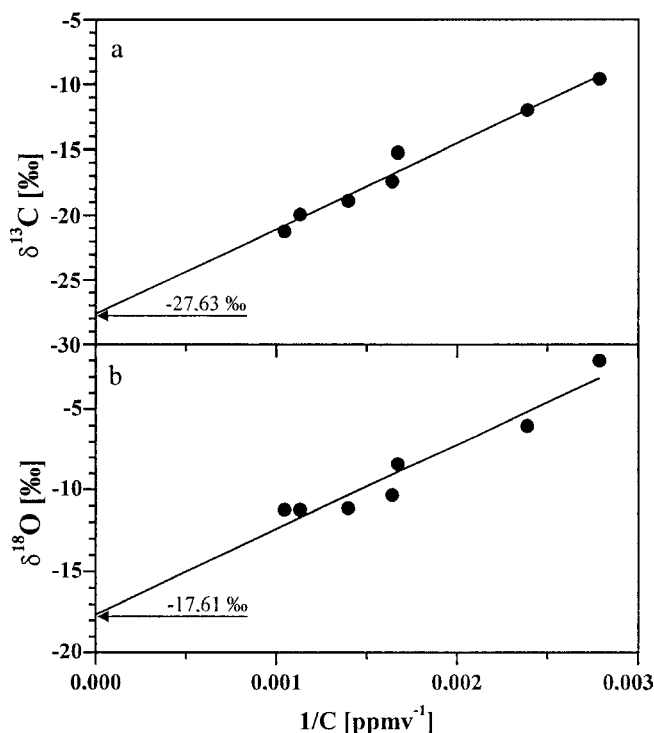
Fig. 3. The $\delta^{13}C$ and $\delta^{18}O$ values of CO_2 under the inverted metal container, plotted *vs.* reciprocal of the measured CO_2 concentration (the mixed forest site sampled on January 28, 1999). The extrapolation of the data points (fitted by least squares) yields the isotopic composition of the soil CO_2 flux equal $-27.6 \pm 0.9\%o$ and $-17.6 \pm 1.2\%o$ for $\delta^{13}C$ and $\delta^{18}O$, respectively.

Depth profiles

Information about the flux and isotopic composition of the soil CO_2 can be obtained also through sampling of the soil air at different depths in a soil column. The field equipment used for this purpose is presented schematically in Fig. 1c. In the framework of this study, the soil air was extracted only from two depths in the soil profile (40 and 80 cm). Approximately 15 litres of air was pumped from the selected depth intervals into special sampling bags made of polyvinyl fluoride (Cole–Parmer Int.). The CO_2 was then extracted cryogenically in the laboratory on a specially designed vacuum line [21] and its concentration in the sampled soil air was calculated from the measured volume of the exctracted CO_2 and the volume of the collected air sample. The ^{13}C and ^{18}O isotope composition of the extracted CO_2 was measured by mass spectrometry. For ^{14}C analysis of resident soil CO_2, the ^{14}C activity of the purified CO_2 gas was measured in miniature gas proportional counters [16].

Results

During the period January 1998 – December 2000 several types of measurements have been conducted regularly at the selected sites. First, the monthly mean equilibrium CO_2 concentration in the uppermost soil zone was monitored using an experimental set-up shown in Fig. 1b. The ^{13}C and ^{14}C content in these monthly composite samples of CO_2 was also determined. The results of these measurements

are presented in Fig. 4a, 4b, 4c. In Fig. 4d, the monthly mean values of surface air temperature and the amount of monthly rainfall, as recorded in the meteorological station in Kraków, is shown for comparison. Secondly, regular determinations of the soil CO_2 flux and its stable isotope composition ($\delta^{13}C$, $\delta^{18}O$) at the selected sites using the in-growth method and the experimental set-up shown in Fig. 1a have been performed. The results are summarised in Fig. 5a, 5b, 5c and in Table 1. The mean annual CO_2 flux density and its isotopic composition obtained for each investigated site is compared with the literature data in Table 2. Figure 5d shows the daily temperature and precipitation data for the Kraków meteorological station. It turned out that the surface air temperature and precipitation data for all three investigated sites are well correlated. Finally, the ^{14}C and ^{13}C content in the soil CO_2 collected at 40 cm and 80 cm depth, at all three investigated sites during summer and winter months was measured. The results of those measurements are summarised in Table 3.

Discussion

Figure 4a shows the monthly mean values of the CO_2 concentration inside the inverted metal container measured from January 1998 and December 2000 at three investigated sites. The average CO_2 concentration for the given month was derived from the measured volume of the CO_2 collected in the trap filled with molecular sieve and the volume of air pumped through the trap during that month. The measured CO_2 concentration should closely resemble the equilibrium concentration of carbon dioxide in the upper soil zone. It is apparent from Fig. 4a that equilibrium concentration of CO_2 in the uppermost soil layer depends on the season of year and the type of the soil studied. As expected, the maximum concentrations were observed during summer months. The highest values of the CO_2 concentration were measured for the agricultural field where potatoes were grown (up to 1.4% vol.), to be compared with ca. 0.8% vol. observed at the same time for the grassland site. Worth to note is also the large apparent year-to-year variability of the maximum CO_2 concentration at the given site. For instance, in summer 1999, the maximum CO_2 concentration measured for the agricultural field was ca. 1.4% vol., whereas during the following summer it reached only 0.3% vol. For the mixed forest site similar variations were observed: 1.1% vol. in 1998, 0.8% vol. in 1999 and 0.6% vol. in 2000. The lowest variability was observed for the grassland site.

The observed seasonal and interannual changes of equilibrium CO_2 concentration in the uppermost soil zone are linked to two meteorological variables: (i) surface air temperature stimulating plant growth and decomposition of soil organic matter in the upper soil layer; (ii) amount and frequency of rainfall which regulates the availability of moisture for plants during the growing season and changes free air porosity of the soil. For agricultural fields, the type of plants grown and the type of soil treatment will be also of importance. The relationship between the equilibrium CO_2 concentration and the mean monthly surface air temperature at three investigated sites is shown in Fig. 6. An apparent good correlation between both variables was found using an exponential fitting function (correlation
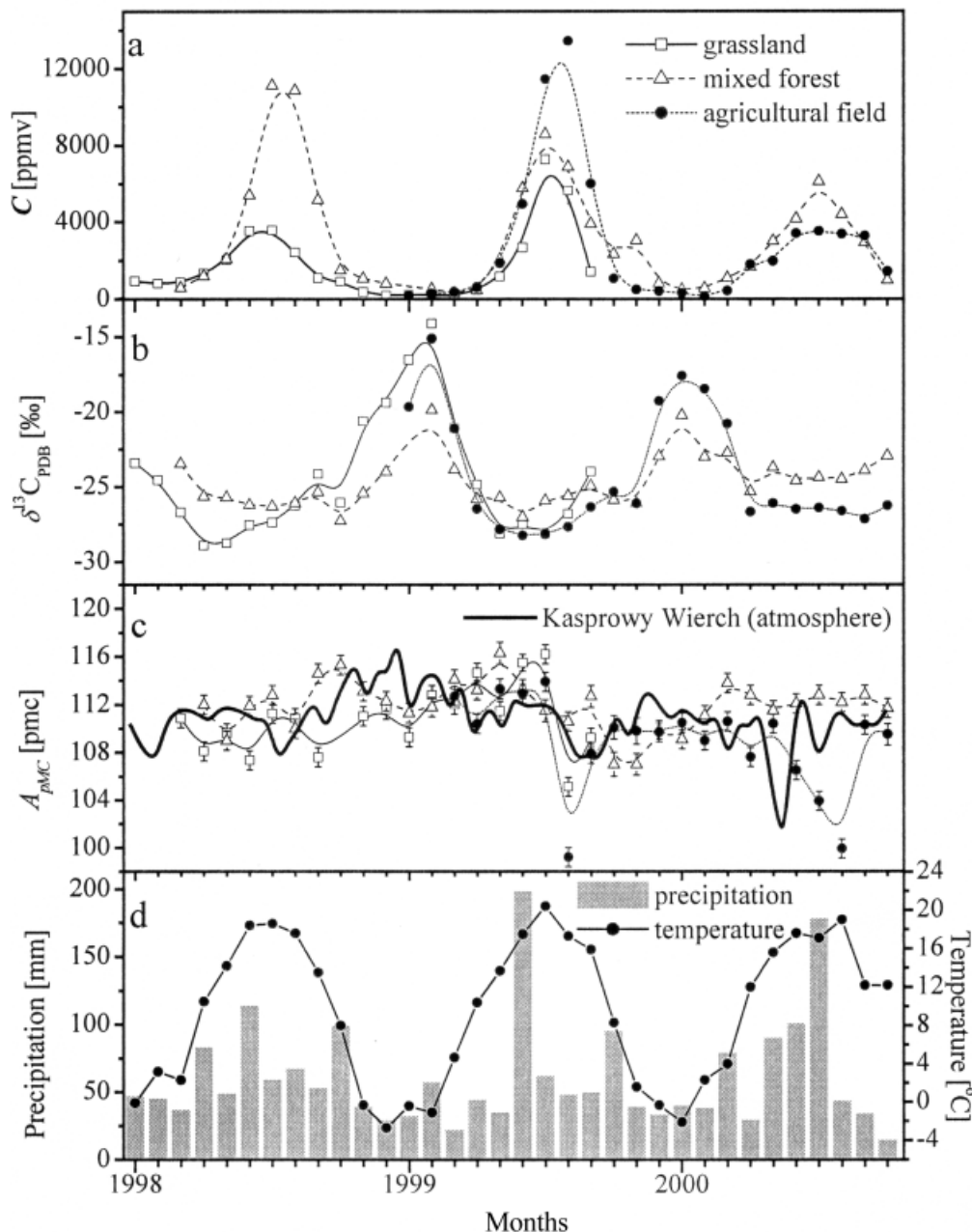
Fig. 4. Seasonal variations of: a – monthly mean values of equilibrium CO$_2$ concentrations in the uppermost soil layer; b – δ^{13}C of the equilibrium CO$_2$ concentrations; c – radiocarbon content in the equilibrium CO$_2$ concentration, monitored at three sites in the southern Poland between January 1998 and December 2000. The ^{14}C content in atmospheric CO$_2$ measured at Kasprowy Wierch, Tatra mountains is also shown. Monthly means of surface air temperature and precipitation amount at Kraków are presented (Fig. 4d).

coefficient varies between 0.66 and 0.85). Similar relationships are reported in the literature [20]. The use of two-parameter fitting function, containing surface air temperature and amount of rainfall as independent variables, did not improve significantly the observed correlation [15]. This suggests that soil moisture was not a limiting factor for plant growth at the investigated sites and also it did not experience large changes over time, which might influence the CO$_2$ transport through the soil column.

The δ^{13}C values of monthly mean CO$_2$ samples representing the uppermost soil layer (Fig. 4b) reveal seasonal fluctuations, with δ^{13}C values between –25‰ and –28‰ during summer and between –20‰ and –15‰ during winter. This apparent seasonality appeared to be mostly an artefact of the sampling method. During winter, when the CO$_2$ flux out of the soil is very low, the CO$_2$ present in the uppermost soil zone contains a significant admixture of atmospheric CO$_2$ which has δ^{13}C value around

–8‰. During summer, the measured δ^{13}C values are close to the expected δ^{13}C values for the CO$_2$ source (root respiration and decay of soil organic matter). Using the δ^{13}C value of the soil CO$_2$ source derived from flux measurements and that of atmospheric CO$_2$, the contribution of the latter component can be calculated. The calculations showed that during summer months the contribution of atmospheric carbon dioxide in the monthly cumulative CO$_2$ samples collected under the inverted container is less than 15%, while during winter it may reach even 70% [15].

The ^{14}C concentration in the monthly cumulative CO$_2$ samples (Fig. 4c) is non-distinguishable from the ^{14}C concentration recorded in the atmosphere during the same period. The atmospheric ^{14}C data originate from the sampling station located at the top of Kasprowy Wierch in the Tatra mountains (T. Kuc – unpublished data). This stems from the fact that most of the CO$_2$ in the uppermost soil zone, which supplies carbon dioxide to the inverted
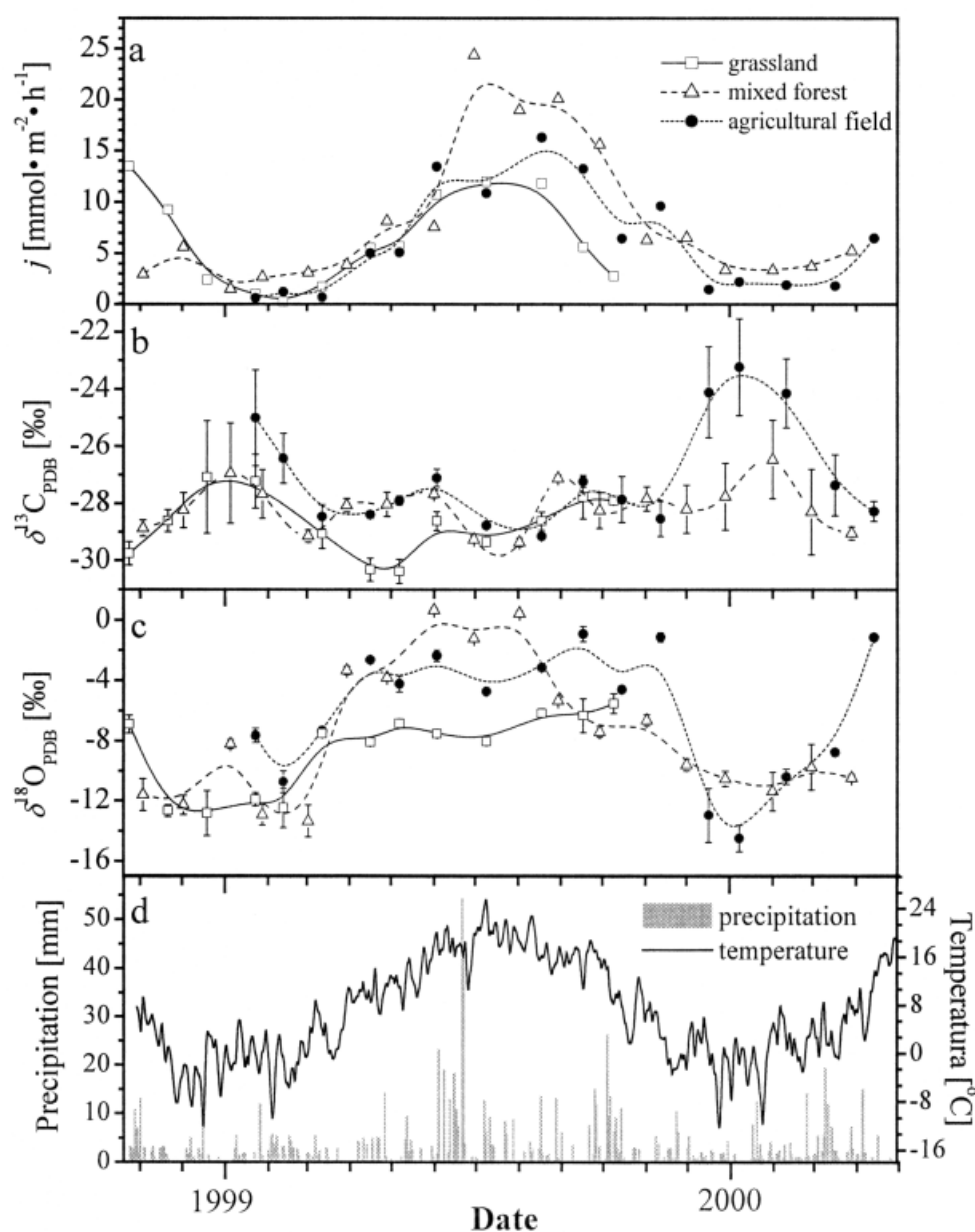
Fig. 5. Seasonal variations of: a – flux density of the soil CO_2 entering the atmosphere; b – $\delta^{13}C$ of the soil CO_2 flux; c – $\delta^{18}O$ of the soil CO_2 flux, monitored at three sites in southern Poland between January 1998 and December 2000. Daily means of surface air temperature and precipitation amount at Kraków for the same period are presented (Fig. 5d).

container, originates from root respiration and partly from the atmosphere (cf. discussion above). The contribution of CO_2 originating from decomposition of organic matter in the deeper soil layers which is characterized by a lower ^{14}C content, apparently plays only a minor role [1]. The origin of relatively low ^{14}C contents in monthly CO_2 samples collected at the agricultural field site in August 1999 and then again in July–August 2000 is not clear. It may partly result from the fact that the green parts of potatoes, which were grown on this field, were gradually drying out in

Table 1. Mean values of the soil CO_2 flux and its isotopic composition ($\delta^{13}C$ and $\delta^{18}O$) observed during summer (May, June, July, August) and winter season (November, December, January) at three investigated sites in southern Poland.

Site	Soil ($mmol \cdot m^{-2} h^{-1}$)		$\delta^{13}C$ of soil CO_2 flux $(‰)_{V-PDB}$		$\delta^{18}O$ of soil CO_2 flux $(‰)_{V-PDB}$	
	Summer	Winter	Summer	Winter	Summer	Winter
Grassland (19°56'E, 50°03'N)	11.5 ± 0.2	1.3 ± 0.2	−29.0 ± 0.2	−27.6 ± 0.7	−7.0 ± 0.2	−12.5 ± 0.5
Agricultural field (19°56'E, 50°03'N)	19.8 ± 0.4	2.9 ± 0.1	−28.4 ± 0.2	−27.7 ± 0.5	−3.3 ± 0.1	−11.0 ± 0.3
Mixed forest (20°23'E, 50°04'N)	13.4 ± 0.2	1.4 ± 0.1	−28.1 ± 0.2	−24.6 ± 0.6	−2.8 ± 0.6	−10.3 ± 0.3

Table 2. Annual mean values of soil CO$_2$ flux into the atmosphere, reported for different types of continental ecosystems.

Type of ecosystem	Location	CO$_2$ flux	Reference
Tallgrass prairie	Temple, Texas, USA	3.9	[20]
Bare soil	Shimane region, Japan	11.4	[22]
Forest Pasture	eastern Amazon basin, Brasil	6.0 2.9	[6]
Grass-covered area Beach/spruce forest	Heidelberg region, Germany	6.6 4.2	[8]
Grass-covered area	Bern region, Switzerland	15.0	[17]
Ficus and eucalyptus forest Pine forest Bare soil	Malaga region, Spain	8.0 4.0 1.8	[11]
Forest Grassland	Moscow region, Russia	1.8 2.4	[19]
Grassland Agricultural field Forest	southern Poland	5.7 7.0 9.8	this work

August. Consequently, the contribution from root respiration to the equlibrium soil CO$_2$ in the uppermost soil layer was gradually decreasing, resulting in the reduction of ^{14}C content in this pool of CO$_2$ (cf. discussion below).

The flux of soil CO$_2$, linked to the equilibrium soil CO$_2$ concentration, was derived from spot measurements at the investigated sites using the in-growth method. Typical evolution of CO$_2$ concentration and its $\delta^{13}C$ and $\delta^{18}O$ values, measured in air samples collected in consecutive time intervals under the inverted container is presented in Fig. 2a, 2b, 2c. The sampling was performed in January 1999 at the mixed forest site. On the basis of CO$_2$ concentration data (Fig. 2a) the flux density of soil CO$_2$ was calculated using eq. (1). It was equal to 2.7 ± 0.3 mmol·m^{-2}h^{-1}. The isotope data presented in Fig. 2b, 2c have been plotted on the δ vs. 1/C diagrams (Fig. 3a, 3b) and the δ_{soil} values of the CO$_2$ flux were derived. They are equal to $27.6 \pm 0.9\%o$ for $\delta^{13}C$ and $-17.6 \pm 1.2\%o$ for $\delta^{18}O$.

The measurements of the soil CO$_2$ flux and its isotopic composition have been performed regularly on all investigated sites over a three-year period. Similarly to CO$_2$ concentration in the uppermost soil layer, the CO$_2$ flux also reveals distinct seasonal fluctuations (Fig. 5a), with the maximum values up to ca. 20 mmol·m^{-2}h^{-1} recorded during summer months and around ten times lower values observed during winter time (Table 1). Significant differences between the monitored sites were also noticed, the CO$_2$ flux density being highest for the mixed forest site and ca. two times lower for the grassland site. The mean annual flux densities of soil CO$_2$ calculated on the basis of the data presented in Fig. 5a are equal to 5.7, 7.0 and 9.8 mmol·m^{-2}h^{-1} for the grassland, agricultural field and mixed forest site, respectively. These values are compared in Table 2 with analogous data reported in the literature, related to different type of ecosystems and different climatic conditions. The mean annual CO$_2$ flux densities summarised in Table 2 vary between 1.8 and 15 mmol·m^{-2}h^{-1}. The values measured in the framework of this work are in good agreement with the data reported for southern Germany [8], obtained under climatic conditions similar to those characterising southern Poland where the present study was conducted.

The relationship between the CO$_2$ flux measured using the in-growth method and the equilibrium monthly mean CO$_2$ concentrations in the uppermost soil layer at three

Table 3. The concentration and isotopic composition of CO$_2$ sampled at two depths in the soil during summer and winter, at three investigated sites in southern Poland.

Site	Sampling period	Depth (cm)	CO$_2$ concentration (ppmv)	$\delta^{13}C$ (‰)$_{V-PDB}$	$\delta^{18}O$ (‰)$_{V-PDB}$	[14]C content[*] (pMC)
Grassland	summer 1999	40	$17,050 \pm 160$	−24.0	−6.7	103.8 ± 1.0
Mixed forest	winter 1998/99	40	1430 ± 40	−19.4	−6.5	109.5 ± 1.1
		80	1490 ± 40	−19.6	−6.7	101.7 ± 1.0
	summer 1999	40	5610 ± 20	−21.9	−6.1	112.8 ± 1.2
		80	5760 ± 20	−22.2	−5.9	101.6 ± 1.2
Agricultural field	winter 1998/99	40	8860 ± 90	−25.8	−5.2	96.0 ± 1.1
		80	$17,360 \pm 170$	−25.0	−4.8	102.2 ± 1.0
	summer 1999	40	$37,400 \pm 1200$	−26.3	−10.3	98.7 ± 1.1
		80	$29,940 \pm 250$	−25.6	−8.6	104.5 ± 1.0

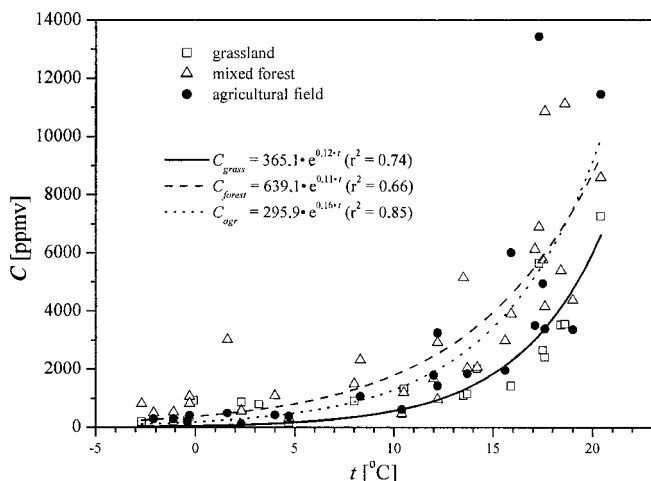[*] radiocarbon concentration is expressed in per cent of Modern Carbon (pMC).

Fig. 6. The relationship between the monthly means equilibrium CO_2 concentration in the uppermost soil layer and the monthly means of surface air temperature for three investigated sites in the southern Poland. The data cover the period from January 1998 till December 2000.

investigated sites is shown in Fig. 7. Relatively good correlation found between both variables (correlation coefficient between 0.63 and 0.71) allows the conversion of the mean equilibrium CO_2 concentrations to the CO_2 flux densities at a given site, provided that the calibration curve of the type shown in Fig. 7 is derived for that site.

The measured $\delta^{13}C$ values of the soil CO_2 flux are summarised in Fig. 5b. They reveal only minor changes in time, fluctuating between ca. $-25‰$ and $-30‰$. The mean $\delta^{13}C$ values calculated for winter and summer months for all three investigated sites are summarised in Table 1. Slightly elevated $\delta^{13}C$ values were recorded during winter months, the largest difference being observed for the agricultural field. Some admixture of atmospheric CO_2, present in significant proportion in the uppermost soil layer and contributing to the CO_2 flux entering the inverted metal container might explain these elevated $\delta^{13}C$ values.

The ^{18}O isotope content of the soil CO_2 flux leaving the surface reveals remarkable seasonality, with distinctly less
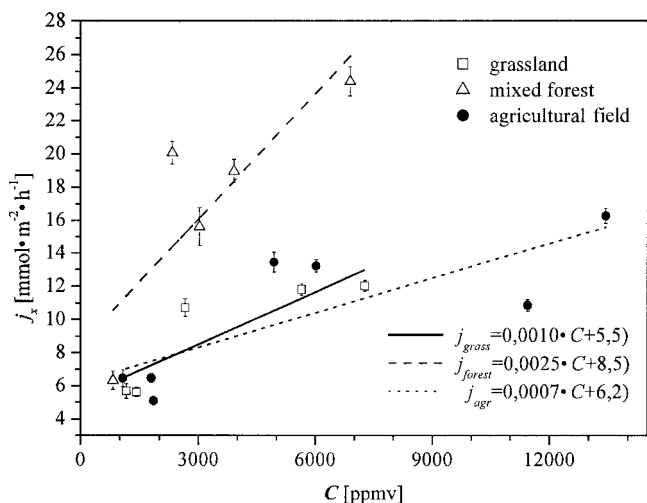

Fig. 7. The relationship between the flux density of soil CO_2 entering the atmosphere and the equilibrium CO_2 concentration in the uppermost soil layer for three investigated sites in the southern Poland. The data cover the period from January 1998 till December 2000.

negative $\delta^{18}O$ values recorded during summer months (Fig. 5b). The average $\delta^{18}O$ values of the soil CO_2 flux calculated for summer and winter months for three investigated sites are reported in Table 1. They vary from $-10.3‰$ (agricultural field) to $-12.5‰$ (grassland) during winter time, and from -2.8 to $-7.0‰$ during summer months, for the agricultural field and the grassland site, respectively. This remarkable seasonality of $\delta^{18}O$ is most likely due to seasonally varying temperature in the uppermost layers of the soil, influencing the magnitute of equilibrium fractionation factor between soil water and CO_2. The seasonal fluctuations of $\delta^{18}O$ of the soil moisture in this region, caused by both the seasonality of ^{18}O signal in rainfall and by the enhanced evaporation of soil water during summer, may also contribute to the observed effect [15, 23].

The seasonal changes in the concentration and isotope characteristics of the resident carbon dioxide at two different depths in the soil profile (40 and 80 cm), were measured at three investigated sites during winter 1998/99 and summer 1999 (at the grassland site only one depth was sampled). The results are summarised in Table 3. The resident CO_2 concentration varies greatly between sites, being the largest for the agricultural field (3.7% vol. during summer) and the lowest for the mixed forest site (0.14% vol. during winter). It is worth to note that the highest CO_2 flux was recorded for the mixed forest site (cf. Table 1). The fact that the highest resident CO_2 concentration does not lead to the highest value of the CO_2 flux leaving the soil is well understood in light of very different properties of the investigated soils: the forest soil had a loose structure proxiding little resistance to CO_2 transport while at the grassland site a brown soil with low air porosity dominated. The resident soil CO_2 is generally enriched in ^{13}C when compared to the CO_2 flux. This apparent enrichment amounts to several per mil and has its origin in kinetic isotope effect associated with the diffusion process (e.g. [3, 7, 8]); molecules of CO_2 containing ^{12}C are favoured in the diffusion process, leaving the bulk CO_2 in the soil enriched in ^{13}C. Relatively high $\delta^{13}C$ values measured for the forest site, when compared to the two other sites, may result from some admixture of atmospheric CO_2 easily penetrating the soil profile at this site during sampling. The $\delta^{18}O$ values of CO_2 at depth reveal minor seasonal fluctuations, being generally smaller than one per mil. The measured $\delta^{18}O$ values reflect the influence of three factors: (i) ^{18}O isotopic composition of the soil moisture at the given depth interval; (ii) temperature at the given depth in the soil controlling the magnitude of isotope fractionation factor between soil moisture and gaseous CO_2; (iii) kinetic isotope effect for ^{18}O associated with diffusion of soil CO_2 into the atmosphere. The radiocarbon content was measured at two depths in the soil for the mixed forest site and the agricultural field site. For the forest site, the ^{14}C content in the soil CO_2 measured at 80 cm depth was ca. 10 pMC lower than that recorded at 40 cm depth. This lower value reflects a larger contribution of the CO_2 originating from decomposition of old organic matter deep in the soil profile. Surprisingly, the agricultural field site revealed an opposite effect: radiocarbon content in soil CO_2 measured at 80 cm depth was by ca. 5 pMC higher than that recorded at 40 cm depth. This might be due to agricultural practices at that site. There was an intensive fertilizer treatment of

this field, the fertilizer containing a significant proportion of CaCO$_3$. During subsequent decomposition of CaCO$_3$ in the soil, significant amounts of CO$_2$, free of ^{14}C, are released within the upper soil zone, thus reducing considerably the ^{14}C content of the soil CO$_2$ in this zone.

Conclusions

The flux and isotopic composition of soil CO$_2$ was investigated at three sites in southern Poland representing most typical ecosystems in this part of Europe (mixed forest, agricultural field and grassland). The measurements revealed distinct seasonal fluctuations of the CO$_2$ flux into the atmosphere, with maximum values up to ca. 20 mmol·m^{-2} h^{-1} during summer months and around ten times lower values recorded during winter time. Differences up to a factor of two between the investigated sites as well as large year-to-year changes of the CO$_2$ flux were observed. The annual mean values of the CO$_2$ flux derived for the investigated sites are in good agreement with the literature data available for similar sites located in comparable climatic conditions.

The ^{13}C content of the soil CO$_2$ flux reveals little seasonal variability, with δ^{13}C values essentially reflecting the isotopic composition of the soil organic matter and the vegetation type. The resident CO$_2$ collected from different depths in the soil is generally enriched in ^{13}C when compared to the CO$_2$ flux. This apparent enrichment amounts to several per mil and has its origin in kinetic isotope effect associated with the diffusion process.

The ^{18}O content of the soil CO$_2$ flux entering the atmosphere reveals remarkable seasonality, with distinctly less negative δ^{18}O values recorded during summer months. This seasonality is greatly reduced in the resident CO$_2$ sampled from different depths in the soil. The measured δ^{18}O values reflect the influence of three factors: (i) ^{18}O isotopic composition of the soil moisture at the given depth in the soil profile; (ii) temperature at the given depth controlling the magnitude of the isotope fractionation factor between soil moisture and gaseous CO$_2$; (iii) kinetic isotope effect for ^{18}O associated with diffusion of soil CO$_2$ into the atmosphere.

The radiocarbon content of the CO$_2$ flux turned out to be non-distinguishable, within the uncertainty of the measurements, from the current ^{14}C level in atmospheric carbon dioxide. This confirms a rather short mean residence time of organic carbon in the soil (approximately 30 years) as well as a significant contribution of CO$_2$ from root respiration to the total CO$_2$ flux leaving the soil. However, significant reduction of the radiocarbon content in soil CO$_2$ was measured at larger depths in the soil reflecting increasing age of soil organic matter with depth.

On the agricultural field site a reversal of the ^{14}C activity in the soil CO$_2$ was observed, with a lower ^{14}C content recorded in the upper soil zone. The most likely reason for this effect is the mineral fertilizer treatment applied at this site, introducing ^{14}C-free carbon into the upper soil zone.

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