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Diurnal variations and vertical distribution of ^{13}C, and concentration of atmospheric and soil CO_2 in a meadow site, SE Poland

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We provide the results of 24-hour observations made in a meadow site located in a small river valley in Central Europe. Samples of atmospheric air were taken from three horizons: near the soil (0.05 m), in the grass (0.5 m) and above the meadow (2 m) at two-hour intervals. At the same time, samples of soil air were collected from two horizons: –0.1 and –0.5 m. We have found a variation of ^{13}C above the ground from –6‰ during the day to –20‰ late at night accompanied by variations in CO_2 concentration from 270 ppm during the day, to various levels late at night at different heights above the ground. The maximum concentration was 1430 ppm at the ground level. The correlation coefficient between ^{13}C and reciprocal of concentration was the highest ($R^2 = 0.984$) for the samples collected 2 m above the ground, the regression line clearly indicating CO_2 mixing from the two sources: atmospheric and biogenic reservoirs. The intercept of the mixing line yields $^{13}C = –23.0$‰ for the biogenic CO_2. In contrast, the diurnal variations in the soil were relatively small, ^{13}C varied from –21.6 to –23.4‰, while CO_2 concentration from 4300 to 8200 and from 24 700 to 34 500 ppm at depths of 0.1 m and 0.5 m respectively, which is less than 2-fold. Small diurnal variations are characteristic of dry soils, where ^{13}C is weakly correlated with CO_2 concentration (in our case R^2 was 0.30 and 0.54, respectively).

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Key words: SE Poland, atmospheric CO_2, carbon dioxide concentration, diurnal observations, ^{13}C, soil CO_2.

INTRODUCTION

The analysis of CO_2 in ice cores shows that for 400 000 years before the industrial revolution began in 1800s, the atmospheric CO_2 concentration had remained between 200 and 280 ppm. The combustion of fuels is continually discharging CO_2 into the atmosphere. The results of almost fifty years of observations at Mauna Loa observatory show that the CO_2 concentration has gradually increased from 315 ppm, observed in 1958, to 376 ppm, observed in 2003 (Keeling and Whorf, 2004). The annual average values of $\delta^{13}C$ observed in clean air in Mauna Loa varied from –7.84‰, observed in 1993, to –8.05‰, observed in 2001 (Allison *et al*., 2003). Long-term observations show a regular decrease of $\delta^{13}C$ in atmospheric CO_2, which results from anthropogenic CO_2; winter-summer variations, caused by a more intense combustion of fuels in winter, were also observed (Keeling *et al*., 1979; Mook *et al*., 1983; Kuc, 1986; Szaran, 1990; Kuc and Zimnoch, 1998).

It is known that the soil organic carbon pools maintain twice as much carbon as the atmosphere, and three times the carbon hoarded by vegetation (Andrew and Schlesinger, 2001). This does not mean that all of the earth's surface is a sink of carbon dioxide. The difference between carbon assimilation and soil respiration determines whether a particular area is a source or a sink. In fact, soil microbial respiration constitutes a carbon flux 10 times greater than that from fossil fuel combustion and 2.5 times greater than the delivery of litter to the soil surface (Andrew and Schlesinger, 2001).

The concentration of carbon dioxide in the atmosphere and its carbon isotopic composition varies according to daylight and plant activity (Kuc, 1991; Szaran, 1998; Zimnoch *et al*., 2004). Plants assimilate CO_2 at daytime, while they only emit CO_2 during the night. These variations are most pronouncing during windless weather which promotes stagnation of the air above the ground.

Another important source of CO_2 is the soil, where carbon dioxide is generated by root respiration and microbial decomposition of soil organic matter. Changes in solar energy within

the 24-hour cycle result in variations of soil temperature and plant activity, which affect the rate of CO_2 production. Small differences between day-time and night-time root respiration rates were observed in laboratory experiments and field investigations on different plant species (Veen, 1981; Scheurwater *et al*., 1998; Widen and Majdi, 2001), and strongly marked diurnal variations when the daylight maximum was more than double the night-time minimum (Harris and van Bavel, 1957). Root respiration is very sensitive to temperature, more than doubling when the temperature increases by 10°C (Palta and Nobel, 1989; Tjoelker *et al*., 1999; Atkin *et al*., 2000).

Soil CO_2 efflux rates were measured in various ecosystems. In eucalyptus open forest in a tropical savanna of northern Australia it was observed that the average soil CO_2 efflux was 19.33 mmol $m^{-2} h^{-1}$ during the wet season and declined to 7.92 mmol $m^{-2} h^{-1}$ during the dry season (Chen *et al*., 2002). Day-time rates of the soil CO_2 efflux rate were consistently higher than nocturnal values. The maximum rates occurred late in the afternoon, when the soil temperatures attained their maximum, whilst the minimum rates were recorded during early mornings. The measurements performed in organic boreal soils (Finland) in summer showed that the mean daily CO_2 flux from grass or barley field (32.5 mmol $m^{-2} h^{-1}$) was 2.5 times higher than from birch forest (Maljanen *et al*., 2002). However, the maximum flux of CO_2 recorded at noon was 25–30% higher than the minimum recorded before dawn. Diurnal changes of carbon dioxide flux from bare soil in an agricultural field in Japan were measured by Nakadai *et al*. (2002). The CO_2 flux showed significant diurnal changes, and these patterns were highly correlated with the soil surface temperature. Its values ranged from 2.1 to 7.0 mmol $m^{-2} h^{-1}$ in August and from 0.4 to 0.9 mmol $m^{-2} h^{-1}$ in February. In forest soils also a reverse behaviour was observed, i.e. the maximum flux of CO_2 occurred in the night (Edwards and Sollins, 1973; Dudziak and Halas, 1996*a*; Scott *et al*., 2004). This kind of variation might be connected with the convection of CO_2 from soil or with air moisture variations.

Variations of carbon isotope composition in soil CO_2 over the 24-hour cycle were observed in Eastern Europe by Dudziak and Halas (1996*a*). Large changes in CO_2 concentration were accompanied by respective distinct changes in $\delta^{13}C$. For example, if the CO_2 concentration doubled, $\delta^{13}C$ decreased by about 4‰. The range of these changes decreased with depth.

The character of diurnal $\delta^{13}C$ and CO_2 concentration variations suggests a simple mixing of clean atmospheric air with a $\delta^{13}C$ value close to –8.0‰ with biogenic carbon dioxide which has a much more negative $\delta^{13}C$ value than that of clean air. The biogenic CO_2 is predominantly produced by plant respiration and microbial decomposition of organic matter in soil. In this paper we present the results of simultaneous observations of diurnal variations in both atmospheric and soil CO_2. The novelty of this study is in demonstrating the vertical distribution of CO_2 concentration and $\delta^{13}C$ from a depth of 0.50 m in the soil to a height of 2.0 m above the ground surface in the air.

STUDY AREA

For this study we have chosen a flat meadow covered with high grass, prior to mowing. The meadow is located in the Bystrzyca River valley, on the left side of the river, 100 m from the waterside trees, 600 m from a local road and 500 m from the nearest farm buildings of the village of Żabia Wola, about 10 km from Lublin (SE Poland); see map in Figure 1. The sampling site was situated in the middle of a rectangular meadow (200 m × 50 m), in the grass, whose overall height was about 0.7 m, whereas the height of single blades reached 1.4 m. We noticed the following species: *Setaria glauca*, *Avena fatua*, *Avena strigosa*, *Agropyron repens*, *Echinochla crus-galli*.

The atmospheric conditions during the sampling (11–12 June 2003) were steady, almost cloudless and windless. A weak breath of air, about 1m/s, was noticed sometimes from the N–NW. The atmospheric pressure was about 100 kPa and it re-

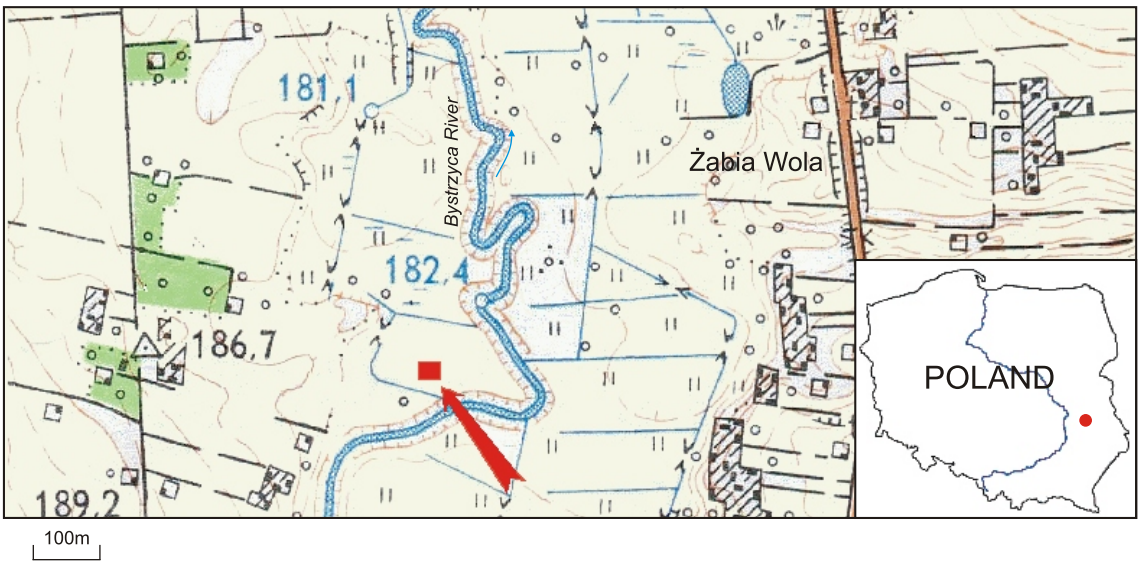

Fig. 1. Location of the study area

Arrow points to a location of the investigated area

mained fairly constant during the observations. The air and soil temperature varied from 9 to 25°C and from 14 to 17°C at depths of 0.1 m and 0.50 m, respectively. The soil was dry; no rainfall had been recorded for over three weeks prior to the observation.

ANALYTICAL METHODS

Samples of atmospheric air were sucked into evacuated glass ampoules (about 500 mL in volume) from three horizons: near the soil (0.05 m above the ground), in the grass (0.5 m above the ground) and above the meadow (2 m above the ground) every two hours. Each time, a sample of atmospheric air was sucked from another part of the meadow, which was covered by similar grass, of similar height and density. The samples were sucked into the glass ampoules by opening a stopcock of large diameter, thereby the sucking time was short - less than 1 second. Such sampling does not induce isotopic fractionation. At the same time, samples of soil air were collected from two horizons: –0.1 and –0.5 m with respect to the soil surface. Soil air was sucked into 50 mL glass syringes with two small stopcocks which allow flushing of the dead volumes by the sampled air. The syringes were connected to a stainless steel probe (see Fig. 2), which was forced into a desired depth and stayed unmoved in the soil over the whole period of the observation. To avoid perturbations in the soil atmosphere, the sampling was performed very slowly, over 20 min. During the sampling, the temperatures of the air above the ground and of the soil were taken by means of mercury thermometers.

The samples of air were immediately transported to the laboratory, where the CO_2 was extracted and analysed mass-spectrometrically (Dudziak and Halas, 1996*b*; Szaran, 1998; Szaran *et al*., 2002). The carbon dioxide was extracted separately from each ampoule and syringe by pumping the residual air through a trap cooled with liquid nitrogen at a pressure reduced to about 10 mbars. An admixture of nitrous oxide (which has the same mass as CO_2, i.e. 44 and 45) was removed by passing the gas through hot copper wires, where N_2O was decomposed (Dudziak and Halas, 1990). Carbon dioxide was purified from the water vapour by fractional sublimation at a temperature of –60°C. The measurements of $\delta^{13}C$ were performed in the Mass Spectrometry Laboratory by means of a dual inlet and triple collector instrument (a modified and modernized *MI 1305* model). The standard uncertainty of $\delta^{13}C$ measurements was 0.08‰.

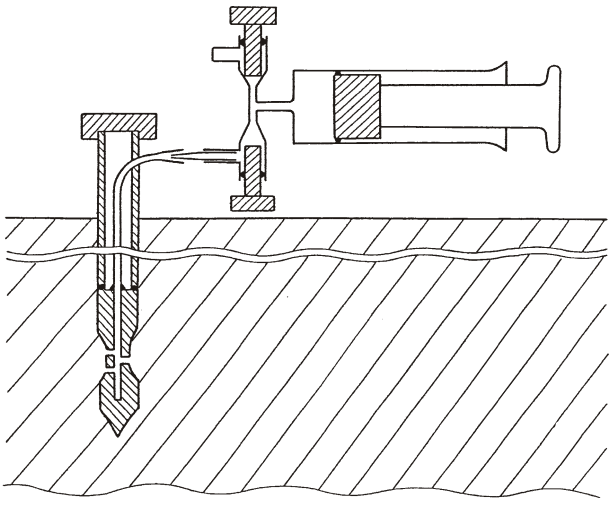

Fig. 2. The sampling of soil air

The absolute CO_2 concentration was determined by means of the same mass spectrometer which was used for $\delta^{13}C$ measurements. We used the linear relationship between the ion beam intensity and gas pressure in the inlet system kept at a constant volume. The relationship was calibrated by $^{12}C^{16}O^{2+}$ ion beams for a given sample and known amounts of CO_2 prepared from pure $BaCO_3$ reagent (McCrea, 1950). The CO_2 concentration was determined with a relative standard uncertainty of 2%.

RESULTS

The results obtained are shown in Tables 1 and 2 and in Figures 3–6. Large diurnal variations in CO_2 concentration and in the $\delta^{13}C$ of the atmospheric air were observed. The maximum values of CO_2 concentration were noticed near the soil surface where the $\delta^{13}C$ value was the lowest. The largest variation in the CO_2 concentration was observed in the air near the ground, where the concentration of CO_2 ranged from 266 ppm to 1430 ppm, and the $\delta^{13}C$ from –8.6 to –20.4‰.

After sunset, the CO_2 concentration in the atmosphere increased while the $\delta^{13}C$ decreased, tending to the value recorded in the soil air. During this time, at the height of 2 m above the ground, CO_2 concentration rose from 280 ppm to 980 ppm, while $\delta^{13}C$ dropped from –7.6 to –18.6‰. Surprisingly, the smallest variations of CO_2 concentration were recorded at the height of 0.5 m above the ground, from 290 to 580 ppm. In contrast we have recorded there the largest variations in $\delta^{13}C$, from –6.2 to –20.2‰. It is worth noting that the air sampling was made in free space between the grass blades, which were dry over the day, but become wet during the night.

At sunrise (4:00 a.m.), the reverse effect was observed: the carbon dioxide concentration decreased, while the $\delta^{13}C$ increased. At the beginning of full daylight (about 6:00 a.m.) these trends stopped. The concentration of carbon dioxide and the isotopic composition of carbon in the air were steady until 8:00 p.m. (before the sunset). After dawn, the CO_2 concentration decreased, while the $\delta^{13}C$ increased, tending to the value of –8.8‰ at the ground, –6.5‰ between the grass and –7.5‰ at 2 m height above the ground. The highest $\delta^{13}C$ and the lowest CO_2 concentration were observed in the air within the grass at 0.5 m level above the ground. The lowest variation of the CO_2 concentration were also recorded at this level.

Other effects were observed in soil, where no distinct diurnal changes were observed. At both horizons, the concentration of carbon dioxide fluctuated slightly, while the carbon isotopic composition remained almost steady. Different values for each of the two horizons, the deeper and shallower, were observed. The carbon dioxide concentration at –0.1 m varied from 4300 to 8200 ppm, while at the –0.5 m horizon it was higher and varied from 24 700 to 34 500 ppm; the $\delta^{13}C$ for these horizons varied from –21.10 to –22.05‰ and from –22.96 to –23.76‰, respectively.

Table 1

Diurnal variations of temperature, concentration and carbon isotopic composition in atmospheric and soil carbon dioxide Żabia Wola 11/12 June 2003

Time	Place	Temperature [°C]	CO_2 conc. [ppm]	$\delta^{13}C$ VPDB [‰]
1	2	3	4	5
20:10	A (2 m)	25.0	540	–14.33
	B (0.5 m)	–	580	–13.20
	C (0.05 m)	19.0	840	–15.85
	D (–0.10 m)	16.5	8 100	–21.94
	E (–0.50 m)	–	27 500	–22.96
21:20	A	20.0	360	–9.86
	B	–	440	–10.20
	C	16.0	660	–14.97
	D	16.0	4 300	–21.21
	E	–	31 900	–23.45
23:00	A	17.0	600	–15.55
	B	–	300	–16.14
	C	16.0	960	–17.66
	D	16.0	7 800	–21.33
	E	–	28 600	–23.28
1:00	A	15.5	610	–15.47
	B	–	470	–19.67
	C	14.5	1 270	–19.59
	D	15.5	4 400	–21.20
	E	–	27 800	–23.35
2:10	A	12.0	870	–17.76
	B	–	500	–20.23
	C	9.0	1 430	–20.37
	D	15.0	8 100	–22.05
	E	–	30 300	–23.18
3:20	A	11.5	980	–18.56
	B	–	490	–19.63
	C	9.0	1 370	–20.27
	D	14.5	n.a.	n.a.
	E	–	n.a.	n.a.
4:30	A	11.0	570	–15.00
	B	–	530	–18.99
	C	10.0	1 300	–20.06
	D	14.0	5 600	–21.98
	E		24 700	–23.17
7:00	A	17.0	320	–8.86
	B	–	390	–7.97
	C	16.0	450	–11.05
	D	14.0	5 200	–21.61
	E	–	32 900	–23.69
9:20	A	21.5	300	–7.77
	B		350	–6.18
	C	20.5	340	–8.91
	D	14.0	6 400	–21.92
	E	–	33 300	–23.59
12:00	A	24.5	310	–7.58
	B	–	290	–6.21
	C	24.5	340	–8.62
	D	15.5	8 200	–21.90
	E	–	30 800	–23.71
14:30	A	24.5	310	–7.75
	B	–	290	–7.32
	C	24.0	450	–12.45
	D	17.0	n.a.	n.a.
	E	–	30 800	–23.43
16:15	A	24.0	280	–7.56
	B	–	310	–6.92
	C	21.0	270	–8.81
	D	17.0	8 200	–21.70
	E	–	27 400	–23.32
18:30	A	22.5	300	–7.64
	B	–	300	–6.90
	C	19.0	350	–8.83
	D	17.0	6 500	–21.39
	E	–	31 300	–23.76
19:45	A	18.0	420	–10.85
	B	–	430	–11.03
	C	17.0	450	–11.84
	D	17.0	7 500	–21.44
	E	–	34 500	–23.64

A, B, C — carbon isotopic composition in atmospheric heights: 2.0, 0.5 and 0.05 m, respectively; D, E — soil carbon dioxide –0.10 and –0.50 m, respectively; n.a. — not analyzed

Table 2

Summary of diurnal observations of carbon dioxide concentration and its carbon isotopic composition in atmosphere and in soil air

Height [m]	Range $C(CO_2)$ [ppm]	Range $\delta^{13}C$ [‰]	Constant A in eq. [1]	R^2
2.0	280 ÷ 990	–7.56 ÷ –18.56	–22.97	0.984
0.5	290 ÷ 580	–6.18 ÷ –20.23	–18.50*	0.82*
0.05	270 ÷ 1430	–8.62 ÷ –20.37	–22.47	0.932
–0.10	4300 ÷ 8200	–21.10 ÷ –22.05	–22.30	0.30
–0.50	24700 ÷ 34500	–22.96 ÷ –23.76	–25.29	0.54

R^2 — squared correlation coefficient
* — for daily data only

The air and soil temperatures recorded during sampling are plotted in Figure 4. These variations were typical for the day-night cycle. They were larger in the air (11–25°C and 9–24.5°C at the 2.0 m and 0.05 m horizons, respectively) than in the soil (at the depth of 0.1 m the temperature varied from 14 to 17°C).

DISCUSSION

There is no doubt that the observed diurnal variations in CO_2 concentration and its carbon isotopic composition predominantly reflect assimilation and respiration processes. Photosynthetic absorption dominates in day-time, while respiration discharges CO_2 at day and night. Plants assimilate $^{12}CO_2$ in preference to $^{13}CO_2$, thereby the CO_2 left in the ambient environment is enriched in ^{13}C. Carbon isotope fractionation during photosynthesis is affected by environmental factors, such as atmospheric CO_2 concentration and temperature (O'Leary, 1988).

CO_2 concentration measured 2 m above the ground varied by about 700 ppm, which is likely the largest change observed so far. This variation was accompanied by $\delta^{13}C$ variation of

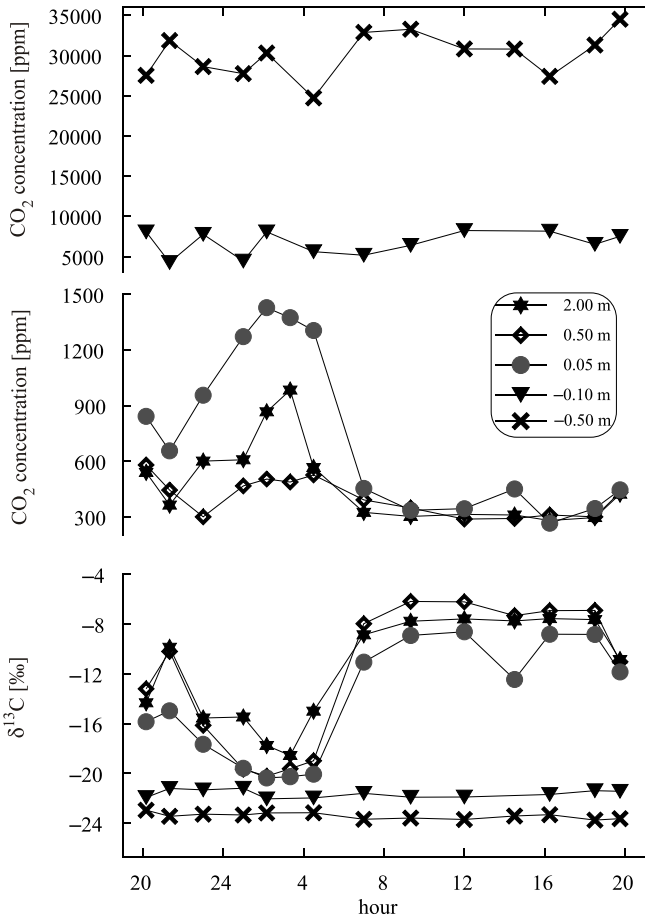

Fig. 3. Diurnal variations of concentration and carbon isotopic composition in soil and atmospheric carbon dioxide at various horizons

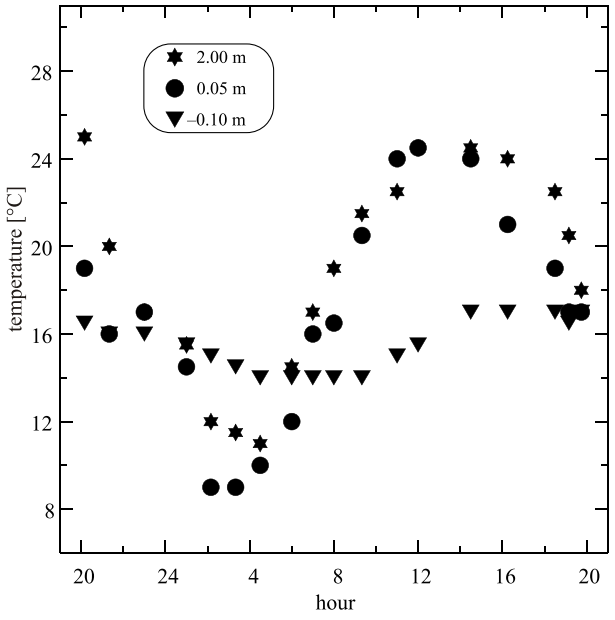

Fig. 4. Diurnal variations of temperature

11‰. Such large variations in $\delta^{13}C$ value were observed previously above meadows covered by grass (Szaran, 1998; Szaran *et al*., 2002). The maximum variations were observed during the specific atmospheric conditions, namely in stagnating air above the meadows covered by high and thick grass. These effects were observed in several meadows located in different regions of eastern Poland (about 100 km south-east of Warsaw and in Roztocze National Park, SE Poland). The greatest ranges observed earlier were: 10.7‰ and 350 ppm (Szaran, 1998), and 10‰ and 480 ppm (Szaran *et al*., 2002). The variations were larger late in the spring than in the summer; for example, they were 10.4‰ and 460 ppm in June, while only 3.9‰ and 120 ppm at the end of August (Szaran *et al*., 2002). Similar observations have been made by Longinelli and Selmo (2005) in Italy at the border of a meadow. They noticed that $\delta^{13}C$ varied by about 4‰ and CO_2 concentration by about 150 ppm. Variations of similar magnitude were observed by Keeling (1961) in a grassland station in Indiana — 200 ppm and 6‰, respectively. In the mass of air situated far away from plants these ranges are smaller. In an observation made on the roof of a building in Kraków (Poland), 20 m above ground level, the CO_2 concentration and $\delta^{13}C$ varied within a narrow range only, the respective amplitudes being 100 ppm and 4‰ (Zimnoch *et al*., 2004). All of these investigations show a strong local effect caused by plants, which is especially large in stagnant air.

Plants and all other organisms in the ecosystem respire over their lifetime using ambient oxygen and produce carbon dioxide in their metabolic processes. It is known that plant respiration and tissue decomposition are accompanied by very little fractionation (Martinelli *et al*., 1991), so the CO_2 which is respired has the same isotope ratio as the living tissue. The carbon isotopic composition of terrestrial plants depends on the photosynthetic pathway. The $\delta^{13}C$ value for C_3 plants (these plants constitute about 90% of all plants today) is in the range from –35 to –20‰, while the C_4 plants, which utilize the four-carbon-photosynthetic-pathway, have $\delta^{13}C$ values from –16 to –9‰ (*cf*. Geyh and Schleicher, 1990).

The carbon isotopic composition of the soil carbon dioxide reflects the isotopic composition of plant bodies. The carbon isotope composition of the CO_2 flux leaving the soil is the same as in that generated during the decomposition of soil organic matter or root respiration, i.e. a mean $\delta^{13}C = –27‰$ for the C_3 plants (Amundson *et al*., 1998). However, the carbon dioxide present in the soil has $\delta^{13}C$ shifted by at least 4.4‰, which results from isotope fractionation during diffusion into the atmosphere (Dörr and Münnich, 1980). That enrichment depends on the depth and on the soil respiration activity (Cerling *et al*., 1991; Hesterberg and Siegenthaler, 1991).

The processes of respiration, and also decomposition of plant relics admit CO_2 enriched in the light isotope into the air, so $\delta^{13}C$ is shifted into the minus, tending to the value corresponding to the isotopic composition of organic matter. When carbon dioxide is not removed by photosynthesis or by convection, its concentration increases whilst its $\delta^{13}C$ value decreases. During day-time, when photosynthetic processes dominate, large amounts of CO_2 are consumed, and so an increase in carbon dioxide concentration is not observed whereas the $\delta^{13}C$ value of CO_2 is almost constant.

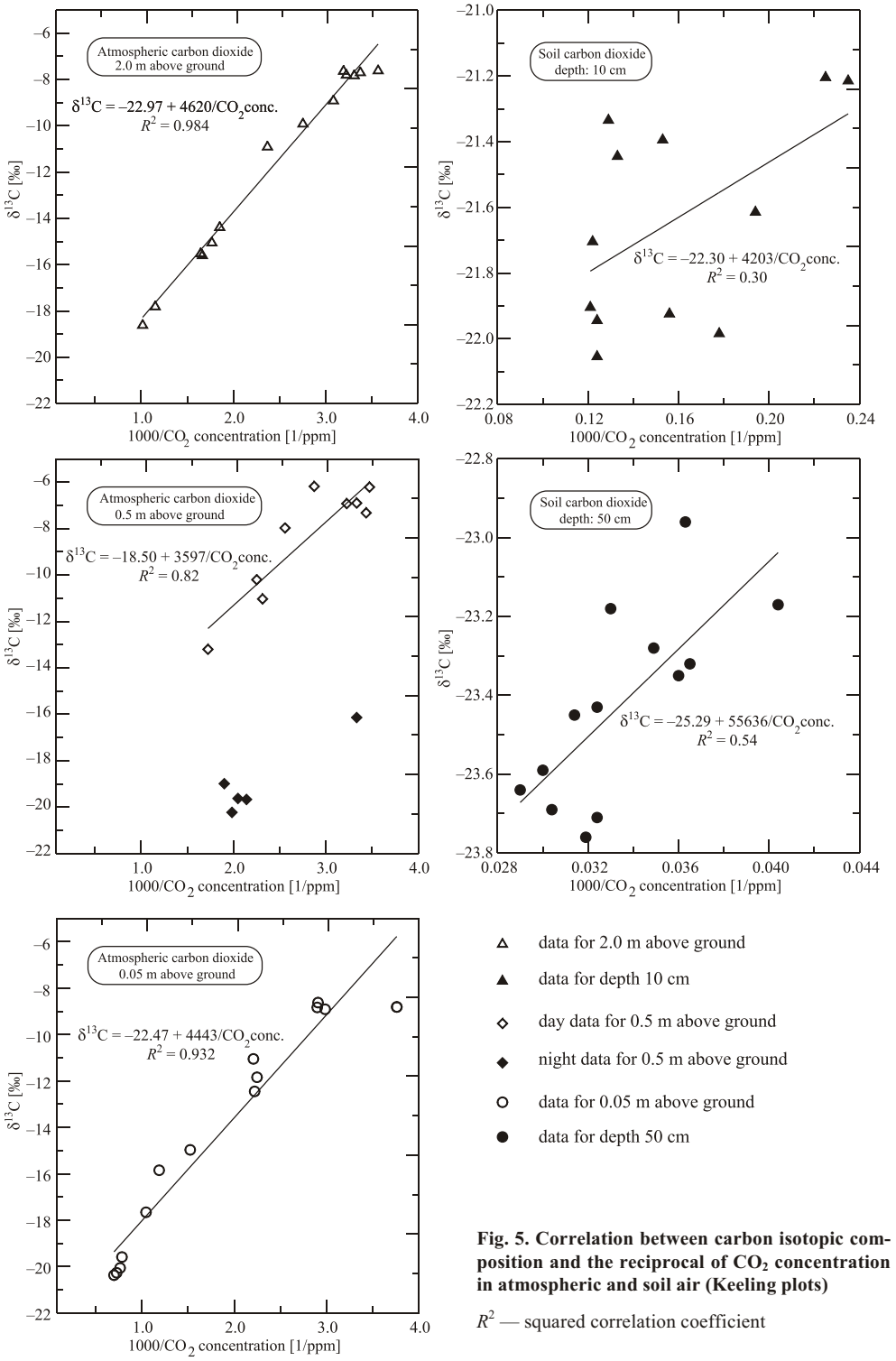

Fig. 5. Correlation between carbon isotopic composition and the reciprocal of CO_2 concentration in atmospheric and soil air (Keeling plots)

R^2 — squared correlation coefficient

In the soil air we did not observe any regular distinct relative variations in the CO_2 concentration nor in $^{13}C/^{12}C$. We can only note a small tendency towards an increased CO_2 content in the morning. The mean diurnal CO_2 concentration at a depth of 0.1m was 6670±1500 ppm, which was 4.5 times lower than at the depth of 0.5 m, where it was 30 150±2800 ppm. The carbon isotope composition did not change by more than 0.8‰. The mean $\delta^{13}C$ values of soil CO_2 were –21.64±0.32‰ and –23.43±0.24‰, at depths of –0.1m and –0.5 m, respectively. These values are significantly different from those recorded in the atmospheric air.

Diurnal variations in the CO_2 of air samples collected at numerous sites were investigated by Keeling (1961). He found that the carbon isotopic composition and the concentration of the atmospheric carbon dioxide of air in forest areas obey the following relationship:

$$\delta^{13}C = A + B/(CO_2conc.) \quad [1]$$

where: A and B are empirical constants.

The above equation presented in the graphical form is known as the Keeling plot.

From this type of plot it is possible to determine the $\delta^{13}C$ of respired CO_2 from the soil or from whole ecosystems. If the carbon dioxide concentration is close to the atmospheric value of 378 ppm, then the sample mostly contains atmospheric CO_2, and the $\delta^{13}C$ value is near –8.0‰. When the CO_2 concentration rises above the atmospheric concentration, it contains a fraction coming from respiration, which has more negative $\delta^{13}C$ values. The intercept, A, of the Keeling plot yields the $\delta^{13}C$ of biogenic CO_2 in the absence of dilution by atmospheric carbon dioxide. In Figure 5, we present the Keeling plots for our observations. The A-values are collected in Table 2 for each sampling series. A very good correlation was noticed between $\delta^{13}C$ and 1/(CO_2conc.) at the horizon of 2 m above the ground (R^2 = 0.984) and near the ground (R^2 = 0.932), whereas at height of 0.5 m the points are split into two groups. The reason for the observed split is discussed below.

The carbon dioxide which is admixed into the air at the level of 2 m above the ground has $\delta^{13}C \approx$ –23.0‰. A similar

value was encountered in the soil, slightly beneath the surface. It was about –22‰, while at the height of 0.5 m above ground level the $\delta^{13}C$ value extrapolated from the Keeling plot for daily values (black points representing night values were excluded) was –18.5‰.The correlation coefficient was weak in this case (see Fig. 5), which indicates a more complicated situation at this horizon.

The low $\delta^{13}C$ value noted near the ground suggests that CO_2 of soil origin dominates in the mixture. A very good correlation observed between $\delta^{13}C$ and $1/(CO_2 conc.)$ indicates the mixing of CO_2 from two distinct sources, enriched with light and heavy isotopes respectively.

The variations observed during night-time can be simply explained by switching off the photosynthesis and stopping vertical mixing in the atmosphere. The lowering of the air temperature at the ground below the soil temperature and below the temperature of the upper layer of air stopped convection and interrupted the flux of carbon dioxide into the upper layer of the atmosphere, so the escape of the soil CO_2 into the atmosphere became slow, while the overall concentration at the bottom of the meadow increased.

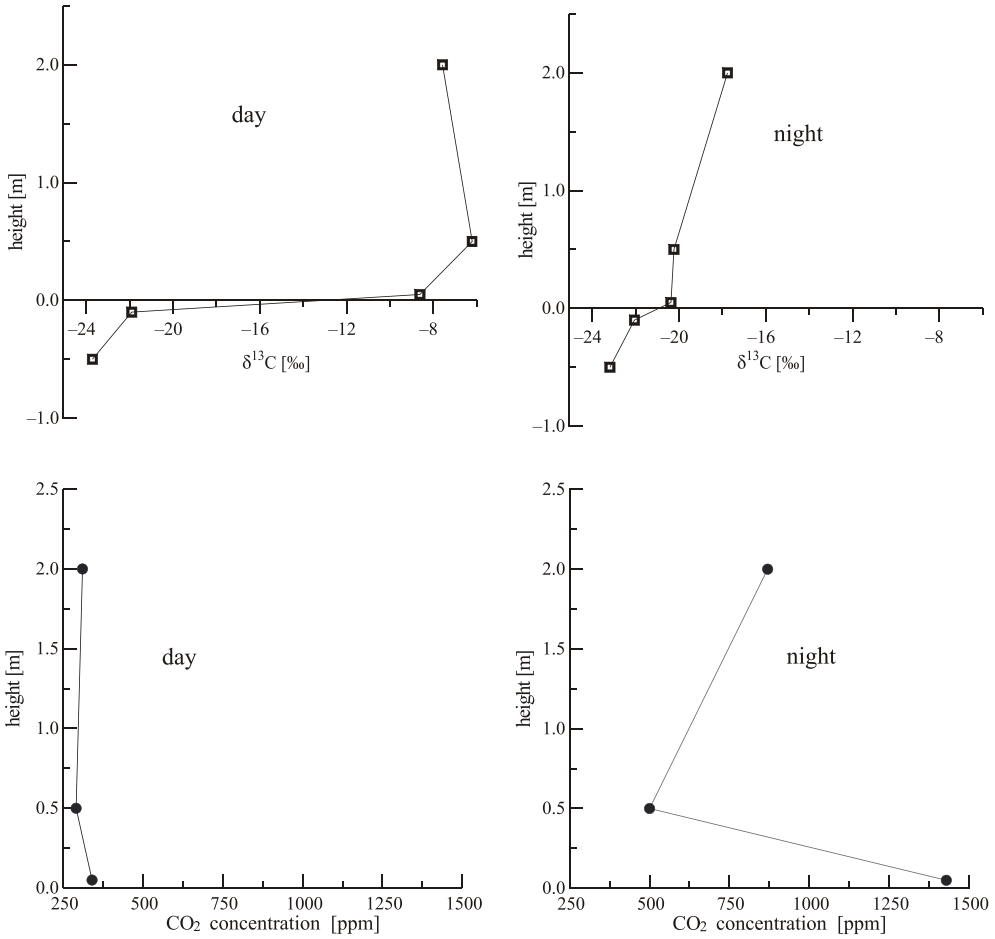

Fig. 6. Vertical distribution of $\delta^{13}C$ and CO_2 concentration recorded at mid-day and at 2:10 a.m.

However, it is more difficult to explain diurnal variations which occur between biologically active parts of grass (at 0.5 m above the ground) on the basis of the Keeling's plot shown in Figure 5. Inasmuch as we observed a significant split in $\delta^{13}C$ between day and night, therefore we have plotted in Figure 6 vertical distributions of $\delta^{13}C$ and CO_2 concentration at mid-day and 2:10 a.m. These plots clearly reveal a major sink of CO_2 at a height (x) of 0.5 m in the night, because the concentration there drops even below that observed at the height of 2 m. From the gradient of CO_2 concentration (c) recorded above, which is: $\frac{dc}{dx} = \frac{(1430-500)\,ppm}{0.45m}$, and from the known coefficient of CO_2 diffusion in air, $D = 1.5 \cdot 10^{-5}$ m^2 s^{-1} at 10^5 Pa and 10°C (Armstrong, 1979), we may estimate the total flux (j), of CO_2 which diffuses from the soil. From Fick's first law, we obtain:

$$j = -D\frac{dc}{dx} = 4.74 \text{ mmol m}^{-2}\text{h}^{-1} \qquad [2]$$

The (j) value obtained in this way falls somewhat below the range of summer flux reported by Gorczyca *et al.* (2003) for a meadow soil in Southern Poland. Taking into account that the soil was rather dry, which implies that CO_2 production was low, the results seem to be reliable. It should be noted that our flux estimate may be underestimated because of the unknown vertical distribution of CO_2 concentration at heights below 0.50 m. Below the 0.50 m horizon the gradient might be somewhat higher. We have selected this horizon because there was a maximum density of the biologically active parts of plants. During the night, atmospheric water condensed at their surface in which CO_2 was dissolved and adsorbed by plants together with the water. That seems to be a reasonable explanation for the sink of CO_2 which was encountered at the height of 0.50 m.

The correlation between $\delta^{13}C$ and $1/(CO_2 conc.)$ in the soil air was weak. The squared correlation coefficients were $R^2 = 0.30$ and 0.54 at depths of 0.1 m and 0.5 m respectively. It is obvious, because this dependence is significant for soils characterised by a large air porosity and small respiration rate, where the CO_2 concentration is small and the process of mixing air, soil and atmospheric origin is more significant at soil horizons. Such an effect was observed in desert soils (Parada *et al.*, 1983; Cerling *et al.*,

1991). In our case, the CO_2 concentration of the soil air is almost a hundred times greater than that in the atmosphere, so the admixture of atmospheric air into the soil air is negligible.

The basic process determining the carbon dioxide content and the carbon isotopic composition in the soil profile is the diffusion of CO_2 into the atmosphere. The composition of the soil air is time-dependent, because the soil parameters (temperature, humidity) vary in a diurnal cycle. Thus the carbon dioxide flux into the atmosphere varies and it would be necessary to use a dynamic model and know more of the soil features in order to calculate it (Nakadai *et al*., 2002). Two steady-state models describing the distribution of CO_2, and its $\delta^{13}C$ were given by Cerling (1984) and Hesterberg and Siegenthaler (1991). They assumed a constant respiration rate in the soil profile in one model and exponentially decreasing respiration activity with depth in another model. It is evident from these models that the parameters describing the soil air depend on: (1) the soil respiration activity and its distribution in the soil profile, (2) coefficients of diffusion and moisture, (3) the concentration of CO_2 in the atmosphere. The diffusion coefficient, depending on air porosity and soil moisture, does not change significantly during over a 24-hour period. On the other hand, soil respiration is very sensitive to temperature changes (Frank *et al*., 2002; Maljanen *et al*., 2002; Murthy *et al*., 2003). We recorded in our study a diurnal variation in temperature of 3°C at a depth of –0.1 m (Fig. 4). As it was the soil layer containing the largest amount of organic matter, we expect regular changes, both in the CO_2 content and in its $\delta^{13}C$. Calculations showed that the changes expected might be diminished due to variations in the boundary conditions. If we assume that the soil activity (q) decreases exponentially with depth (x), i.e. $q(x) = q_0 \exp(-x/x_0)$, then CO_2 concentration is expressed by the following equation:

$$C(x) = C_{atm} + q_0 (x_0^2 / D)(1 - \exp(-x / x_0)) \qquad [3]$$

where: C_{atm} — the concentration of carbon dioxide in the atmosphere, q_0 — soil activity at the soil surface, x_0 — constant, D — the diffusion coefficient.

The concentration of CO_2 increased four-fold during the night near the soil surface. According to that, we estimated that the daylight flux of the soil CO_2 into the atmosphere, from 7:00 a.m. to 4:00 p.m., exceeded the night-time flux by 30±8% (from 1:00 to 5:00 a.m.). These periods were chosen in such a way that CO_2 concentration at 0.05 m above the ground was almost constant there.

The field investigation of the soil respiration rate in the diurnal cycle has shown that its maximum occurs at noon or in the afternoon and may even be more than double the minimum value, which occurs before dawn (Currie, 1975; Nobel and Palta, 1989; Dudziak and Halas, 1996*a*; Frank *et al*., 2002; Nakadai *et al*., 2002). The respiration was strongly correlated with the soil temperature and thus with microbial activity and root respiration.

The increase in mean values of $\delta^{13}C$ observed from 0.5 m to 0.1 m depth by 1.8‰ can be explained by applying one of the two diffusion models mentioned above. They make it possible to determine the carbon isotope composition as a function of depth (Cerling, 1984; Hesterberg and Siegenthaler, 1991). In the deep soil layers, due to isotope fractionation during diffusion, carbon is enriched in ^{13}C and $\delta^{13}C$ is shifted by 4.4‰ in comparison to the respired CO_2. Also, CO_2 concentration is the highest there. On going to the top layer, the enrichment in ^{13}C becomes greater, and the carbon dioxide concentration lower, as we have observed. Of course these changes depend on the soil respiration rate and on the soil parameters. The most rapid changes occur in the thin layer at the soil surface, where the isotope composition and CO_2 concentration become equal to that in the atmospheric air.

The influence of temperature on CO_2 concentration and its isotopic composition were investigated. A correlation between the air temperature and the concentration of CO_2 as well as $\delta^{13}C$ were observed. This correlation was strong near the ground surface ($R^2 = 0.70$ and 0.64), while at the level of 2 m this dependence was rather weak ($R^2 = 0.50$ and 0.51). It is not surprising, because sunbeams do not heat the air directly, but heat the ground and subsequently the ground heats the air. Diurnal variations of temperature at various horizons change the air convection. This is probably the strongest influence of the temperature variations on the variations of CO_2, especially noticeable at the ground. This effect is weak at a higher level because plants consume large amounts of CO_2 during photosynthesis.

Statistically insignificant correlations between the soil temperature and the carbon dioxide concentration and $\delta^{13}C$ were noticed in the soil air. The calculated R^2 coefficients were very small, ranging from 0.05 to 0.15.

SUMMARY AND CONCLUSIONS

RESULTS FOR ATMOSPHERIC AIR

1. The isotopic composition is a very sensitive indicator of biogenic activity, more sensitive than CO_2 concentration only.

2. After the sunset, the CO_2 concentration increases and its $\delta^{13}C$ decreases (the extreme values are reached before the dawn). After the dawn, the CO_2 concentration decreases, while $\delta^{13}C$ tends to –8.0‰.

3. Near the soil surface the maximum of CO_2 concentration in the atmospheric air was noticed, whilst $\delta^{13}C$ value was the lowest.

4. The highest $\delta^{13}C$ values and the lowest CO_2 concentrations were observed in the air between the grass-blades, at 0.5 m above the ground. The variation in CO_2 concentration was the smallest at this level.

5. The largest variation in the CO_2 concentration was observed in the air near the ground.

6. A very good correlation was noticed between $\delta^{13}C$ and $1/(CO_2 conc.)$ at 2 m above the ground ($R^2 = 0.984$) and near the ground ($R^2 = 0.932$), whereas inside the grass the plot is split into day and night parts.

RESULTS FOR SOIL AIR

1. CO_2 concentration in the soil air at 0.5 m depth was higher than at 0.1 m depth and in the atmospheric air. The $\delta^{13}C$ values measured in soil air at 0.5 m depth was lower than at 0.1 m depth and in the atmospheric air.

2. The relative variations as well as the CO_2 concentration and $\delta^{13}C$ were insignificant in the soil air.

3. The correlation between $\delta^{13}C$ and $1/(CO_2 conc.)$ in the soil air was weak. The squared correlation coefficients were $R^2 = 0.30$ and 0.54 at depths of 0.1 m and 0.5 m, respectively.

4. The diffusive transport of CO_2 from the soil to the atmosphere was significantly influenced by a four-fold increase of CO_2 concentration at the ground surface in the night.

TEMPERATURE DEPENDENCE

Diurnal variations of temperature induce mixing of air by convection, the intensity of which is forced by the vertical temperature gradient. The largest influence of the temperature variations on the variations of CO_2 parameters was encountered at the ground surface.

MIXING PROCESS

The strong diurnal variations and the correlation between $\delta^{13}C$ and CO_2 concentration in the atmospheric air indicate a mixing line, from which the $\delta^{13}C$ of the biogenic CO_2 has been inferred. The extrapolation of the straight line to the zero value of the $1/(CO_2$ conc.) yields $\delta^{13}C = -23.0‰$. Small diurnal variations are characteristic of dry soil, where $\delta^{13}C$ is weakly correlated with CO_2 concentration.

CO_2 FLUX ESTIMATION

On the basis of the vertical gradient of CO_2 concentration recorded near the ground surface, the CO_2 flux was estimated from the Fick's first law to be 4.7 mmol m^{-2} h^{-1} at night-time. The daily flux was estimated to be *ca*. 30% higher than that.

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