Seasonal and diurnal variations of $\delta^{13}C$ and concentration of atmospheric CO_2 at Parma, Italy

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The $\delta^{13}C$ of atmospheric CO_2 from discrete air samples collected at the University campus, Parma, Italy, was measured at time intervals of about five days over a period of 18 months. Some day and night samples were measured along with three daily time series to evaluate the daily variations of $\delta^{13}C$ values and CO_2 concentrations. The following patterns were revealed: (1) the least negative $\delta^{13}C$ values show a seasonal evolution with slightly more negative values during winter and less negative values during summer. Home heating systems probably contribute to this behaviour; (2) four samples collected in downtown Parma show more negative values than those collected at the same time at the University campus, probably because of car engine pollution; (3) occasionally, quite negative $\delta^{13}C$ values were obtained at the campus. The expansion of polluted air masses from downtown to the suburban area may be responsible for these negative events; (4) one sample showed a $\delta^{13}C$ of –17.67‰. The nearby fields had been extensively manured and the contribution from organic matter fermentation may explain the exceptionally negative result; (5) the diurnal changes in $\delta^{13}C$ are relatively low from January to May; (6) in July and September the major daily changes take place in the late evening and in the early morning and are very fast. During the night the CO_2 concentration increases by no more than some 50–60%, this behaviour differing from observations by other authors in different areas; (7) the set of daily samples collected in August shows a different behaviour, clearly related to the heavy rain that lasted for several hours during the night.

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INTRODUCTION

Thanks to the pioneer investigations on atmospheric CO_2 carried out in the late fifties and early sixties by Keeling (1958, 1961) we know the concentration and $\delta^{13}C$ of atmospheric CO_2 at that time so we can now evaluate the growth rate of the former variable through time and the decrease rate of the latter variable. Uptake and release of CO_2 by terrestrial vegetation and soil, anthropogenic production of CO_2, essentially by combustion of fossil fuel, and air-sea fluxes control both variables. However, the variations in atmospheric CO_2 concentrations and in its $\delta^{13}C$ are not uniformly distributed in space and time (Keeling, 1958, 1961; Ciais *et al.*, 1995; Denning *et al.*, 1995; Keeling *et al.*, 1995, 1996; Flanagan and Ehleringer, 1998; Szaran, 1998, *etc.*). The contribution by plants is related essentially to their photosynthetic pathway (C_3, C_4 and CAM) and their stomatal conductance (Craig, 1954; Park and Epstein,

1960): C_3 plants have a carbon isotope composition ranging between about –20 and –35‰ *vs*. PDB-1 while C_4 plants have $\delta^{13}C$ values between about –9 and –16‰: CAM plants may show $\delta^{13}C$ values within the whole range of C_3 and C_4 plants. However, at the latitude of Parma, C_3 plants comprise the great majority of all plants. Plant photosynthesis dominates during daylight hours, determining a preferential assimilation of $^{12}CO_2$ molecules from the atmosphere while at night respiration dominates, the $\delta^{13}C$ of respired CO_2 being equal to the mean isotopic value of the plant tissue. Accordingly, higher CO_2 concentrations and lower isotope values should be observed at night, particularly when favoured by low night-time temperatures that substantially reduce the vertical mixing of the atmosphere. Keeling (1958, 1961) found that the variation in relative abundance of the carbon stable isotopes is proportional to the reciprocal of the CO_2 concentration. A simple, two-component mixing model is generally used, according to this relationship, when studying the local balance of CO_2. We assume that the

ambient CO_2 (CO_{2amb}) near the ground level is the sum of two components with distinct concentrations and carbon isotope values: background CO_2 (C_{bg} and $\delta^{13}C_{bg}$) and CO_2 from surface emissions (C_{surf} and $\delta^{13}C_{surf}$), surface emissions including soil emissions, plant biological activity, anthropogenic contributions, *etc*. It follows that:

$$C_{am} = C_{bg} + C_{surf}$$

and:

$$C_{amb}\delta^{13}C_{amb} = C_{bg}\delta^{13}C_{bg} + C_{surf}\delta^{13}C_{surf}$$

the following relationship can be derived from the isotope mass balance:

$$\delta^{13}C_{amb} = C_{bg}(\delta^{13}C_{bg} - \delta^{13}C_{surf})\, 1/C_{amb} + \delta^{13}C_{surf}$$

The intercept of the least squares fit line calculated for the $\delta^{13}C$ and $1/C$ values of each single measurement represents the carbon isotope composition of the mean local surface emissions. Obviously, the anthropogenic contribution to atmospheric CO_2 concentration and isotopic composition is mainly related to industrial pollution, discharge from car engines and domestic heating, particularly during the cold season. The burning of fossil fuel, whose $\delta^{13}C$ values are always very negative, is then the main cause of the increase in atmospheric pollution. However, studying short term variations in these two variables, it is rather difficult to separate the anthropogenic contribution from the natural contribution of plant respiration. In fact, in the case of C_3 plants, that constitute about 90% of all terrestrial plants today, the

very negative $\delta^{13}C$ of the respired CO_2 can hardly be distinguished from the CO_2 produced by the combustion of fossil fuel that on average, and despite minor variations, is at about –27/–28‰ ±2‰. To overcome this problem, Zimnoch *et al*. (2004) proposed a different approach, taking into consideration both the $\delta^{13}C$ and the $\delta^{18}O$ of CO_2 and considering a three-component model: background CO_2, local contribution from the biosphere, and the local anthropogenic component. The isotope mass balance equations can be solved "for selected time intervals provided that the isotopic composition of individual components is constant during the selected time interval and the corresponding values are known or can be assessed". However, the suggested model cannot be applied during air mass changes and this is a strong limitation of this procedure.

The carbon isotope composition of atmospheric CO_2, the importance of plant activity, and its contribution to the daily variations have been discussed in several papers, from the very first paper by Craig (1954), the fundamental paper by Park and Epstein (1960), the contributions by Keeling (1958, 1961) and the most recent papers on this subject (Inoue and Sogimura, 1984; Keeling *et al*., 1995, 1996; Szaran, 1998; Szaran *et al*., 2002, 2004; Demény and Haszpra, 2002; Zimnoch *et al*., 2004). A detailed knowledge of the CO_2 distribution in space and time, and of the variability of its carbon isotope composition, is of primary importance to evaluating the environmental damage resulting from the anthropogenic contribution and its variability through time, and in developing reliable global carbon budget models. The results reported up to now show that different areas are characterized by different behaviours, so that the need for knowledge of local/regional environmental conditions increases as we plan to integrate these local contributions and to model the evolution of environmental conditions over extended areas.
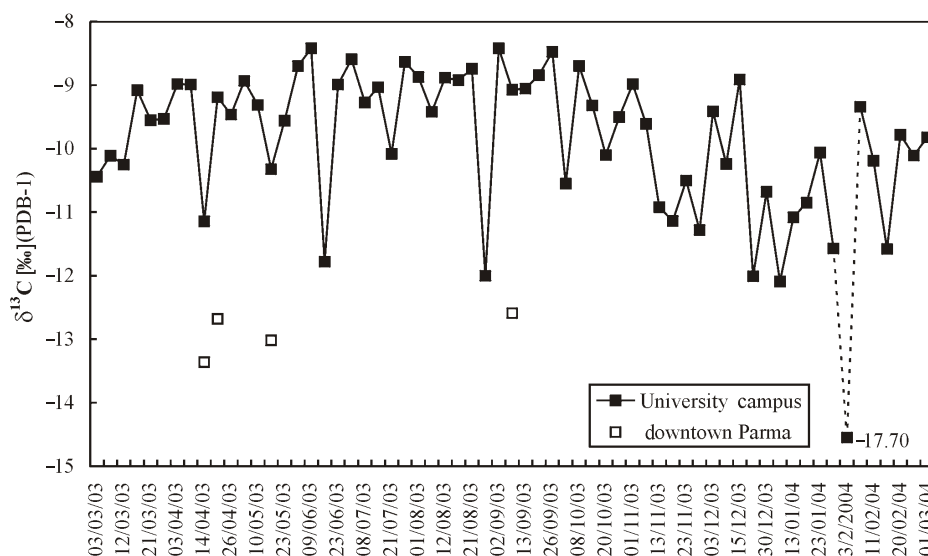

Fig. 1. Carbon isotopic composition of CO_2 from discrete air samples collected periodically between March 2003 and March 2004 at the University campus, Parma, Italy

Four samples were collected in downtown Parma for a comparison with the samples collected simultaneously in a suburban area (University campus); the $\delta_{13}C$ values are reported versus PDB-1 since our working standard is calibrated periodically versus NBS-19 and NBS-20 which, in turn, have been calibrated directly versus the original PDB-1 carbonate

SAMPLING SITE AND ANALYTICAL TECHNIQUES

This study was carried out at Parma, Italy, a town with about 180 000 inhabitants, located at 44°47'59" N, 10°20'24" E, at an elevation of 55 m.a.s.l. on the Po River plain; the mean annual temperature is 13±1°C; the lowest monthly mean value (January) is +1°C and the highest (July) is +25°C. Mean annual precipitation is about 800 mm and its mean $\delta^{18}O$ value (2001–2004) is –8.01‰ (V-SMOW). The town is supposed to represent a moderately polluted area. Discrete air samples were collected from March 2003 to August 2004 with a mean frequency of one sample every five days. Almost all the samples were collected in the late morning between 11 and 12. Some samples were also collected at about midnight while sets of samples to detect daily variations in detail were collected with a frequency of one sample every two or three hours. Samples were collected in 4-litre Pyrex flasks, carefully evacuated to about 10^{-3} mm Hg and always opened at the same place within the University campus, at the border of a fairly large meadow, at about 1.5 m above the soil surface. The University campus is located in a suburban area in the southern section of the town. CO_2 samples were separated by slowly pumping the flask air through a vacuum line and freezing the water vapour and the CO_2 in a liquid nitrogen-cooled spiral trap. The air flow through the trap was about 8 ml/minute, a Swagelock microvalve regulating the air flow. After pumping down the flask to about 10^{-3} mm Hg, the spiral trap was isolated by means of high vacuum stopcocks and heated to about –80°C by means of an ethyl alcohol-liquid nitrogen slash. The CO_2 was then collected in a sample tube and measured in a *Finnigan Delta S* mass spectrometer. The standard used was CO_2 from very pure Carrara marble with an isotopic composition, measured repeatedly and periodically against NBS-19 and NBS-20, equal to +2.45‰ ($\delta^{13}C$) and –2.45‰ ($\delta^{18}O$); for these calibrations the NBS standards were taken equal to +1.95‰ ($\delta^{13}C$) and –2.20‰ ($\delta^{18}O$) for NBS-19 and –1.06 ($\delta^{13}C$) and –4.14‰ ($\delta^{18}O$) for NBS-20. As in the case of all our measurements of atmospheric CO_2 their standard deviation is frequently evaluated using several air samples collected simultaneously in the same place and at the same time and treated in the same way for the extraction and measurement of atmospheric CO_2. The standard deviation of these measurements is 0.03±0.01‰ (1σ). In this case, due to the relatively small contribution of N_2O to the isotopic measurements (in general between 0.1 and 0.2‰) and the fact that extremely accurate measurements are not necessary for the purpose of this study, the correction for the N_2O contribution was not carried out. In the case of sets of daily samples, for which the evaluation of the variations through time of the CO_2 concentrations is important, and because of the lack of an analyser for a direct and accurate measurement, these values were calculated on the basis of the intensity in the mass spectrometer of the $^{12}C^{16}O_2^+$ ion beam of each sample and known amount of CO_2 prepared for calibration. The calibration was carried out by means of repeated measurements of synthetic air samples whose CO_2 concentration was determined by comparison with primary standards currently used at the Monte Cimone Observatory (Modena, Italy) working on this subject from 1979 and connected to the global network. The CO_2 concentrations were 345 ppmv, 375 ppmv and 393 ppmv; the reproducibility of our measurements was between 0.3 and 0.4%. With the existing mean natural CO_2 concentrations this means that the most probable error is close to about ±1/1.5 ppmv and does not affect the entity of the gradients evaluated between different samples in daily sequences. This method can be considered reasonably accurate also because the air volume collected is always the same (4000 ml), and the extraction technique of CO_2 is the same for all the samples.

RESULTS OBTAINED

The results obtained from the first year of sampling (March 2003 to March 2004) are shown graphically in Figure 1. The long-term variations of $\delta^{13}C$ values show a well-defined seasonal trend, the summer values being, on average, definitely less negative than the winter values. In fact, while the least negative winter values range from about –9.0‰ to about –10.5‰ (Fig. 1), the least negative summer values are close to –8.5‰. Surprisingly enough, these values are very close to those exhibited by the background air samples collected in the Central Indian Ocean at the end of 2003 (–8.3‰; Longinelli *et al.*, Tellus B, in press) in an area very far from continental pollutants, suggesting a basically clean state of the atmosphere at the University campus area during the warm semester. However, the overall trend of these results is periodically interrupted by some samples that show considerably more negative values. $\delta^{13}C$ values as low as –12‰ were found also during spring and summer, showing that variable conditions very often modify the $\delta^{13}C$ values. The first hypothesis taken into consideration to explain these negative events relates to meteorological conditions and, particularly, to wind speed and direction that may have carried air masses from highly polluted areas over Parma. However, these negative results were obtained under quite different conditions (wind blowing from the NW, NE and E with variable speeds from 1–2 up to 12–13 km/h). Four samples collected at the same time at the University campus and in downtown Parma (April, May and September 2003) show considerably lighter $\delta^{13}C$ values in the latter samples (Fig. 1). This effect can be reasonably related to a large contribution of exhaust gases from car engines that are obviously heavier downtown, the University campus being located in a suburban area, at some distance from the main polluting area. Movements of air masses from the city to the campus area could perhaps explain the negative events measured occasionally at the University campus.

The $\delta^{13}C$ of the sample collected on February the 3rd 2004 is –17.67‰ and the CO_2 concentration is considerably higher that usual. During the previous day the nearby fields had been extensively manured and probably the contribution of CO_2 from fermentation and oxidation processes of the organic matter can explain the anomalous $\delta^{13}C$ obtained, favoured by relatively low air temperatures (max. 8.8°C, min. –0.7°C), humidity from 77 to 98%, an average wind speed of 1.7 km/h, and reduced vertical mixing.

The results obtained from the second period of sampling (March to August 2004) are reported graphically in Figure 2.

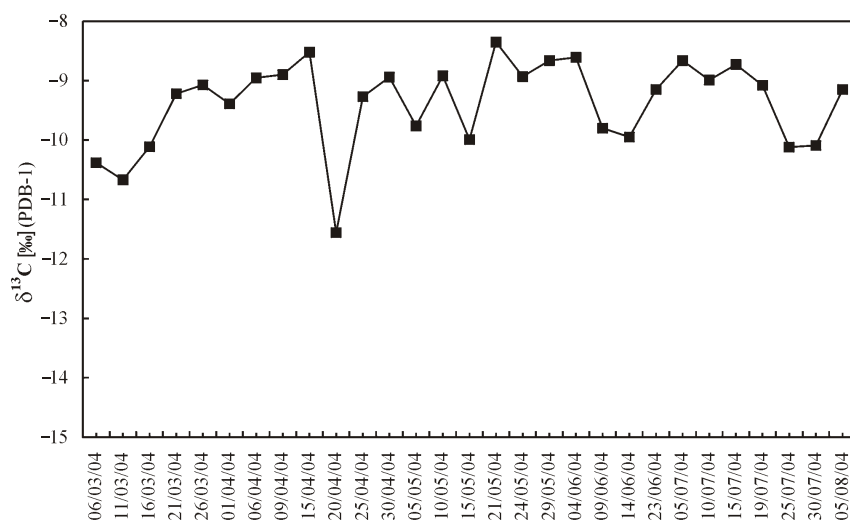**Fig. 2. Carbon isotopic composition of CO$_2$ from discrete air samples collected periodically between March 2004 and August 2004 at the University campus, Parma, Italy**

They show a trend in fairly good agreement with that of the first year of measurements. The least negative summer values are not far from those measured in the previous year and negative events were observed also in this period, even though only one of them is substantially negative (–11.56‰).

   The carbon isotope data obtained from day-time and night-time samples collected between January and May 2004

are shown in Table 1. The Δδ values (Δδ is equal to night-time δ^{13}C–day-time δ^{13}C) between January and May are relatively small, ranging from –0.33 to –3.22, considerably smaller than those reported in previous studies (Inoue and Sugimura, 1984; Szaran, 1998; Szaran *et al.*, 2002, 2004; Demény and Haszpra, 2002). Szaran (1998) reported a daily variation during May 1990 of –10.7‰; such a large gradient had never been reported previously. This may be due to very particular local conditions (temperature range from 24 to 0.6°C): the marked inversion of air temperature may have caused stagnant conditions, absence of vertical and/or horizontal mixing, and accumulation near the soil surface of the CO$_2$ from plant respiration. In the case of our May samples the largest temperature gradient was lower than 10°C and there was always some wind, albeit very slow. However, Szaran (1998) found an isotopic gradient of –8.2‰ between day and night also in June 1990 when the temperature gradient was 16°C. In June 1991 the isotopic gradient was about the same (–8.4‰) but the temperature gradient was only 11°C. In October 1990 and February 1992 the same author found very small isotopic gradients (1–2‰); our results from January to May are in fairly good agreement with the latter results. Szaran *et al.* (2002) again found large isotopic gradients between day and night in 1998. At the beginning of June a Δδ^{13}C of about 11‰ was found in a meadow area while a hill area and a forest showed lower gradients (about –9 and –7‰ respectively). The authors attributed the observed effect to the higher biomass concentration in the meadow environment. The difference between the biomass of a meadow and of a forest environment seems to be debatable, the latter environment producing normally important amounts of biomass. However, a few years later Demény and Haszpra (2002) at the K-puszta station in Hungary found considerably lower gradients, systematically lower than 3‰, in a large clearing in a forest. Szaran *et al.* (2004) again found very large isotopic gradients (about –12‰) at a meadow site. One should conclude that, apart from differences

T a b l e 1

Environmental data and measured values for CO$_2$ from discrete day-time and night-time air samples collected between January and May 2004 at the University campus, Parma, Italy

Sample no.	Date	Hour	Temperature [°C]	Wind direct.	Wind speed [km/h]	δ^{13}C [‰] (PDB-1)	Δδ night-day
58	January 26	23.30	–1	no wind	–	–12.02	–0.65
59	January 27	12.30	2	NW	8	–11.37	
62	February 6	11.30	13	E	4	–9.14	–1.64
63	February 6	23.30	2	E	4	–10.78	
82	May 10	12.00	19	E–NE	6	–8.72	–0.69
83	May 10	23.30	14.5	W-SW	8	–9.41	
84	May 15	11.30	18	E–SE	16	–9.79	–2.98
85	May 15	23.30	14	SW	8	–12.77	
86	May 21	11.30	27	E–SE	4	–8.15	–0.55
87	May 21	23.30	17.5	W–NW	16	–8.70	
88	May 24	11.30	20	E–SE	8	–8.73	–0.28
89	May 24	23.30	13	SE	8	–9.01	
90	May 29	11.30	20	SE	8	–8.46	–2.17
91	May 29	23.30	16	S	3	–10.63	
92	June 4	11.15	26	W–NW	2	–8.41	–2.42
93	June 4	23.15	20	E	3	–10.83	
95	June 14	11.30	18	NW	2	–9.95	–3.22
96	June 14	23.30	15.5	no wind	–	–13.17	
97	June 23	12.00	25.5	E	3	–9.15	–0.33
98	June 23	24.00	19.5	W	4	–9.48	

T a b l e 2

Environmental data, measured and calculated values for CO_2 from a set of discrete air samples collected between July 19 and 20, 2004, at the University campus, Parma, Italy

Sample no.	Date	Hour	Tempera-ture [°C]	Wind direct.	Wind speed [km/h]	$\delta^{13}C$ [‰] (PDB-1)	CO_2conc. [ppmv]	10^3 [l/CO_2conc.]
103	19/07/04	13.00	26	NW	8	−9.08	375	2.66
104	19/07/04	16.00	26	N–NE	6	−9.05	384	2.60
105	19/07/04	19.00	27	NW	2	−9.57	375	2.66
106	19/07/04	22.00	24	W–NW	2	−13.55	523	1.91
107	20/07/04	1.00	22	SW	7	−13.03	461	2.16
108	20/07/04	4.00	21	no wind	–	−13.00	485	2.06
109	20/07/04	7.00	20	SW	1	−10.30	418	2.39
110	20/07/04	10.00	28.5	NW	7	−9.17	378	2.63
111	20/07/04	13.00	31	E–SE	2	−9.19	386	2.59

T a b l e 3

Environmental data, measured and calculated values for CO_2 from a set of discrete air samples collected between August 5 and 6, 2004, at the University campus, Parma, Italy

Sample no.	Date	Hour	Tempera-ture [°C]	Wind direct.	Wind speed [km/h]	$\delta^{13}C$ [‰] (PDB-1)	CO_2conc. [ppmv]	10^3 [l/CO_2conc.]
114	05/08/04	14.00	28.5	E	2	−9.15	365	2.74
115	05/08/04	17.00	29	W	2	−9.15	361	2.77
116	05/08/04	20.00	26	E	1	−9.55	393	2.54
117	05/08/04	22.00	19	W–NW	8	−9.88	448	2.23
118	05/08/04	24.00	19.5	W	2	−9.74	385	2.59
119	06/08/04	2.00	19.5	W	6	−9.56	391	2.55
120	06/08/04	4.00	20	W–SW	11	−9.68	373	2.68
121	06/08/04	6.00	19.5	W	8	−10.23	360	2.78
122	06/08/04	9.00	23	NW	3	−9.13	410	2.44
123	06/08/04	12.00	28	NW	8	−8.88	375	2.66

T a b l e 4

Environmental data, measured and calculated values for CO_2 from a set of discrete air samples collected between September 1 and 2, 2004, at the University campus, Parma, Italy

Sample no.	Date	Hour	Tempera-ture [°C]	Wind direct.	Wind speed [km/h]	$\delta^{13}C$ [‰] (PDB-1)	CO_2conc. [ppmv]	10^3 [l/CO_2conc.]
124	01/09/04	11.00	21	E–SE	12	−8.86	392	2.55
125	01/09/04	14.00	25	SE	10	−8.95	341	2.93
126	01/09/04	17.00	26	SE	6	−8.65	381	2.62
127	01/09/04	19.00	24	E–NE	2.5	−9.11	397	2.52
128	01/09/04	21.00	20	no wind	–	−12.97	517	1.93
129	01/09/04	23.00	19	E	2	−12.24	485	2.06
130	02/09/04	1.00	17	E	1	−12.61	422	2.37
131	02/09/04	3.00	16	no wind	–	−12.19	497	2.01
132	02/09/04	5.00	15	S	2	−13.33	460	2.17
133	02/09/04	7.00	14	no wind	–	−13.73	560	1.78
134	02/09/04	9.00	20	W–NW	4	−10.18	355	2.81
135	02/09/04	12.00	26	E	6	−8.73	350	2.85

determined by local temperature and/or other environmental conditions, meadow environments are responsible for the largest day-night isotopic gradients; this means that in this environment the amount of respired CO_2 is the largest for each emitting surface unit. This does not seem to be the case with our collection site even though, in this case, we are not able to compare the amount of biomass and the emitting surface at our site with the same variable at the sites studied by other authors. Differences between local environmental conditions are probably responsible for the large isotopic differences observed at different sites and periods.

Interesting results were obtained from the three sets of samples collected in July 19–20, in August 5–6 and in September 1–2, 2004 for a detailed picture of the diurnal variations (the reported hours refer to daylight saving time). The samples collected, the environmental conditions and the results obtained from the three sets of samples are shown in Tables 2, 3 and 4: the $\delta^{13}C$ values are also shown graphically in Figure 3. In the case of July daily samples (Table 2, Fig. 3A) the $\delta^{13}C$ and CO_2 concentrations of the samples collected during the day (clear sky and low wind speed) are very similar to one another: in the late evening a rapid evolution of these variables takes place, decreasing the $\delta^{13}C$ values by about four per mil while the CO_2 concentration increases by about 35%. These values undergo only minor changes through the night and begin to evolve towards daylight values only in the early morning. This behaviour is rather different from those reported by previous authors. In the case of Inoue and Sugimura (1984) the daily variations measured in June and September showed a V-shaped trend with the maximum concentration of CO_2 and the most negative isotope value at about five a.m. These measurements were carried out long ago (1982): the background CO_2 concentration was considerably lower than today (about 333 ml.l^{-1}) as well as the day/night gradient (about 67 ml.l^{-1} in June and about 40 ml.l^{-1} in September).

In the case of Szaran (1998) a V-shaped trend was apparent in May, June and October 1990 and in June 1991, while very low variations of both CO_2 concentration and $\delta^{13}C$ were observed in April 1991 and in February 1992, when both variables remained almost constant throughout the 24 hours. The trend of our July daily values is very different from that trend as well as the range of values (both CO_2 concentrations and $\delta^{13}C$) which is considerably smaller.

In the case of Szaran *et al*. (2002) a V-shaped trend was again apparent in June 1998 while an almost flat trend was obtained in August of the same year. The study carried out by Demény and Haszpra (2002) at K-puszta (Hungary) showed a rather flat trend with almost negligible daily variations of the CO_2 concentration during autumn-winter 1999 and 2000 and variations lower than 30% between noon and early morning during spring-summer with isotopic variations systematically lower than about 3‰. Zimnoch *et al*. (2004), measuring the isotopic composition of atmospheric CO_2 in the urban area of Kraków (Poland) in March, July and December 1992 obtained daily $\delta^{13}C$ variations equal to or lower than 4‰. The range of our isotope daily results is quite close to this value. However, strangely enough, the range of values measured in December at Kraków was extremely low (less than 2‰) and the mean $\delta^{13}C$ value was around –9.5‰. This is surprising, bearing in mind

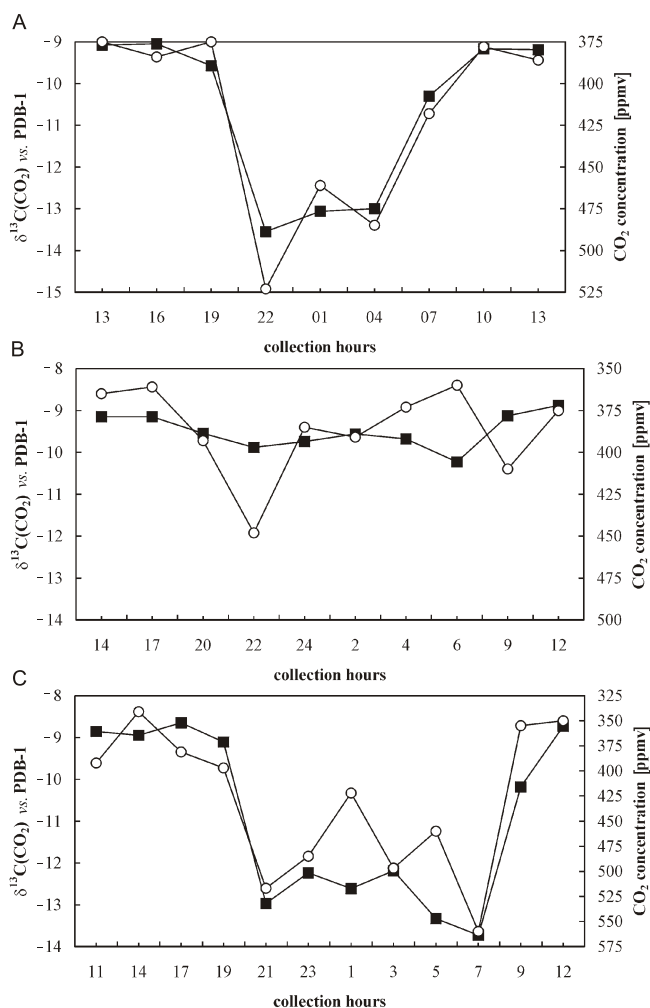**Fig. 3. Diurnal changes in the isotopic composition $\delta^{13}C$ and concentration of atmospheric CO_2 from discrete air samples collected at the University campus, Parma, Italy**

A — the air samples were collected on July 19–20, 2004, at the border of a meadow, about 1.5 m above the soil surface, under clear sky and calm conditions; **B** — the air samples were collected on August 5–6, 2004, at the border of a meadow, about 1.5 m above the soil surface, under overcast conditions during the day and heavy rain almost all night through; **C** — the air samples were collected on September 1–2, 2004, at the same location of A and B, under clear sky and low wind speed conditions; the CO_2 concentrations are shown on a reversed Y axis to draw attention to the relationship between the two variables; black squares — $\delta^{13}C$, open circles — atmospheric CO_2

that during winter only the home heating, essentially the burning of coal (measurements refer to 12 years ago), should have heavily contributed to atmospheric pollution, while the mean $\delta^{13}C$ value is not far from those measured in July when the contribution of home heating in that area should be null. At the 2004 ESIR workshop Szaran *et al*. (2004) presented further results on this subject, obtained in June 2003 from an area relatively close to the city of Lublin (Poland): in this case both the variables exhibited an almost sinusoidal trend, quite different from the trend observed in Parma, as well as from the (V-shaped) trends observed previously by the same author. The range of the values measured at Parma is also very far from those reported by Szaran *et al*. (2004), whose $\delta^{13}C$ values range

from about –8 to about –20‰, while the CO_2 concentrations change by about 300%. A mixing line between atmospheric CO_2 and biogenic CO_2 was suggested in the case of Lublin samples but this is fairly obvious since the night-time contribution of CO_2 from plant respiration is apparent according to the ^{12}C enrichment of the isotopic values and the increase in CO_2 concentrations. However, it is difficult to understand the marked differences observed also because the enormous increase of the night-time CO_2 concentration in the Lublin samples is difficult to reconcile with a normal respiratory activity of soil plants. As far as we know, these huge changes in CO_2 concentration have never been reported in previous studies.

Table 3 and Figure 3B show the results obtained from the second set of daily samples collected in August 2004. During the afternoon of August 5 the sky was overcast and rain was forecast during the night. The set of air samples was collected with the main purpose of checking the effect of rain on the concentration of atmospheric CO_2 and its carbon isotope values. The results obtained clearly show the cleaning effect of rain that decreases the addition of biogenic CO_2, thus limiting the evolution of the $\delta^{13}C$ towards lighter values. These are, as far as we know, the only results obtained from a set of daily samples collected under rainy conditions: the effect of rain on the variables studied is in good agreement with the results foreseen.

Table 4 reports the values obtained from the third set of daily samples (September 1 and 2, 2004) along with the environmental parameters. The $\delta^{13}C$ and CO_2 concentrations are also shown graphically in Figure 3C. The trends of the two variables are similar to those observed for the July set of samples and also the absolute values are not far from those of the first set. The main difference between these two sets refers to the evolution of the CO_2 concentrations during the night. In Figure 3C the night-time variations of this variable are considerably larger. This particular behaviour may hardly be referred to the wind that, during the night, was absent or extremely weak, or to the daily temperature gradient that was considerably larger than that of July.

Figure 4 shows the plot of the carbon isotope composition of the three sets of daily samples *versus* the inverse of CO_2 concentrations: this plot reveals the compositions of the mixing end-members. It must be pointed out that the sets of July and September samples were collected under fine weather conditions (sunny days and clear nights) while the August set of samples was collected under rainy weather conditions, with over six hours of rain from about 8.30 in the evening to about 5 a.m. with a dry interval of a couple of hours at about 10 p.m. The lines that can be calculated for the three sets of samples are quite different from one another and clearly show the "cleaning"effect of the rain, likely related to the solubility of CO_2 in water. The isotopic values that can be calculated for the end-member compositions are given by the intercepts of the regression lines and clearly show that, in the case of the July and September sets of values, the end-member composition may be referred to the $\delta^{13}C$ of CO_2 from the respiration of C_3 plants. This is not the case with the set of August samples whose end-member carbon isotope composition is only slightly more negative than the background CO_2, probably due to minor additions of respiratory CO_2, large amounts of which have been dissolved into rain water.
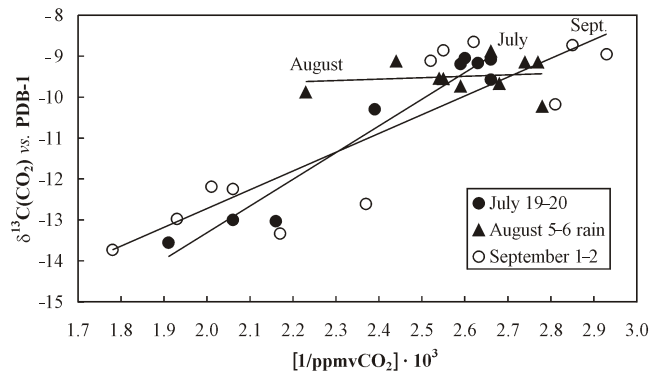

Fig. 4. Carbon isotope composition of the diurnal sets of samples *versus* the inverse of CO_2 concentration

The equations of the regression lines are the following: July: $y = 6.52x - 26.35$, August: $y = 0.34x - 10.39$, September: $y = 4.58x - 21.8$ the intercepts on the Y axis are the end-member carbon isotope compositions (surface CO_2 added to the background CO_2); these values clearly reflect the differences between the environmental conditions under which the three sets of samples have been collected

CONCLUSIONS

The results obtained and the comparison with the data reported in previous papers allow the following conclusions:

1. A marked seasonal effect can be observed on the $\delta^{13}C$ of atmospheric CO_2 samples collected in a suburban area at Parma, Italy; this effect can be related to general meteorological conditions but an apparent seasonal effect of home heating systems is very probable.

2. A few very negative $\delta^{13}C$ values have been measured, independent of seasons and environmental conditions. The origin of these events is not fully understood even though slow movements of air masses from downtown Parma to the suburban area may be responsible for these negative values.

3. As expected, a marked isotope gradient can be observed between the more polluted downtown area and the suburban area.

4. Extensive episodic manuring of the fields may contribute large amounts of isotopically light CO_2 of biogenic origin.

5. Diurnal changes of $\delta^{13}C$ and CO_2 concentration are rather small from January to May, and definitely increase during summer, at least under fine weather conditions: however, even during summer, both variables, when compared to the values measured by previous authors in other countries, show considerably low values.

6. Very rapid changes were observed (July and September) for the day-night-day variations, the values remaining fairly homogeneous during daylight and somehow less homogeneous during the night. Also in this case the observed trends are rather different from those reported by previous authors for other countries. This difference cannot be easily explained.

7. There is a marked effect of rain water on the normal processes of diffusion of respiratory CO_2 from plants taking place at night: the expected increase of CO_2 concentration is drastically reduced by the withdrawal of CO_2 from the atmosphere related to the solubility of CO_2 in water.

8. The plot of $\delta^{13}C$ values versus the inverse of CO_2 concentrations clearly suggests that the atmospheric CO_2 at night is a mixture of two end-members whose $\delta^{13}C$ values (under fine weather conditions) are close to –8.3‰ (background CO_2) and range from about –22 to about –26‰ (mainly plant respiratory CO_2).

REFERENCES

CIAIS P., TANS P. P., TROLIER M., WHITE J. W. C. and FRANCEY R. J. (1995) — A large northern hemisphere terrestrial CO_2 sink indicated by the $^{13}C/^{12}C$ ratio of atmospheric CO_2. Science, **269**: 1098–1102.

CRAIG H. (1954) — Carbon-13 in plants and the relationship between carbon-13 and carbon-14 variations in nature. J. Geol., **62**: 115–149.

DEMÉNY A. and HASZPRA L. (2002) — Stable isotope composition of CO_2 in background air and at polluted sites in Hungary. Rapid Comm. Mass Spectrom., **16**: 797–804.

DENNING A. S., FUNG I. Y. and RANDALL D. (1995) — Latitudinal gradient of atmospheric CO_2 due to seasonal exchange with land biota. Nature, **376**: 240–243.

FLANAGAN L. B. and EHLERINGER A. R. (1998) — Ecosystem-atmosphere CO_2 exchange: interpreting signals of change using stable isotope ratios. Trends Ecol. Evol., **13**: 10–14.

INOUE H. and SUGIMURA Y. (1984) — Diurnal change in $\delta^{13}C$ of atmospheric CO_2 at Tsukuba, Japan. Geochem. J., **18**: 315–320.

KEELING C. D. (1958) — The concentration and isotopic abundances of carbon dioxide in rural areas. Geochim. Cosmochim. Acta, **13**: 322–334.

KEELING C. D. (1961) — The concentration and isotopic abundances of carbon dioxide in rural and marine air. Geochim. Cosmochim. Acta, **24**: 277–298.

KEELING C. D., CHIN E. L. S. and WHORF T. P. (1996) — Increased activity of northern vegetation inferred from atmospheric CO_2 measurements. Nature, **382**: 666–670.

KEELING C. D., WHORF T. P., WAHLEN M. and VAN DER PLICHT J. (1995) — Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. Nature, **375**: 666–670.

PARK R. and EPSTEIN S. (1960) — Carbon isotope fractionation during photosynthesis. Geochim. Cosmochim. Acta, **21**: 110–126.

SZARAN J. (1998) — Seasonal variations of $\delta^{13}C$ values and CO_2 concentration in the air during vegetation growth. Isot. Environ. Health Stud., **34**: 341–348.

SZARAN J., DUDZIAK A., TREMBACZOWSKI A., NIEZGODA H. and HALAS S. (2004) — Diurnal variations of $\delta^{13}C$ and concentrations of atmospheric and soil carbon dioxide in a meadow site. ESIR VII Abstracts: 137–140.

SZARAN J., NIEZGODA H. and TREMBACZOWSKI A. (2002) — Respiration and assimilation processes reflected in the carbon isotopic composition of atmospheric carbon dioxide. Nukleonika, **47** (1): S59–S61.

ZIMNOCH M., FLORKOWSKI T., NECKI J. and NEUBERT R. E. M. (2004) — Diurnal variability of $\delta^{13}C$ and $\delta^{18}O$ of atmospheric CO_2 in the urban atmosphere of Kraków, Poland. Isot. Environ. Health Stud., **40** (2): 129–143.