

CHANGES OF CARBON ISOTOPES IN ATMOSPHERIC CO₂ OF THE KRAKOW REGION IN THE LAST FIVE YEARS

TADEUSZ KUC

Institute of Physics and Nuclear Techniques, The Academy of Mining and Metallurgy, Al Mickiewicza 30, 30-059 Kraków, Poland

ABSTRACT. The Krakow Radiocarbon Laboratory has been measuring isotope composition of atmospheric CO₂ and its natural concentration in the Kraków region for the last five years. We have been sampling on a continuous basis in two-week intervals at ca 20m above ground level, close to the center of Kraków. CO₂ was sorbed while slow pumping atmospheric air through a molecular sieve. After recovery by heating, the CO₂ was converted to benzene and ¹⁴C measured in a liquid scintillation spectrometer. In a small portion of CO₂ ^δ¹³C was determined in a mass spectrometer. Concentration of CO₂ was assessed by measurement of the volumes of the sorbed CO₂ and the pumped air. A five-year record (1983-1987) reveals a multi-annual linear trend and winter-summer oscillations. Calculated parameters of the regression line (intercept and slope) for the measured ^δ¹⁴C, ^δ¹³C and concentration are: 222‰ (Jan 1983) and -15.5‰/yr, -9.57‰ (Jan 1983) and -0.042‰/yr, 336ppm (Jan 1983) and 1.4ppm/yr, respectively.

INTRODUCTION

Anthropogenic changes in natural composition of tropospheric air, especially in concentration of CO₂, are distinct and have been measured at various localities (Bacastow & Keeling, 1981; Bischof, 1981; Perman & Breadmore, 1984; Elliot, Machta & Keeling, 1985; Wong *et al*, 1984) thus providing useful data for modeling carbon circulation. Differences in carbon isotope composition between "dead" CO₂ and that present in "clean air" enables identification of the source and assessment of its input (Freyer, 1979; Mook *et al*, 1983; Keeling, Carter & Mook, 1984).

Isotopic composition of atmospheric CO₂ has been continuously measured in Kraków for five years, supplemented by determination of its concentration. Preliminary results of the first two-year record were discussed and published earlier (Kuc, 1986). The following paper is a continuation of these investigations, and the results comprised in Table 1 cover the period 1985-1987.

SAMPLING AND MEASUREMENT

The sampling point was located in Kraków (53°3'N, 19°54'E), not far from the city and close to recreation grounds. We continuously sampled atmospheric CO₂ by sorption in a molecular sieve in two-week intervals at ca 20m above ground level. After thermal recovery of the sorbed CO₂, its atmospheric concentration (C), radiocarbon activity (^δ¹⁴C), and stable carbon isotope ratio (^δ¹³C), were determined by volume measurement, liquid scintillation counting and mass-spectrometric measurement, respectively (Florkowski *et al*, 1975; Kuc, 1986). We assessed CO₂ concentration as a volume ratio of the sorbed CO₂ and the pumped air with an estimated error of <5%. We measured stable isotope composition in a mass spectrometer Micromass 602 C and ¹³C/¹²C ratio was expressed *vs* the PDB standard using ^δ¹³C notation with an error of a single measurement <0.1‰.

Presence of N₂O in the measured CO₂ was not investigated. It is very likely that N₂O decomposes while heating the molecular sieve (thermal decomposition on catalytic compounds) and/or is trapped with water vapor. $\delta^{13}\text{C}$ results were not corrected for N₂O. We determined ¹⁴C activity in a liquid scintillation spectrometer TRI-CARB model 3320, Packard Instrument International SA, after converting the CO₂ to benzene and mixing with scintillation cocktail PPO/POPOP. Results are reported as $\delta^{14}\text{C}$ according to Stuiver and Polach (1977) with 1 σ error of ca 10‰. Results for 1985–1987 (Table 1) represent a mean value for two-week sampling periods.

TABLE 1
Samples of atmospheric CO₂

Sample (Lab no.)	Colln date (Year, month, day)	$\delta^{14}\text{C}$ ‰	$\delta^{13}\text{C}$ ‰	C ppm	Week of sampling
POW-55	12/31-01/15	101	-10.88	365	106
-56	1985 01/22-02/04	181	- 9.86	333	109
-57	02/05-02/18	144	- 9.91	352	111
-58	02/18-03/04	-	-10.00	347	113
-59	03/05-03/18	146	-10.39	372	115
-60	03/18-04/01	170	- 9.86	341	117
-61	04/01-04/15	206	- 9.30	335	119
-62	04/15-04/29	227	- 9.68	322	121
-63	04/29-05/13	171	- 9.51	349	123
-64	05/14-05/31	185	- 9.39	308	125
-65	05/31-06/14	180	- 8.88	328	127
-66	06/14-06/28	179	- 9.12	325	129
-67	07/02-07/16	172	- 9.15	327	132
-68	07/16-07/29	193	- 9.38	334	134
-69	07/29-08/12	187	- 8.88	322	136
-70	08/12-08/26	175	-10.39	347	138
-71	08/26-09/09	143	- 8.92	330	140
-72	09/09-09/23	137	- 9.73	353	142
-73	09/23-10/07	144	-10.09	358	144
-74	10/07-10/21	119	- 9.18	346	146
-75	10/21-11/04	108	- 9.88	354	148
-76	11/04-11/18	146	- 9.75	344	150
-77	11/18-12/02	165	-10.27	324	152
-78	12/02-12/16	120	- 9.78	335	154
-79	12/16-12/30	189	-10.02	324	156
-80	12/30-01/13	140	-10.27	461	158
-81	1986 01/13-01/27	229	- 8.68	322	160
-82	01/27-02/10	190	-10.16	361	162
-83	02/10-02/24	170	- 9.87	350	164
-84	02/24-03/10	170	-10.66	362	166
-85	03/11-03/24	164	- 9.95	354	168

TABLE 1. continued

Sample (Lab no.)	Colln date (Year, month, day)	$\delta^{14}\text{C}$ ‰	$\delta^{13}\text{C}$ ‰	C ppm	Week of sampling
-86	03/24-04/07	157	- 9.68	336	170
-87	04/07-04/21	158	- 9.76	344	172
-88	04/21-05/05	232	- 9.99	329	174
-89	05/05-05/19	256	- 9.42	363	176
-90	05/21-06/02	101	- 9.72	-	178
-91	06/02-06/16	167	- 8.90	336	180
-92	06/16-06/30	179	- 8.64	326	182
-93	06/30-07/14	218	- 9.08	338	184
-94	07/14-07/28	228	- 9.04	325	186
-95	07/28-08/11	202	- 9.96	327	188
-96	08/11-08/26	162	- 9.32	328	190
-97	08/26-09/08	219	- 8.93	342	192
-98	09/08-09/22	158	- 9.45	312	194
-99	09/22-10/06	170	- 9.28	307	196
-100	10/06-10/20	146	-10.30	350	198
-101	10/20-11/03	174	- 9.54	344	200
-102	11/03-11/17	115	-10.64	342	202
-103	11/17-12/01	104	-10.93	374	204
-104	12/01-12/15	128	-10.08	361	206
-105	12/15-12/29	176	- 9.48	342	208
-106	12/29-01/12	171	- 9.88	349	210
-107	1987 01/12-01/26	98	-10.81	376	212
-108	01/27-02/09	114	-10.84	369	214
-109	02/09-02/23	96	-10.83	363	216
-110	02/24-03/09	162	- 9.34	323	218
-111	03/09-03/23	158	- 9.99	309	220
-112	03/24-04/06	152	- 9.65	337	222
-113	04/06-04/21	187	- 9.41	286	224
-114	04/21-05/04	146	- 9.69	338	226
-115	05/04-05/18	158	- 8.99	341	228
-116	05/19-06/01	-	- 8.99	313	230
-117	06/01-06/16	128	- 9.57	294	232
-118	06/16-06/29	196	- 9.05	337	234
-119	06/29-07/13	210	- 9.43	322	236
-120	07/13-07/28	-	-	-	238
-121	07/28-08/13	187	- 8.91	344	240
-122	08/17-08/31	88	- 9.36	345	243
-123	08/31-09/14	171	- 9.73	332	245
-124	09/15-09/28	186	- 9.78	345	247
-125	09/28-10/12	100	-10.44	375	249
-126	10/12-10/26	164	-10.12	358	251
-127	10/27-11/09	165	- 9.96	353	253
-128	11/10-11/23	177	- 8.78	339	255
-129	11/23-12/07	137	- 9.93	337	257
-130	12/07-12/21	186	-10.39	357	259

LINEAR TREND AND ANNUAL OSCILLATIONS

As observed earlier in Kraków, superposition of two components (secular and seasonal) describing changes with time of CO₂ concentration, δ¹³C and δ¹⁴C is well confirmed by 5-yr measurements (Figs 1 and 2). Similar changes with time at different sites were observed and reported by Mook *et al* (1983), Nydal and Lövseth (1983), Levin *et al* (1985).

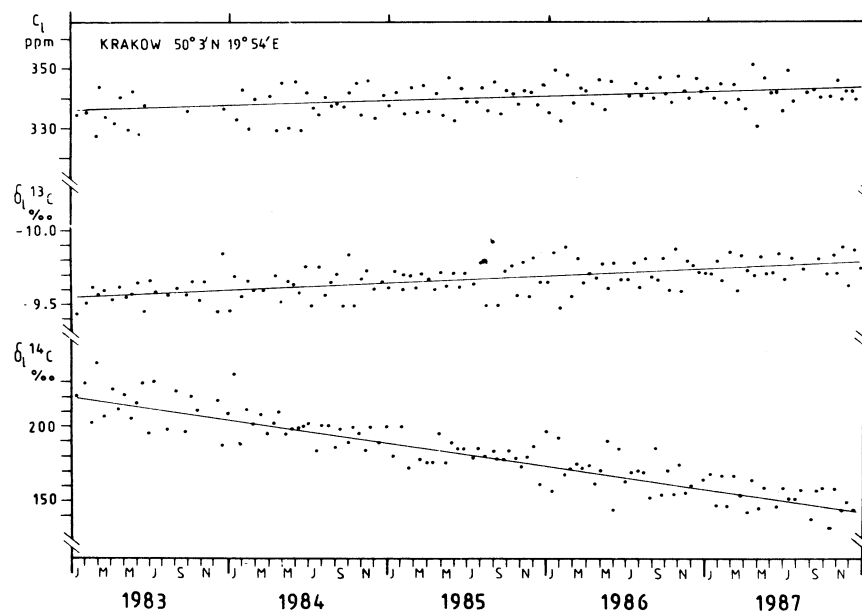


Fig 1. Time plot of the separated linear component of ¹⁴C activity, δ¹⁴C, ratio of stable carbon isotopes, δ¹³C and atmospheric CO₂ concentration, C₁.

The applied procedure for trend analysis is the same as used earlier by Kuc (1986) and similar to that described by Mook *et al* (1983). Separated linear components can be expressed by the equations:

$$\begin{aligned} C_1(t) &= a + b * t && (\text{CO}_2 \text{ concentration}) \\ \delta_1^{14}\text{C}(t) &= d + e * t && (\delta^{14}\text{C}) \\ \delta_1^{13}\text{C}(t) &= p + q * t && (\delta^{13}\text{C}) \end{aligned}$$

Parameters and their errors were calculated applying the procedure of straight line fitting and cubic spline fitting combined in a simple computer program. The detailed procedure was the following: First, a rough estimate was made of linear trend by a least square fit to the measured data. Then "detrended" values were simply calculated by subtracting linear trend from the measured data. Thus obtained detrended values were smoothed by cubic splines that yielded an oscillating component, which, in the next step,

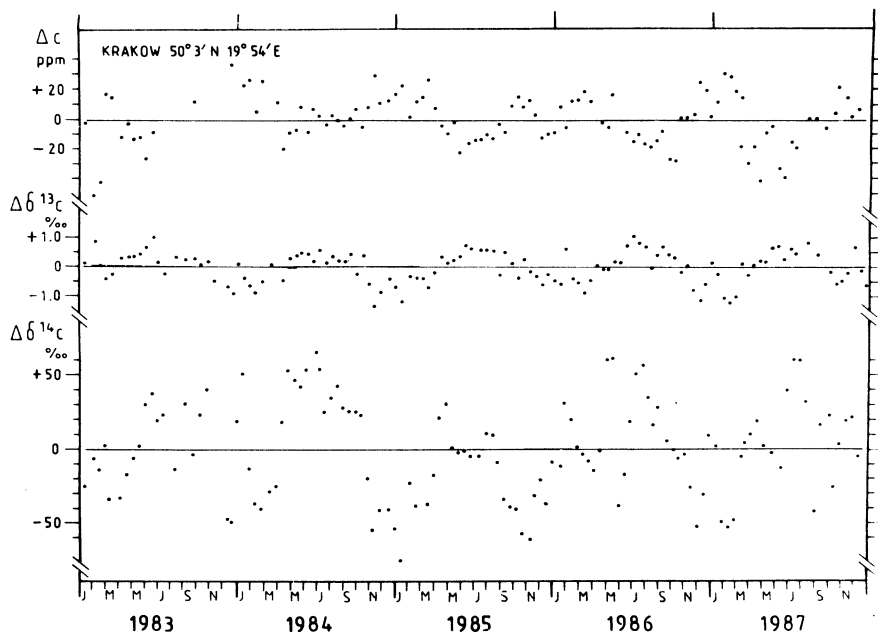


Fig 2. Time plot of the separated oscillation component of ¹⁴C activity, $\Delta\delta^{14}\text{C}$, ratio of stable carbon isotopes, $\Delta\delta^{13}\text{C}$ and atmospheric CO₂ concentration, ΔC .

was subtracted from the measured data. Finally, the linear trend was calculated by a least square fit to the “deoscillated” values. In practice there is only a small difference between parameters of the straight line obtained in the first and last step. Final results are the following:

$$\begin{array}{ll} a = 336 \pm 1\text{ppm} & b = 1.4 \pm 0.3\text{ppm/yr} \\ d = 222 \pm 1\text{‰} & e = -15.5 \pm 0.4\text{‰/yr} \\ p = -9.57 \pm 0.01\text{‰} & q = -0.042 \pm 0.003\text{‰/yr} \end{array}$$

Oscillations (Fig 2) have their extremes in winter and summer and their average amplitude for concentration, ΔC , ¹⁴C, $\Delta\delta^{14}\text{C}$, and stable carbon isotopes, $\Delta\delta^{13}\text{C}$, is ca 20ppm, 50‰, and 0.85‰, respectively.

BRIEF REMARKS

Concentration of CO₂. The average value obtained for January 1983 from the straight line, “a”, is 336, which is ca 8 and 5ppm lower than extrapolated for La Jolla and Mauna Loa, respectively. Relatively low CO₂ concentration calculated at Krakow in 1983 can be explained by geographically different metabolic activity between sampling sites. Also, a small shift can be due to the extrapolation of Mauna Loa results as well as to imposing a straight line fit to the Krakow data. The rate of increase, “b”, 1.4ppm/yr is

in the range observed for the central Pacific, South Pole and La Jolla (Mook *et al.*, 1983).

Stable Carbon Isotopes. The calculated value for January 1983, "p", is -9.57‰ and is ca 1.6 and 1.7‰ more negative than extrapolated for La Jolla and uncontaminated marine air (central Pacific). Annual decrease, "q", equal to -0.042‰/yr , is the same as reported for La Jolla (Mook *et al.*, 1983).

Radiocarbon. The calculated linear decrease of atmospheric ^{14}C activity, "e", ca 16‰/yr , as a mean value for 1983–1987 is ca 3‰/yr higher than reported by Levin, Münnich & Weiss (1980) for clean air in 1976–1979 and close to an estimated decrease (1981–1985) for Scandinavia (Olsson, pers commun, 1987). $\delta^{14}\text{C}$ obtained for January 1983, "d", is 222‰ which, recalculated to $\Delta^{14}\text{C}$, gives a value of ca 50‰ smaller than proposed by Levin *et al.* (1985) for "clean air" in 1983.

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