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CHANGES OF CARBON ISOTOPES IN ATMOSPHERIC CO_2 OF THE KRAKOW REGION IN THE LAST FIVE YEARS

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ABSTRACT. The Krakow Radiocarbon Laboratory has been measuring isotope composition of atmospheric CO_2 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. CO_2 was sorbed while slow pumping atmospheric air through a molecular sieve. After recovery by heating, the CO_2 was converted to benzene and ^{14}C measured in a liquid scintillation spectrometer. In a small portion of CO_2 $\delta^{13}C$ was determined in a mass spectrometer. Concentration of CO_2 was assessed by measurement of the volumes of the sorbed CO_2 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 $\delta^{14}C$, $\delta^{13}C$ 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 CO_2, 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" CO_2 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 CO_2 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 CO_2 by sorption in a molecular sieve in two-week intervals at ca 20m above ground level. After thermal recovery of the sorbed CO_2, its atmospheric concentration (C), radiocarbon activity ($\delta^{14}C$), and stable carbon isotope ratio ($\delta^{13}C$), were determined by volume measurement, liquid scintillation counting and mass-spectrometric measurement, respectively (Florkowski *et al*, 1975; Kuc, 1986). We assessed CO_2 concentration as a volume ratio of the sorbed CO_2 and the pumped air with an estimated error of <5%. We measured stable isotope composition in a mass spectrometer Micromass 602 C and $^{13}C/^{12}C$ ratio was expressed *vs* the PBD standard using $\delta^{13}C$ notation with an error of a single measurement <0.1‰.

Presence of N_2O in the measured CO_2 was not investigated. It is very likely that N_2O decomposes while heating the molecular sieve (thermal decomposition on catalytic compounds) and/or is trapped with water vapor. $\delta^{13}C$ results were not corrected for N_2O. We determined ^{14}C activity in a liquid scintillation spectrometer TRI-CARB model 3320, Packard Instrument International SA, after converting the CO_2 to benzene and mixing with scintillation cocktail PPO/POPOP. Results are reported as $\delta^{14}C$ according to Stuiver and Polach (1977) with 1σ error of ca 10‰. Results for 1985–1987 (Table 1) represent a mean value for two-week sampling periods.

TABLE 1

Samples of atmospheric CO_2

Sample (Lab no.)	Colln date (Year, month, day)		$\delta^{14}C$ ‰	$\delta^{13}C$ ‰	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)		$\delta^{14}C$ ‰	$\delta^{13}C$ ‰	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 CO_2 concentration, $\delta^{13}C$ and $\delta^{14}C$ 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).

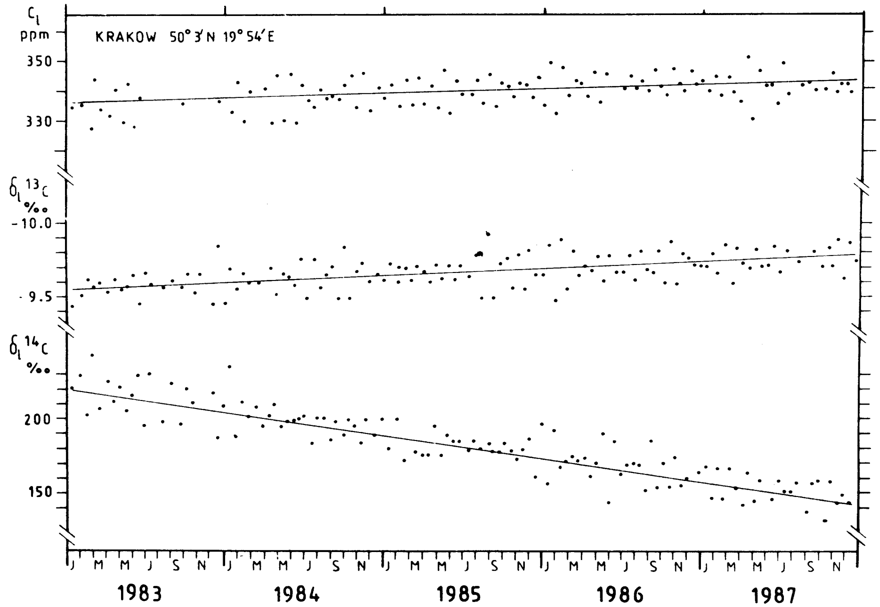

Fig 1. Time plot of the separated linear component of ^{14}C activity, $\delta_1{}^{14}C$, ratio of stable carbon isotopes, $\delta_1{}^{13}C$ and atmospheric CO_2 concentration, C_1.

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:

$$C_1(t) = a + b * t \qquad (CO_2 \text{ concentration})$$

$$\delta_1{}^{14}C(t) = d + e * t \qquad (\delta^{14}C)$$

$$\delta_1{}^{13}C(t) = p + q * t \qquad (\delta^{13}C)$$

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,

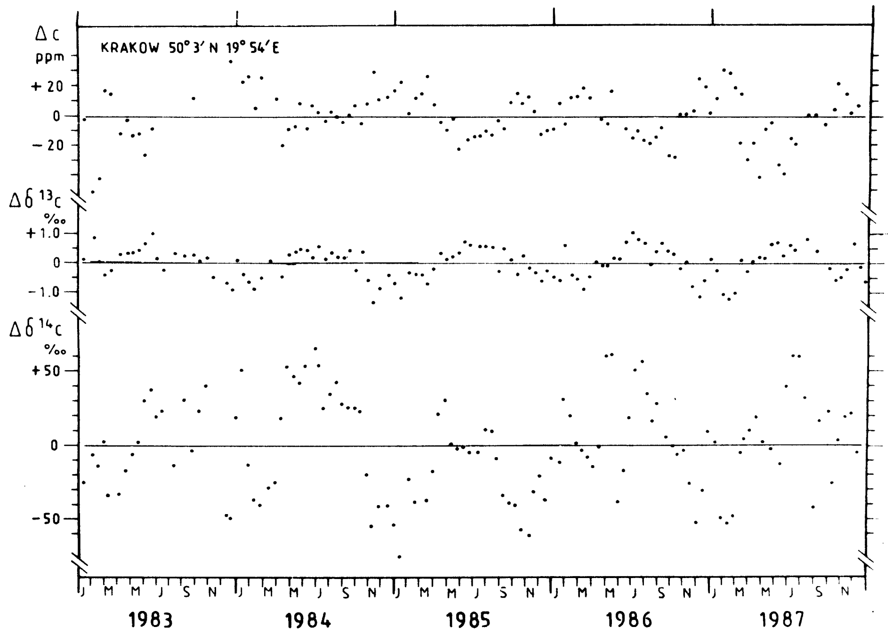

Fig 2. Time plot of the separated oscillation component of ^{14}C activity, $\Delta\delta^{14}C$, ratio of stable carbon isotopes, $\Delta\delta^{13}C$ and atmospheric CO_2 concentration, ΔC.

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:

a = 336 ± 1ppm	b = 1.4 ± 0.3ppm/yr
d = 222 ± 1‰	e = −15.5 ± 0.4‰/yr
p = −9.57 ± 0.01‰	q = −0.042 ± 0.003‰/yr

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

BRIEF REMARKS

Concentration of CO_2. 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 CO_2 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). $\delta^{14}C$ obtained for January 1983, "d", is 222‰ which, recalculated to $\Delta^{14}C$, gives a value of ca 50‰ smaller than proposed by Levin *et al* (1985) for "clean air" in 1983.

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