[RADIOCARBON, VOL 28, NO. 2A, 1986, P 649–654]

CARBON ISOTOPES IN ATMOSPHERIC CO_2 OF THE KRAKOW REGION: A TWO-YEAR RECORD

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ABSTRACT. We have been measuring concentration of atmospheric CO_2 and its carbon isotope composition in the Kraków region for about two years. Samples are continuously collected at two-week intervals at ca 20m above ground level, close to the center of the industrialized urban area. Sampled atmospheric CO_2 is sorbed in a molecular sieve and, after recovery by heating, is converted to benzene. ^{14}C is measured in a liquid scintillation spectrometer, and $\delta^{13}C$ of the CO_2 is determined in a mass spectrometer. The annual record shows winter–summer variation of ^{14}C, ^{13}C, and CO_2 concentration. A long-term trend for 1983 and 1984 indicates a slight decrease of ^{14}C activity (122.0 in January 1983; −1.2% per year), a permanent decrease of $\delta^{13}C_{PDB}$ (−9.3‰ in January 1983; −0.3‰ per year) and an increase of CO_2 concentration (344ppm in January 1983; 1.4ppm per year).

INTRODUCTION

A steady growth of carbon dioxide released to the atmosphere during the burning of fossil fuels increases global concentration of this gas with simultaneous changes of its $^{13}C/^{12}C$ ratio. Anthropogenic CO_2 is free of ^{14}C contrary to "biospheric" carbon of almost constant activity. This enables distinction between "dead" CO_2 and that present in "clean" air. These anthropgenic effects are known in the literature (Freyer, 1979; Mook *et al*, 1983; Keeling, Carter & Mook, 1984). Seasonal variation of the $^{13}C/^{12}C$ ratio, influenced by photosynthesis, respiration, and decomposition of soil, makes the separation of anthropogenic changes more complex.

Isotopic composition of atmospheric CO_2 has been continuously measured in Kraków for more than two years, supplemented by the determination of its concentration. Collected data should reveal fossil CO_2 influences on local atmosphere and determine to what extent global trends are covered by these disturbances. The present study is an extention of measurements from the mid-1970's (Florkowski & Kuc, 1979) and is foreseen for the next few years.

SAMPLING

The sampling point is located in Kraków (50° 3′ N, 19° 54′ E), not far from the city center and close to recreation and sports grounds. Kraków and its suburbs belong to a densely populated area with concentrated industry employing mainly coal as its energy source.

Atmospheric CO_2 is continuously sampled in 2-week intervals (Table 1) and $15m^3$ of air necessary for one sample is taken at the height of ca 20m above ground level. Sampling is done by continuously passing the pumped air through a column with silica gel for trapping water and then through a stainless steel container filled with molecular sieve 4 Å where CO_2 is sorbed. The volume of the pumped air is measured by a gas meter[1] at the inlet and the flow rate is controlled by a flow indicator mounted at the outlet (Fig 1). A simple membrane or water pump can be used for pumping.

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[1] Commercially produced for recording volume of the coal-gas supplied to consumers

TABLE 1
Isotopic composition of carbon in atmospheric CO_2
Concentration values, C_{FT}, taken from broken line fitting

Sample (Lab no.)	Colln date (Year, month, day)	$\delta^{14}C$ (0/00)	$\delta^{13}C$ (0/00)	C_{FT} (ppm)	Week of sampling
POW-7	1983 1/5–1/17	192	−9.44	368	2
-8	1/26–2/7	222	−8.60	359	5
-9	2/9–2/21	182	−9.56	351	7
-10	2/22–3/7	247	−9.94	347	9
-11	3/10–3/21	168	−9.84	341	11
-12	3/29–4/11	188	−9.13	332	14
-13	4/12–4/25	—	−9.30	327	16
-14	4/26–5/9	212	−9.16	321	18
-15	5/9–5/25	207	−9.22	315	20
-16	5/25–6/6	243	−9.12	308	22
-17	6/7–6/20	265	−8.43	315	24
-18	6/24–7/8	204	−9.63	321	26
-19	7/8–7/21	248	−9.89	328	28
-21	8/4–8/18	173	−9.25	341	32
-22	8/18–9/13	250	−9.43	353	35
-23	9/13–9/26	184	−9.37	361	38
-24	9/26–10/8	237	−9.60	368	40
-25	10/11–10/24	247	−9.42	374	42
-26	10/25–11/19	—	−10.16	381	44
-27	11/30–12/13	165	−10.12	392	49
-28	12/13–12/20	132	−10.75	383	50
-29	12/20–1/2	223	−9.42	376	52
-30	1984 1/5–1/14	292	−9.93	369	54
-31	1/17–1/29	170	−10.12	362	56
-32	2/1–2/13	171	−10.56	355	58
-33	2/14–2/27	156	−9.94	348	60
-34	3/6–3/19	176	−9.52	345	63
-35	3/20–4/3	166	—	331	65
-36	4/3–4/16	215	−10.35	325	67
-37	4/16–4/30	261	−9.25	329	69
-38	4/30–5/13	237	−9.35	330	71
-39	5/16–5/30	233	−9.27	332	73
-40	5/30–6/11	247	−9.23	333	75
-41	6/13–6/25	260	−9.73	335	77
-42	6/26–7/9	251	−8.88	336	79
-43	7/9–7/23	200	−9.69	337	81
-44	7/23–8/6	233	−9.25	339	83
-45	8/7–8/20	239	−9.53	340	85
-46	8/20–9/3	209	−9.62	342	87
-47	9/3–9/17	218	−9.03	343	89
-48	9/17–10/1	210	−10.08	344	91
-49	10/2–10/15	219	−9.05	346	93
-50	10/15–10/31	174	−10.26	347	95
-51	10/31–11/16	123	−11.17	349	97
-52	11/16–12/1	153	−10.36	350	99
-53	12/4–12/19	144	−9.94	352	102
-54	12/19–12/30	144	−10.30	354	104

The adsorbed CO_2 is recovered by heating the container with the molecular sieve to a temperature of 420° C while simultaneously pumping released gases through a line of traps for separating CO_2 by freezing at −196°C. A test experiment of the applied procedure indicated the total sorption of atmospheric CO_2 (accuracy ca 1%) and entire recovery of the CO_2 from the

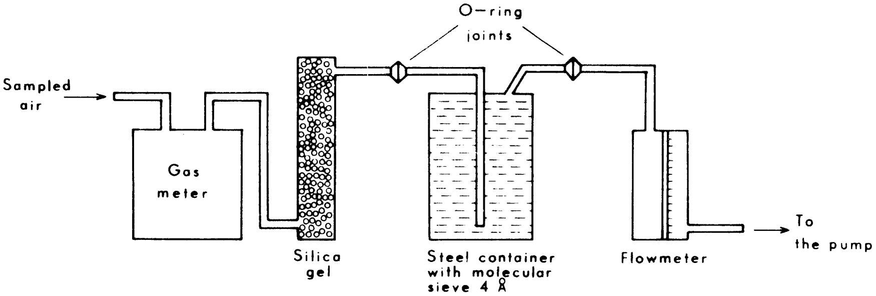

Fig 1. Scheme of sampling device used for continuous collection of atmospheric CO_2. H_2O and CO_2 are sorbed, respectively, in 800g of silica gel and 1600g of molecular sieve 4 Å. Flow rate of the pumped air is ca $60dm^3/h$.

molecular sieve: there was found no detectable quantity of the CO_2 in the gas which passed through the sieve and, after completed recovery there was no additional release of the CO_2 when the sieve overheated to 550°C and pumped to the vacuum better than 10^{-1} torr. Before further processing the volume of purified CO_2 is measured and the small fraction is separated into a glass container for mass spectrometric $^{13}C/^{12}C$ determination. Measurements of $\delta^{13}C$ in CO_2 directly frozen (−196°C) from the air and in CO_2 obtained from the sieve showed a discrepancy within the measurement error for a single measurement. Concentration of N_2O in the released CO_2 was not investigated.

MEASUREMENT OF CO_2 CONCENTRATION AND ISOTOPIC COMPOSITION

CO_2 concentration is assessed as a ratio of measured volumes: the sorbed CO_2 and the pumped air. The estimated error is $<5\%$.

The stable isotope composition is measured in the mass spectrometer, Micromass 602 C and the $^{13}C/^{12}C$ ratio is expressed *vs* the PDB standard using generally accepted $\delta^{13}C$ notation. The long-term record of laboratory standards and numerous control measurements show that the accuracy of a single measurement is better than 0.1‰. The sample is stored before measurement for ca 1 week in a tightly closed glass container. The results without correction for N_2O are comprised in Table 1.

The ^{14}C activity of the sorbed CO_2 is determined using liquid scintillation. The carbon-forming CO_2 molecules is quantitatively converted to benzene following the well-known procedure (Florkowski *et al,* 1975). The benzene obtained after about two-weeks' refrigeration (for decay of possible radon contamination) is mixed with the scintillation cocktail and measured in a specially-constructed teflon-copper vial (Kuc & Różański, 1979). A concentration of PPO and POPOP dissolved in toluene used as the scintillation cocktail as well as settings of liquid scintillation spectrometer TRI-CARB model 3320, Packard Instrument International SA were optimized (Grabczak *et al,* 1983). Results are reported as $\delta^{14}C$:

$$\delta^{14}C = \left(\frac{A_s}{A_{on}} - 1\right) \cdot 1000‰ \qquad (1)$$

where A_s = sample activity, A_{on} = 0.95 activity of NBS oxalic acid in 1950. The error of the results in Table 1 is ca 10‰.

ANALYSIS OF TREND AND ANNUAL VARIATION

Changes with time of the CO_2 concentration, $\delta^{13}C$, and $\delta^{14}C$ (Figs 2, 3) are superposition of two components. One component varies linearly in time while the second shows seasonal oscillations for one year. Two harmonics of the CO_2 concentration were fitted by a broken line (Fig 2). Each segment was found by fitting measured values to a straight line in a time-range the ends of which were defined by highest or lowest concentration. From this broken line time-fitted concentrations, C_{FT}, in two-week intervals were taken for further analysis, the procedure of which was very similar to that described by Mook *et al* (1983). If fitted C_{FT} values to equation:

$$C_{LT}(t) = a + b \cdot t \tag{2}$$

expressing the linear trend parameters found were following: a = 344ppm ± 7.5ppm and b = 1.4ppm/y ± 1.1ppm/y, while t = 0 corresponds to January 1, 1983. Errors were assessed on the basis of relative error when the measured values fitted directly to a straight line. Maximum amplitude of annual oscillations reached ca 40ppm in winter 1983–1984.

A similar procedure of fitting $\delta^{14}C$ to a straight line

$$^{14}C_{LT}(t) = d + e \cdot t \tag{3}$$

resulted in d = 220‰ ± 12‰ and e = −12‰/y ± 10‰/y that indicates a slight decrease of ^{14}C activity. Maximum amplitude was ca 50‰.

After examining the $\delta^{13}C$ trend assuming its linear time dependence

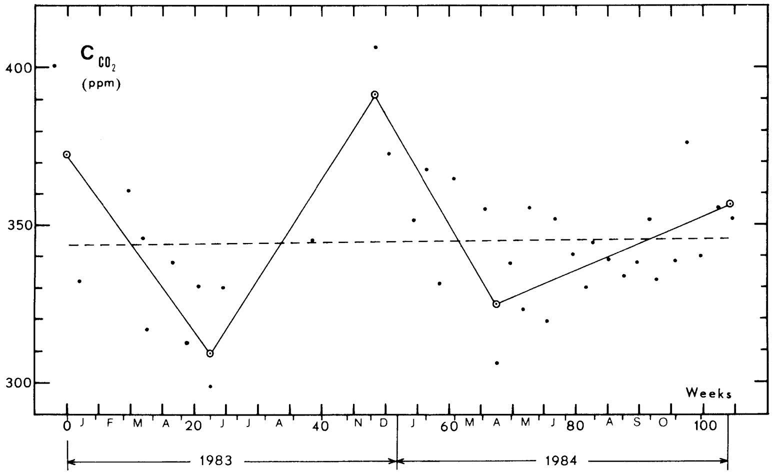

Fig 2. Time plot of the CO_2 concentration in 1983–1984. Seasonal variation is represented by the broken line which was obtained as a linear fit to the data points in about half-year periods.

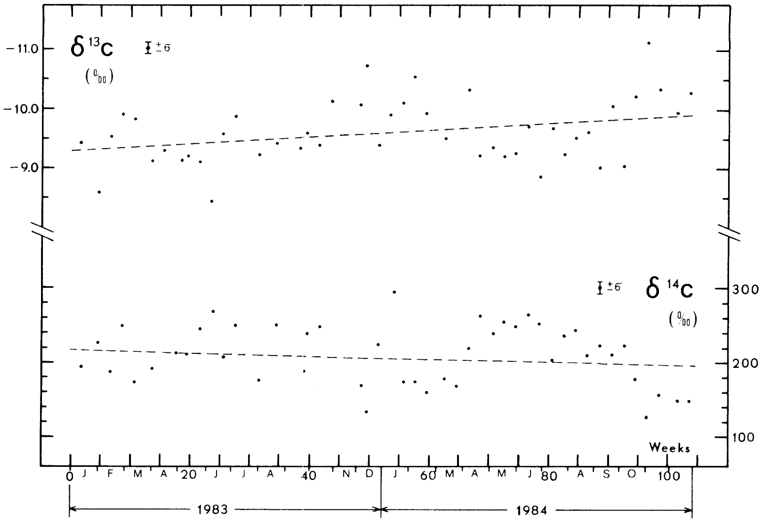

Fig 3. Time plot of $\delta^{13}C$ and $\delta^{14}C$ of atmospheric CO_2 collected in 1983–1984 in 2-week periods. Dashed lines present regression line fitting.

according to equation

$$^{13}C_{LT}(t) = p + q \cdot t \qquad (4)$$

the following parameters were obtained: $p = -9.3‰ \pm 0.16‰$ and $q = -0.3‰/y \pm 0.13‰/y$. If an iteration procedure for assessment δ_I^{13} (Mook *et al,* 1983) is applied, value $\delta_I^{13} = -13.7‰$ is obtained indicating stable isotopic composition of CO_2 which is added or substracted to produce the observed concentration fluctuation.

The same procedure for ^{14}C was used to determine $\delta_I^{14} = 0‰$.

DISCUSSION OF DATA

1) The averaged concentration of CO_2 reached in January 1983 was $C_{LT} = 344ppm$, which is ca 1ppm and 4ppm higher than reported for La Jolla and Mauna Loa, respectively (Mook *et al,* 1983). The rate of increase 1.4ppm/y is close to the observed global value.

2) The linear trend of $^{13}C/^{12}C$ ratio is represented by the value of $^{13}C_{LT} = -9.3‰$ in January 1983, ca 1.5‰ more negative as compared to the "non-contaminated" marine air. Similarly, the decrease of $-0.3‰/y$ is nearly one order of magnitude greater.

3) The ^{14}C activity for the two-year period was slightly decreasing, $\delta^{14}C = 200‰$ in January 1983, and $-12‰/y$. If measurements are integrated for May, June and the first half of July (highest vegetation activity) the obtained value is $\delta^{14}C = 246‰$ in 1984.

4) Assuming that changes of carbon isotope composition were induced by different sources (or sinks) of various $\delta^{13}C$ and $\delta^{14}C$ values, it is possible to separate components contributing to this CO_2. Local

influences consist of three components: fossil CO_2 (δ^{13}C = −26.5‰, δ^{14}C = −1000‰), biogenic origin (δ^{13}C = −25.0‰, δ^{14}C = 250‰) and uncontaminated "clean" air (δ^{13}C = −8.0‰ (La Jolla), δ^{14}C = 250‰ (in 1984)). Using δ_I^{13}, δ_I^{14} and applying simple mass balance we can calculate the contribution of each component, respectively: 20%, 12%, and 68%. An explanation of the unexpected dominating "clean" air component needs further investigation especially when observed oscillations of CO_2 are relatively high.

5) Considering only changes in isotopic composition for the Kraków region "summer" air has δ^{13}C = −9.29‰ and δ^{14}C = 246‰, representing the average values of summer (30.04–09.07.1984) and comparing with respective values −10.41‰ and 148‰ for winter (15.10–30.12.1984) the "winter" contribution of fossil, f, and biogenic, b, carbon dioxide was estimated. From δ^{14}C, f = 7.8% was obtained and from δ^{13}C, b + f = 6.7%. Both values are close to the estimated concentration increase of winter 1984 when ca 5.2% of CO_2 should be of fossil and biogenic origin.

6) The CO_2 concentration record for the Kraków region shows maximum concentration in December and minimum in April–May (Fig 2) and is inversely well correlated with δ^{13}C. For the "clean" stations of the Northern Hemisphere maximum CO_2 concentration and minimum δ^{13}C is at the end of spring, while the next extreme values are in early fall. This 5-month "shift in phase" can be explained as an effect of burning fossil fuels which is most intensive in this region from 15 October to 15 April. δ^{14}C shows also its minimum in December–February (the greatest fall-out of "dead" CO_2) and maximum in May–June, which is good synchrony with CO_2 concentration and δ^{13}C.

The presented computations, based on relatively few measurements made over a period of two years, have a rather quantitative character. The more exact assessments of the trends and the contribution of fossil and biogenic CO_2 can be possible after obtaining more data, including also meteorologic observations.

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