

CARBON ISOTOPES IN ATMOSPHERIC CO₂ OF THE KRAKÓW REGION: A TWO-YEAR RECORD

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ABSTRACT. We have been measuring concentration of atmospheric CO₂ 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 CO₂ is sorbed in a molecular sieve and, after recovery by heating, is converted to benzene. ¹⁴C is measured in a liquid scintillation spectrometer, and δ¹³C of the CO₂ is determined in a mass spectrometer. The annual record shows winter–summer variation of ¹⁴C, ¹³C, and CO₂ concentration. A long-term trend for 1983 and 1984 indicates a slight decrease of ¹⁴C activity (122.0 in January 1983; –1.2% per year), a permanent decrease of δ¹³C_{PDB} (–9.3‰ in January 1983; –0.3‰ per year) and an increase of CO₂ 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 ¹³C/¹²C ratio. Anthropogenic CO₂ is free of ¹⁴C contrary to “biospheric” carbon of almost constant activity. This enables distinction between “dead” CO₂ and that present in “clean” air. These anthropogenic effects are known in the literature (Freyer, 1979; Mook *et al.*, 1983; Keeling, Carter & Mook, 1984). Seasonal variation of the ¹³C/¹²C ratio, influenced by photosynthesis, respiration, and decomposition of soil, makes the separation of anthropogenic changes more complex.

Isotopic composition of atmospheric CO₂ has been continuously measured in Kraków for more than two years, supplemented by the determination of its concentration. Collected data should reveal fossil CO₂ influences on local atmosphere and determine to what extent global trends are covered by these disturbances. The present study is an extension 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 CO₂ is continuously sampled in 2-week intervals (Table 1) and 15m³ 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 CO₂ is sorbed. The volume of the pumped air is measured by a gas meter¹ 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.

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

TABLE 1
Isotopic composition of carbon in atmospheric CO₂
Concentration values, C_{FT}, taken from broken line fitting

Sample (Lab no.)	Colln date (Year, month, day)	δ ¹⁴ C (0/00)	δ 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 CO₂ 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 CO₂ by freezing at -196°C. A test experiment of the applied procedure indicated the total sorption of atmospheric CO₂ (accuracy ca 1%) and entire recovery of the CO₂ from the

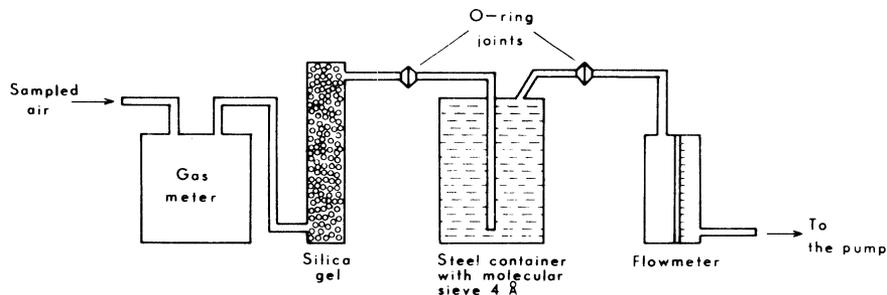


Fig 1. Scheme of sampling device used for continuous collection of atmospheric CO₂. H₂O and CO₂ are sorbed, respectively, in 800g of silica gel and 1600g of molecular sieve 4 Å. Flow rate of the pumped air is ca 60dm³/h.

molecular sieve: there was found no detectable quantity of the CO₂ in the gas which passed through the sieve and, after completed recovery there was no additional release of the CO₂ when the sieve overheated to 550°C and pumped to the vacuum better than 10⁻¹ torr. Before further processing the volume of purified CO₂ is measured and the small fraction is separated into a glass container for mass spectrometric ¹³C/¹²C determination. Measurements of δ¹³C in CO₂ directly frozen (-196°C) from the air and in CO₂ obtained from the sieve showed a discrepancy within the measurement error for a single measurement. Concentration of N₂O in the released CO₂ was not investigated.

MEASUREMENT OF CO₂ CONCENTRATION AND ISOTOPIC COMPOSITION

CO₂ concentration is assessed as a ratio of measured volumes: the sorbed CO₂ and the pumped air. The estimated error is <5%.

The stable isotope composition is measured in the mass spectrometer, Micromass 602 C and the ¹³C/¹²C ratio is expressed *vs* the PDB standard using generally accepted δ¹³C 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 N₂O are comprised in Table 1.

The ¹⁴C activity of the sorbed CO₂ is determined using liquid scintillation. The carbon-forming CO₂ 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 & Rózański, 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 δ¹⁴C:

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

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, $\delta^{13}\text{C}$, and $\delta^{14}\text{C}$ (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:

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

expressing the linear trend parameters found were following: $a = 344\text{ppm} \pm 7.5\text{ppm}$ and $b = 1.4\text{ppm/y} \pm 1.1\text{ppm/y}$, 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 $\delta^{14}\text{C}$ to a straight line

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

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

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

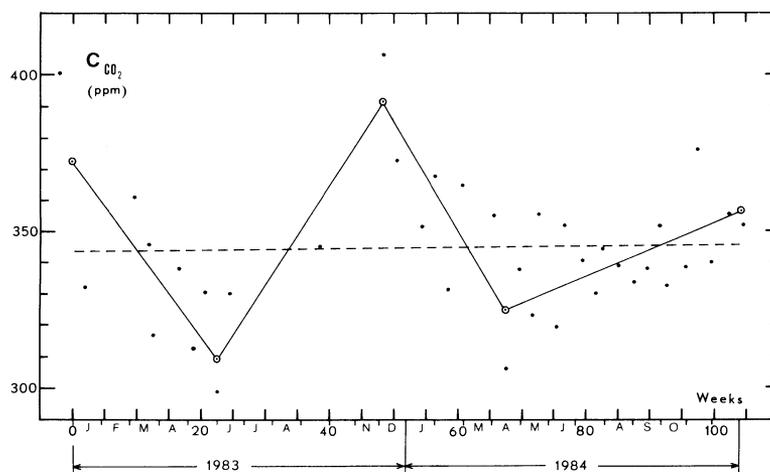


Fig 2. Time plot of the CO_2 concentration in 1983–1984. Seasonal variation is represented by the broken line which was obtained as a linear fit to the data points in about half-year periods.

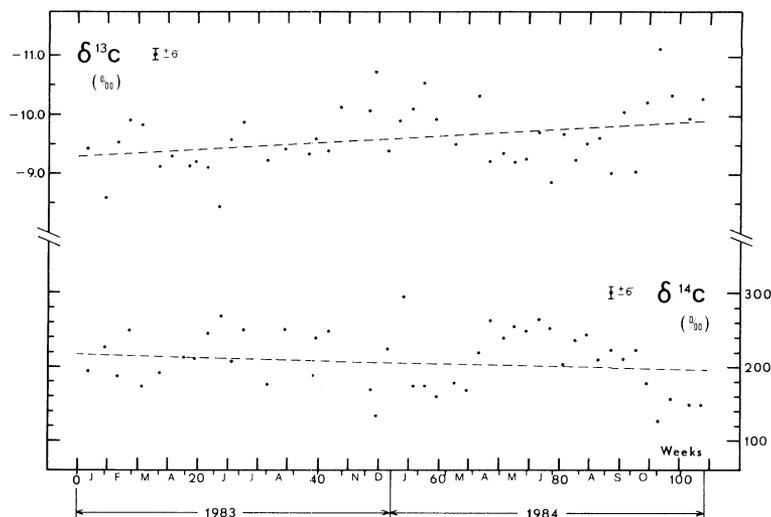


Fig 3. Time plot of $\delta^{13}\text{C}$ and $\delta^{14}\text{C}$ of atmospheric CO_2 collected in 1983–1984 in 2-week periods. Dashed lines present regression line fitting.

according to equation

$$^{13}\text{C}_{\text{LT}}(t) = p + q \cdot t \quad (4)$$

the following parameters were obtained: $p = -9.3\text{‰} \pm 0.16\text{‰}$ and $q = -0.3\text{‰}/\text{y} \pm 0.13\text{‰}/\text{y}$. If an iteration procedure for assessment δ_1^{13} (Mook *et al.*, 1983) is applied, value $\delta_1^{13} = -13.7\text{‰}$ is obtained indicating stable isotopic composition of CO_2 which is added or subtracted to produce the observed concentration fluctuation.

The same procedure for ^{14}C was used to determine $\delta_1^{14} = 0\text{‰}$.

DISCUSSION OF DATA

1) The averaged concentration of CO_2 reached in January 1983 was $\text{C}_{\text{LT}} = 344\text{ppm}$, 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 $^{13}\text{C}/^{12}\text{C}$ ratio is represented by the value of $^{13}\text{C}_{\text{LT}} = -9.3\text{‰}$ in January 1983, ca 1.5‰ more negative as compared to the “non-contaminated” marine air. Similarly, the decrease of $-0.3\text{‰}/\text{y}$ is nearly one order of magnitude greater.

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

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

influences consist of three components: fossil CO₂ ($\delta^{13}\text{C} = -26.5\text{‰}$, $\delta^{14}\text{C} = -1000\text{‰}$), biogenic origin ($\delta^{13}\text{C} = -25.0\text{‰}$, $\delta^{14}\text{C} = 250\text{‰}$) and uncontaminated “clean” air ($\delta^{13}\text{C} = -8.0\text{‰}$ (La Jolla), $\delta^{14}\text{C} = 250\text{‰}$ (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 CO₂ are relatively high.

5) Considering only changes in isotopic composition for the Kraków region “summer” air has $\delta^{13}\text{C} = -9.29\text{‰}$ and $\delta^{14}\text{C} = 246\text{‰}$, 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 $\delta^{14}\text{C}$, $f = 7.8\%$ was obtained and from $\delta^{13}\text{C}$, $b + f = 6.7\%$. Both values are close to the estimated concentration increase of winter 1984 when ca 5.2% of CO₂ should be of fossil and biogenic origin.

6) The CO₂ concentration record for the Kraków region shows maximum concentration in December and minimum in April–May (Fig 2) and is inversely well correlated with $\delta^{13}\text{C}$. For the “clean” stations of the Northern Hemisphere maximum CO₂ concentration and minimum $\delta^{13}\text{C}$ 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. $\delta^{14}\text{C}$ shows also its minimum in December–February (the greatest fall-out of “dead” CO₂) and maximum in May–June, which is good synchrony with CO₂ concentration and $\delta^{13}\text{C}$.

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 CO₂ can be possible after obtaining more data, including also meteorologic observations.

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