Tellus (1991), *43B*, 373–378

Concentration and carbon isotopic composition of atmospheric CO_2 in southern Poland*

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(Manuscript received 19 December 1989; in final form 3 June 1991)

ABSTRACT

The isotopic composition of atmospheric CO_2 and its concentration in the Krakow region has been measured since 1983. Air samples have been collected in bi-weekly intervals close to the center of Krakow. The six years records (1983–1988) of these data reveal multi-annual linear trends and winter–summer oscillations. The calculated parameters of the individual regression lines (intercept and slope) for the measured $\Delta^{14}C$, $\delta^{13}C$ and CO_2 concentration, C, are: 173 °/oo (January 1983) and -10.7 °/oo yr^{-1}, -9.58 °/oo (January 1983) and -0.038 °/oo yr^{-1}, 371 ppmv (January 1983) and 1.0 ppmv yr^{-1}, respectively. The ^{14}C activity in tree leaves collected in a mountain region, about 60 km from Krakow was also assessed. The parameters of the linear decrease of ^{14}C activity in tree leaves are: 239 °/oo (January 1983) and 21 °/oo yr^{-1}.

1. Introduction

Measurements of the carbon isotopic composition in the naturally-occurring carbon compounds have been carried out for the last 10 years in the Department of Environmental Physics of the Institute of Physics and Nuclear Techniques. Investigations of this type became more interesting once the problem of anthropogenic changes in the environment assumed global significance.

Southern Poland, and particularly the highly industrialized Silesia district where numerous coal mines are located, with associated metallurgic, machinery and chemical industries, is an area of greatest hazard for the natural environment. Krakow, about 60 km east of the Silesia district is mostly influenced by pollutants coming from the west as well as by discharges from the local industry.

Measurements of the isotopic composition of carbon dioxide together with its concentration in the atmosphere, yielded useful information on the degree of anthropogenic changes; they were started in our Institute in 1983.

2. Sampling site and techniques

The Krakow sampling site is located to the west of the city, bordering recreation and sports grounds. The air inlet for the sampling device is about 17 m above ground level on the roof of a detached building of the Institute.

Sampling is continuously carried on at bi-weekly intervals by means of a sorption technique in molecular sieve 4 Å (the sampling device is illustrated in Fig. 1). Gases recovered from the molecular sieve during heating in an electric oven to a temperature of 420°C, are dried, and CO_2 is separated while passing through a vacuum-cryogenic line. The volume of the obtained CO_2 is then carefully measured. The concentration of the CO_2, averaged over the sampling period, is assessed as the volume ratio of the absorbed CO_2 and the atmospheric air passing through the moleclar sieve; the error is not exceeding 5%.

The stable carbon isotopic composition of a small portion of the CO_2 is measured in a mass

* This contribution was presented at the 3rd International Conference on Analysis and evaluation of atmospheric CO_2 data, present and past which was held in Hinterzarten, Germany, 16–20 October 1989 (see *Tellus 43B*: 2, 1991).

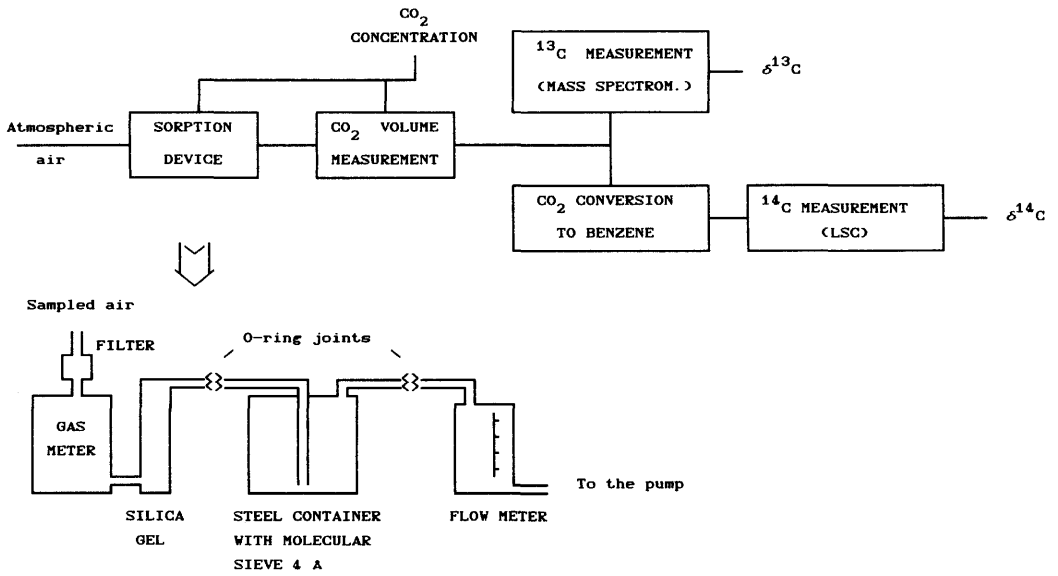

Fig. 1. Block diagram of the apparatus for measurement of CO_2 concentration, ^{13}C and ^{14}C. The sampling device is shown in details.

spectrometer Micromass 602C, the results being expressed versus the PDB standard as $\delta^{13}C$. A test experiment of absorption of the same air several times as consecutive samples showed no detectable influence of the sampling procedure (within mass-spectrometer error) on the $\delta^{13}C$ results. The error of a mass-spectrometric measurement of $\delta^{13}C_{PDB}$ is $\pm 0.07\,^{o}/_{oo}$, calculated as a standard deviation of a single measurement in a series of separately prepared samples of the same CO_2. Including the long-term stability of the mass-spectrometer, the total error of $\delta^{13}C_{PDB}$ is $\pm 0.1\,^{o}/_{oo}$. N_2O, which could be present in the absorbed air was not investigated, but probably decomposes during heating of the molecular sieve.

The ^{14}C activity of the CO_2 is determined in a liquid scintillation spectrometer: TRI-CARB model 3320, Packard. For this purpose, the CO_2 is routinely converted to benzene; the benzene sample obtained is mixed with a scintillation coctail PPO/POPOP-toluene and measured in a special teflon-copper vial (Florkowski et al., 1975; Kuc and Różański, 1979). The results reported as $\delta^{14}C$, are recalculated to $\Delta^{14}C$ according to Stuiver and Polach (1977). The measurements error of about $8\,^{o}/_{oo}$ for atmospheric CO_2 includes the counting errors of the sample, both standard (NBS oxalic acid, SRM-4990), and background (each one measured on one run). The total error, including the benzene synthesis reproducibility, is estimated to be $\pm 10\,^{o}/_{oo}$. The long-term drift of the standard count rate is small compared with the error of a single measurement.

A block diagram of the whole measurement procedure is presented in Fig. 1.

3. Results

3.1. Seasonal and secular variations in atmospheric samples

The changes with time of the three mentioned parameters of atmospheric CO_2 (concentration, C, stable carbon isotopes, $\delta^{13}C$, and radiocarbon, $\delta^{14}C/\Delta^{14}C$) reveal seasonal oscillations overlapping with a linear trend. The separation of these two components needed a special computer program which was a combination of straight line and cubic spline fitting. The procedure for trend analysis was earlier used by Kuc (1989), and similar to that described by Mook et al. (1983).

The measured values of the above-mentioned parameters (C, $\delta^{13}C$, $\Delta^{14}C$) are shown in Fig. 2,

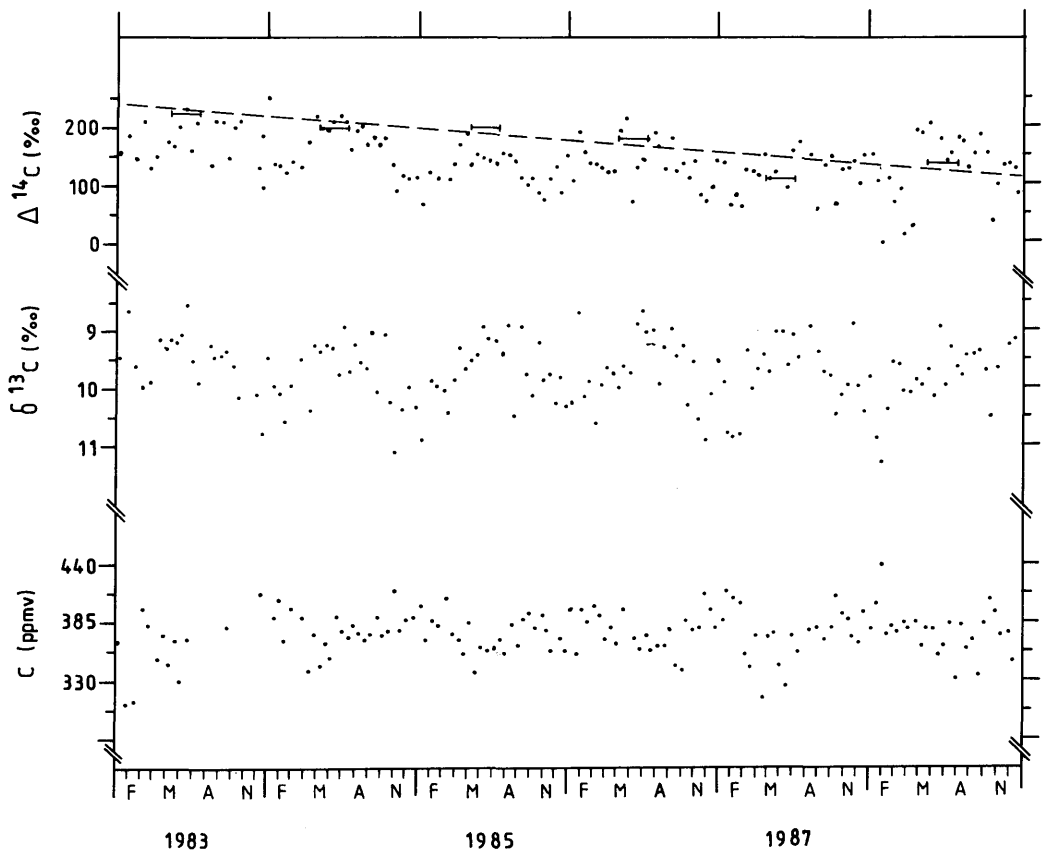

Fig. 2. Time plot of the atmospheric CO_2 concentration, C, ratio of stable carbon isotopes, $\delta^{13}C_{PDB}$, and radiocarbon activity, $\Delta^{14}C$. The broken line presents straight line fitting of the $\Delta^{14}C$ in organic matter (tree leaves) sampled in a region recognized as a "clean" area, about 60 km to the south of Krakow, in a mountain district. The measured values are indicated as the bars.

and the separated linear components expressed by the following equations (t in years):

$C_1(t) = a + b \times t$ (CO_2 concentration)

$\Delta_1{}^{14}C(t) = d + e \times t$ ($\Delta^{14}C$)

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

with calculated parameters:

$a = 371 \pm 1$ ppmv (January 1983),

$b = 1.0 \pm 0.3$ ppmv yr^{-1}

$d = 173 \pm 2\,‰$ (January 1983),

$e = -10.7 \pm 0.5\,‰$ yr^{-1}

$p = -9.58 \pm 0.02\,‰$ (January 1983),

$q = -0.038 \pm 0.005\,‰$ yr^{-1}

Indicated errors of the straight line parameters are the standard deviations calculated in conventional way on the basis of about 150 points.

The averaged amplitudes for the oscillation components (extremes fall in winter and summer) of concentration, C, stable isotopes, $\delta^{13}C$, and radiocarbon, $\Delta^{14}C$, are 24 ppmv, 0.85‰, and 50‰, respectively.

3.2. *^{14}C activity in organic matter*

In the last 10 years, ^{14}C activity has been measured in tree leaves (*Fagus silvatica L.*)

collected in a mountain region regarded as a representative "baseline" of southern Poland. The sampling period was August/September 1975–1988 (four samples in 1975, one in 1976, and one sample per year in 1982 to 1988). Dried and milled material after combustion to CO_2 was measured for ^{14}C activity in the same way as atmospheric CO_2. The observed decrease of ^{14}C activity (Fig. 2) expressed as $\Delta^{14}C$ (Stuiver and Polach, 1977), for easier comparison with the atmospheric data, was fitted by a straight line, which was chosen as the simplest function (relative to the small number of points with the long time gaps), yielded the following equation:

$$\Delta^{14}C(t) = (239 \pm 5.7) - (20.9 \pm 1.3) \times t \,{}^{o}/_{oo}$$

$t = 0$ in January 1983.

$\Delta^{14}C$ was calculated using individually measured $\delta^{13}C_{PDB}$ values.

4. Discussion

The CO_2 concentration calculated at Krakow in 1983 is about 27 and 30 ppmv higher than extrapolated for La Jolla and Mauna Loa, indicating a remarkable fossil CO_2 contamination. The rate of increase 1.0 ppmv yr^{-1} (in 1983–1986 was about two times higher) is in the range observed for the central Pacific, South Pole and La Jolla (Mook et al., 1983).

The calculated value of stable carbon isotopes in the Krakow region for January 1983 is $-9.58\,{}^{o}/_{oo}$, about $1.7\,{}^{o}/_{oo}$ and $1.8\,{}^{o}/_{oo}$ more negative than extrapolated for La Jolla and uncontaminated marine air. This difference can be due to the higher content of the fossil-fuel as well as biogenic CO_2. The annual decrease, $-0.038\,{}^{o}/_{oo}\,yr^{-1}$, is very close to that reported for La Jolla (Mook et al., 1983).

The linear decrease of atmospheric ^{14}C activity, $10.7\,{}^{o}/_{oo}\,yr^{-1}$, as a mean value for 1983–1988, is about $1.8\,{}^{o}/_{oo}\,yr^{-1}$ lower than reported by Levin, et al. (1980) for clean air in 1976–1979, and about $1.0\,{}^{o}/_{oo}\,yr^{-1}$ lower than the value extrapolated by Levin et al. (1989) for Jungfraujoch (the differences if compared to the measurement error are: $3.6\,\sigma$ and $2\,\sigma$, respectively), and close to an estimated value by Olsson (1989) for Scandinavia in the last years ($15\,{}^{o}/_{oo}\,yr^{-1}$ to $20\,{}^{o}/_{oo}\,yr^{-1}$ before 1985 and about $10\,{}^{o}/_{oo}\,yr^{-1}$ after that date). The ^{14}C activity, originally calculated and published as $\delta^{14}C$ (Kuc, 1989), was recalculated to $\Delta^{14}C$ applying a $\delta^{13}C_{PDB}$ of $-9.6\,{}^{o}/_{oo}$ (constant value for each sample), and for January 1983 gives a value of $173\,{}^{o}/_{oo}$ - about $60\,{}^{o}/_{oo}$ less than the $235\,{}^{o}/_{oo}$ proposed by Levin et al. (1985) for 1983 "clean air" in central Europe (southern Germany).

The regression line calculated for $\Delta^{14}C$ in organic matter from southern Poland (Fig. 2) yields values of $239\,{}^{o}/_{oo}$ for January 1983 and $229\,{}^{o}/_{oo}$ if averaged over the whole year 1983, comparing well with the above-mentioned "clean air" value. Four organic samples collected in 1975 and one in 1976 show $\Delta^{14}C = 392\,{}^{o}/_{oo}$ (mean) and $378\,{}^{o}/_{oo}$, respectively which are $16\,{}^{o}/_{oo}$ and $18\,{}^{o}/_{oo}$, respectively higher than those estimated for central Europe. On the other hand, the fitted regression line in Fig. 2 shows a steeper decrease with time than is reported for Jungfraujoch and observed in the Krakow atmospheric samples during summer, resulting in lower values for recent years, e.g., in January 1988, the difference is about $40\,{}^{o}/_{oo}$. This indicates that our ^{14}C data from tree leaves cannot serve as the best reference for ^{14}C background in the Krakow region.

Applying a simple additive model for the atmospheric CO_2, i.e., presence of only two components which fulfill the equation: $CO_{2observed} = CO_{2background} + CO_{2fossil}$ and using the different ^{14}C activities for each component, i.e., $^{14}C_{fossil} = 0$ pmc, it is possible to estimate the fossil component. We followed the simple equation used by Levin (1989): $CO_{2fossil} = CO_{2background} \times (^{14}C_{background} - {}^{14}C_{observed})/{}^{14}C_{observed}$, where: CO_2 (ppmv), ^{14}C (pmc), and assumed a $CO_{2background}$ of 350 ppmv suggested by Levin et al. (1989), following Conway et al. (1988). For $^{14}C_{background}$, we used the Jungfraujoch trend (Levin et al., 1989). The monthly-mean values of the $CO_{2fossil}$ were calculated, and averaged for 1983–1988; the results are presented in Fig. 3. In this figure are also marked the Heidelberg values, following Levin et al. (1989). Systematically higher fossil fuel concentrations are observed at Krakow, if compared to Heidelberg. In 1983–1988, the yearly-mean values (Fig. 3 - upper part) show variations from about 17 ppmv to 26 ppmv, while for the individual samples, the observed spread is from small negative values to about 67 ppmv. No significant shift of the CO_2 concentration from

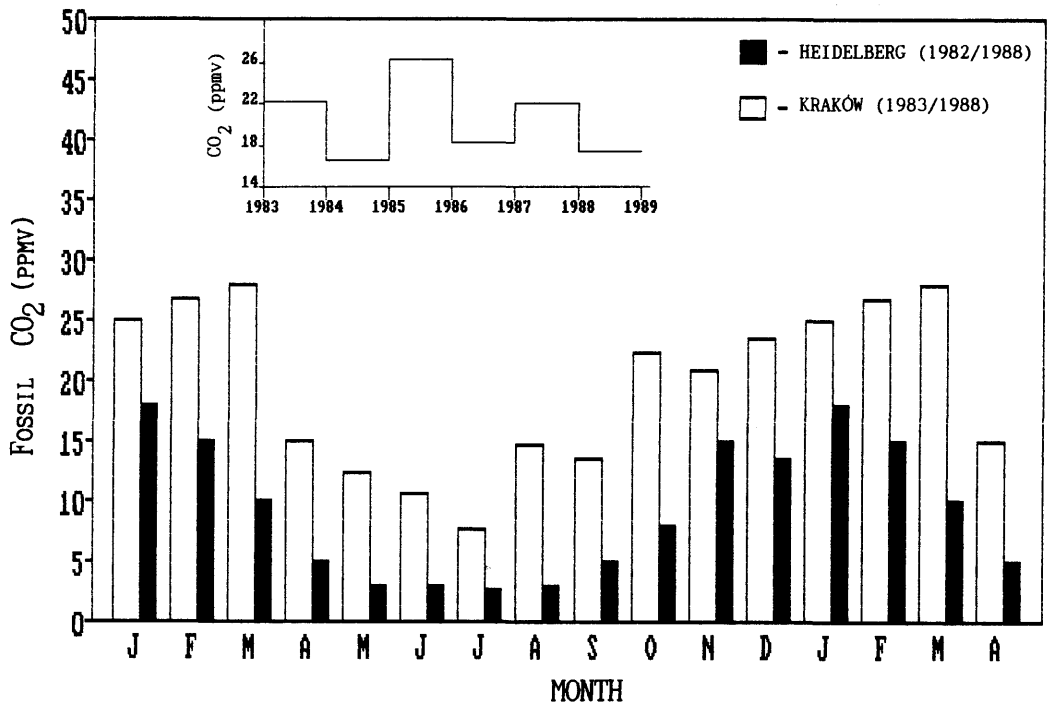

Fig. 3. Concentration of the fossil fuel CO_2 at the Krakow sampling site, calculated assuming: $CO_{2\text{background}} = 350$ ppmv and $^{14}C_{\text{background}}$ = Jungfraujoch trend. The Heidelberg values are taken from Levin et al. (1989). In the upper part, the yearly-mean values of Krakow are presented.

fossil-fuels was found; however, a small increase before 1985 and also a small decrease after, both within the 1σ error, were noticed.

The calculated mean value for the whole period (132 points) is 21 ppmv. Subtracting this value from the mean CO_2 concentration in 1983–1988 (374 ppmv), one obtains 353 ppmv for "clean" air, which agrees quite well with the background CO_2 value used.

Observations in southern Poland in spring 1986, following the Chernobyl accident, indicated a small increase of ^{14}C atmospheric concentration (about 10 pmc), lasting less than 3 weeks after the accident. A questionable increase of ^{14}C activity immediately after the accident, and more pronounced two months later was reported from Scandinavia by Olsson (1989). Similarly, the higher ^{14}C activity measured in Krakow in July 1986 (Kuc, 1987) indicates an appearance of a higher atmospheric radiocarbon activity, lasting about 1 month.

5. Conclusions

The contribution of the fossil-fuel CO_2 calculated on the basis of the $\Delta^{14}C$ measured in air samples at the Krakow sampling site corresponds well with the high total CO_2 concentration observed. This contribution does not show any significant trend during the period 1983–1988; however, the total CO_2 concentration increases, although in recent years the observed tendency shows a decrease. The assessed component of the "clean" air CO_2 concentration for the Krakow samples is in good agreement with that reported for central Europe.

The ^{14}C activity in organic matter (tree leaves) collected in a "clean" area of southern Poland reveals a steeper decrease than that measured for central Europe (the $\Delta^{14}C$ values are most close in 1983). It is expected that samples collected in the coming years will help in clarifying this discrepancy.

6. Acknowledgments

This study was partly founded by the Central Program of Fundamental Research: CPBP # 03.01.24.01, available through the Institute of Geophysics, The Academy of Mining and Metallurgy, Krakow. The author is truly grateful to Ingeborg Levin for a critical reading of the manuscript, and valuable suggestions. Thanks are also due to B. Lewandowska and J. Fiedorowicz for collection and preparation of the samples, and to P. Obrocki for mass-spectrometric measurements.

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