CHANGES OF THE CO_2 SOURCES AND SINKS IN A POLLUTED URBAN AREA (SOUTHERN POLAND) OVER THE LAST DECADE, DERIVED FROM THE CARBON ISOTOPE COMPOSITION

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ABSTRACT. Time series of $\delta^{14}C$, $\delta^{13}C$, and concentration of atmospheric CO_2 covering the last 12 years are available at the Kraków sampling site (southern Poland) representing an urban area exposed to anthropogenic pollution of both local and regional origin. The samples represent continuous monitoring in biweekly intervals. Observations covering the time period 1983–1994 show a linear decrease of the $^{13}C/^{12}C$ ratio ($\delta^{13}C = -9.6‰$ in Jan. 1983) with a slope of $-0.02‰$ a^{-1}. The decreasing tendency in the case of ^{14}C ($\delta^{14}C = 227‰$ in January 1983) is weaker with a broad minimum in 1991 ($\delta^{14}C = 124‰$) and subsequent gradual increase by *ca.* 10‰, coinciding with a substantial reduction of coal consumption in Poland (26% reduction in 1991–1994 for heat and electricity production), partly compensated in agglomerations by increased gas consumption. The 12-year record of the CO_2 concentration in Kraków points to a constant value fluctuating at a high level (average: 373 ppmv) reaching a maximum yearly average of 376 ppmv. These carbon isotope signatures were used for the separation of fossils from biogenic and "background" components, reflecting the strength of relevant sources. The monthly mean of the fossil component varies from *ca.* 10 ppmv in June to 27.5 ppmv in March while the yearly mean decreased *ca.* 16 ppmv since 1991.

INTRODUCTION

Temporal and spatial changes of the carbon isotope composition of atmospheric CO_2 yield information on the circulation of this element between the atmosphere, biosphere and introduced anthropogenic disturbances. Studies of atmospheric CO_2 were initiated in the early 1950s by Keeling (1958). Systematic measurements of carbon isotope composition in tropospheric CO_2 have been performed since 1983 at the Department of Environmental Physics, University of Mining and Metallurgy. The sampling point site is in Kraków (50°3′N, 19°54′E), at *ca.* 25 m above the ground level (on the roof of the Faculty building), in the area bordering the recreation and sports grounds and the university campus. The Kraków area, with about a million inhabitants, is influenced by local sources as well as by anthropogenic pollution from the west (the Silesia coal-mining district and heavy industry with high consumption of fossil fuels). Transformation in industrial technologies since the early 1990s has resulted in reduced usage of coal as fuel. In 1990–1994, the total use of coal in Poland for power and heating stations decreased from 82.0 Mt to 60.7 Mt (Rocznik Statystyczny 1996). At the same time, the use of gas for heating and other municipal purposes increased. For instance, in the Kraków region, consumption of natural gas has doubled, partly replacing coal (Raport z Prac Fazy I 1995). In the Kraków region there are also remarkable emissions from local industrial sources including a large steel factory (Huta Tadeusza Sendzimira) at the eastern outskirts of the city. The location of the sampling point is representative of the area of town. The Kraków region is in the transition zone between a maritime climate, with prevailing influence of Atlantic Ocean, and a continental climate, characterized by northeast and east circulation.

The aim of the present work is: 1) to quantify changes in the carbon isotope ratio in atmospheric CO_2 and calculate the fossil component over an industrial and highly urbanized area (Kraków region) during intensive reconstruction of heavy industry and significant lowering of coal usage, and 2) to document the increasing contribution of CO_2 from natural gas (using the stable isotope signal), and provide an estimate of this effect.

METHODS

At the Kraków sampling station, atmospheric CO_2 is continuously sampled by sorption in a molecular sieve in biweekly intervals. Sampled air (usually *ca.* 15 m^3) is pumped through a container with a molecular sieve, and after thermal desorption, >5 dm^3 of CO_2 is obtained, from which $\delta^{14}C$ and $\delta^{13}C$ are measured (Florkowski *et al.* 1975; Kuc 1991). The CO_2 concentration is measured by the volumetric method, albeit with a relatively high error (<5%). For carbon isotopic measurements ($\delta^{14}C$, $\delta^{13}C$), we use liquid scintillation spectrometers (Tri-Carb®, Canberra-Packard), and mass spectrometers (VG Micromass 602 C and Finnigan Mat Delta S), respectively. The overall measurement error is *ca.* ±8‰ for $\delta^{14}C$, and ±0.09‰ for $\delta^{13}C$.

The radiocarbon results are reported as $\delta^{14}C$ in per mil (‰) *versus* NBS Oxalic Acid (contemporary standard for ^{14}C-dating laboratories) following the generally accepted notation (Stuiver and Polach 1977), and corrected for decay since 1950. The stable carbon isotope ratio, $\delta^{13}C$, is reported on the VPDB scale (Coplen 1995; Allison *et al.* 1995). N_2O was not determined in the samples, and correction for presence of this gas was not included. This could make a difference of *ca.* +0.2‰ at the atmospheric concentration of N_2O *ca.* 300 ppb (Mook and Jongsma 1987).

RESULTS AND DISCUSSION

During 1983–1994, the carbon isotope composition in atmospheric CO_2 at the Kraków sampling site showed well-pronounced seasonal oscillations superimposed on the long-term trends. Linearization of data, permissible for shorter time intervals (Kuc 1991) for this 12-year period, does not reflect the behavior of the isotope signals. Exponential smoothing of points measured biweekly reflects seasonal fluctuations; the long-term trend is approximated by a second-order polynomial (Fig. 1). Both $\delta^{14}C$ and $\delta^{13}C$ are gradually decreasing with time ($\Delta\delta^{14}C \approx -92‰$, $\Delta\delta^{13}C \approx -0.24‰$ for the 12-year interval). However, fits to ^{14}C data point to a broad minimum in 1991 (Fig. 1a) with an increase following by *ca.* 10‰ to end of 1994. The observed decrease in $\delta^{13}C$ (Fig. 1b) is well represented by a straight line. The record of CO_2 concentrations reveals a constant level (within measurement error) with overlapping seasonal oscillations. The 12-year average value is *ca.* 373 ppmv; the highest yearly mean (376 ppmv) was recorded in 1991. A small decrease is evident over the last 3 years. At Schauinsland station (Germany), the yearly mean concentration increased from 345.0 to 357.7 ppmv between 1983 and 1991 (Levin *et al.* 1995); over the same period at K-Puszta station (Hungary), the increase was from 355.7 to 372.3 ppmv. However, since 1988, fluctuations of *ca.* 369 ppmv have been observed (Haszpra 1994). The station is subject to significant biospheric effects due to its location.

The atmospheric $^{14}CO_2$ concentration at the Kraków site is systematically lower than the reported background fit for Europe (Levin *et al.* 1995). The difference reaches 44‰ in January 1983, showing a tendency decreasing to 41‰ in January 1993. However, the local minimum of $\delta^{14}C$ observed at Kraków, and the following small increase, diminishes this difference significantly after 1991. This effect is probably of regional significance, resulting from a remarkable reduction in the use of coal as fuel, mainly for industrial purposes and heating the city, since 1990.

The $\delta^{13}C$ values of atmospheric CO_2 at Kraków in 1983–1994, fitted with a second-order polynomial, show a linear decrease with the slope of −0.02‰ a^{-1} (Fig. 1a). The $\delta^{13}C$ value in 1983 (−9.9‰) is *ca.* 1.7‰ more negative than the uncontaminated marine air in the Northern Hemisphere (Mook *et al.* 1983), and *ca.* 0.95‰ more negative compared to the Schauinsland data (Levin *et al.* 1995). The $\delta^{13}C$ of the upper envelope spot samples collected at Kraków in 1992–1993 (Fig. 3) corresponds with biweekly means for Schauinsland (Levin and Kromer 1997), and are more positive than the Kraków biweekly means. The Kraków values are *ca.* 1.5‰ more negative than the Schauinsland data.
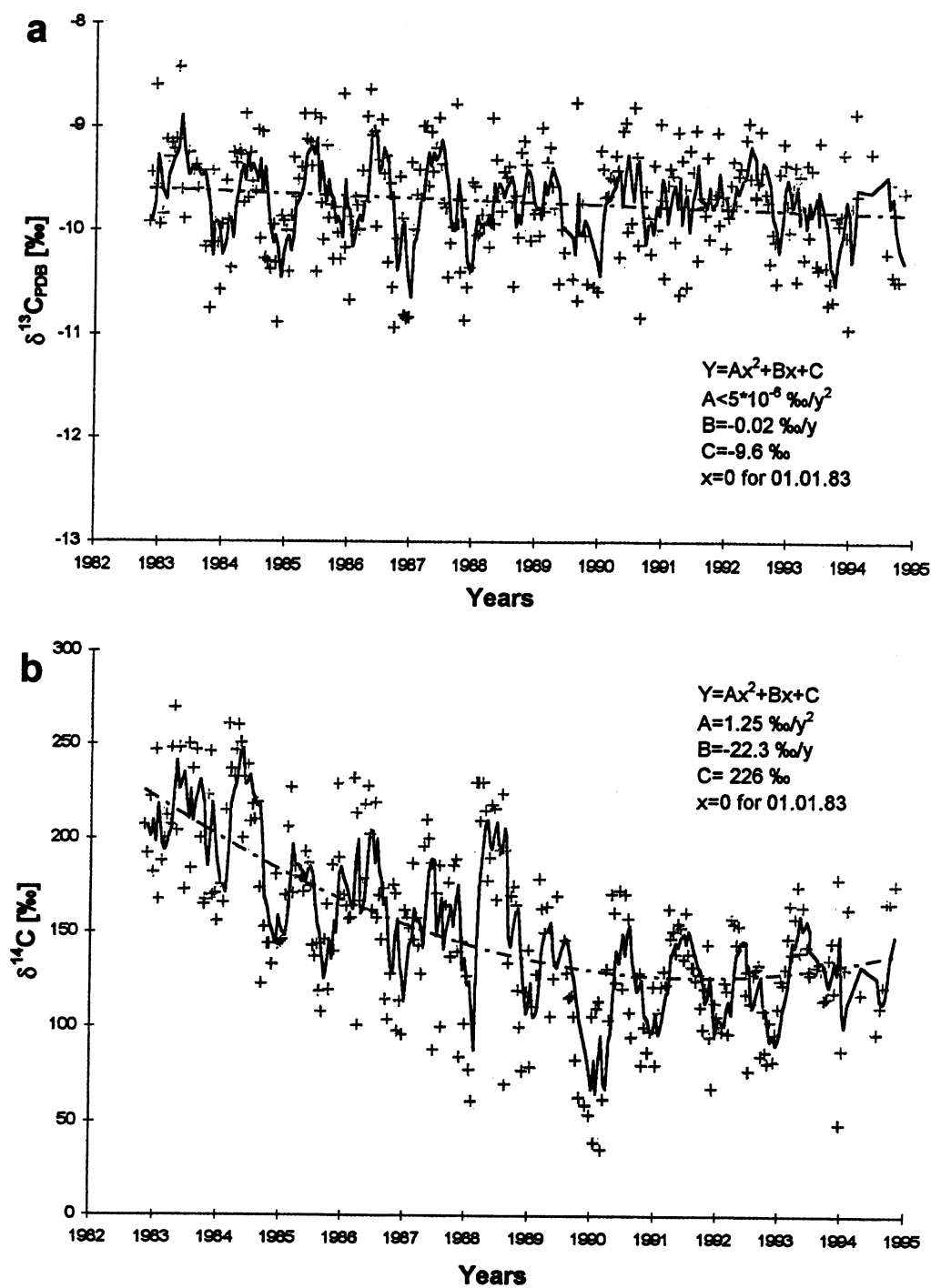
a

$$Y=Ax^2+Bx+C$$
$$A<5*10^{-6} \%o/y^2$$
$$B=-0.02 \%o/y$$
$$C=-9.6 \%o$$
$$x=0 \text{ for } 01.01.83$$

b

$$Y=Ax^2+Bx+C$$
$$A=1.25 \%o/y^2$$
$$B=-22.3 \%o/y$$
$$C= 226 \%o$$
$$x=0 \text{ for } 01.01.83$$

Fig. 1. Trends of $\delta^{13}C$ (a), and $\delta^{14}C$ (b) in atmospheric CO_2 in 1983–1994 at the Kraków sampling site. Biweekly means (crosses) are exponentially smoothed (solid line). The long-term trend (broken line) is represented by fit to second-order polynomial (polynomial coefficients indicated below graph a, and above graph b).
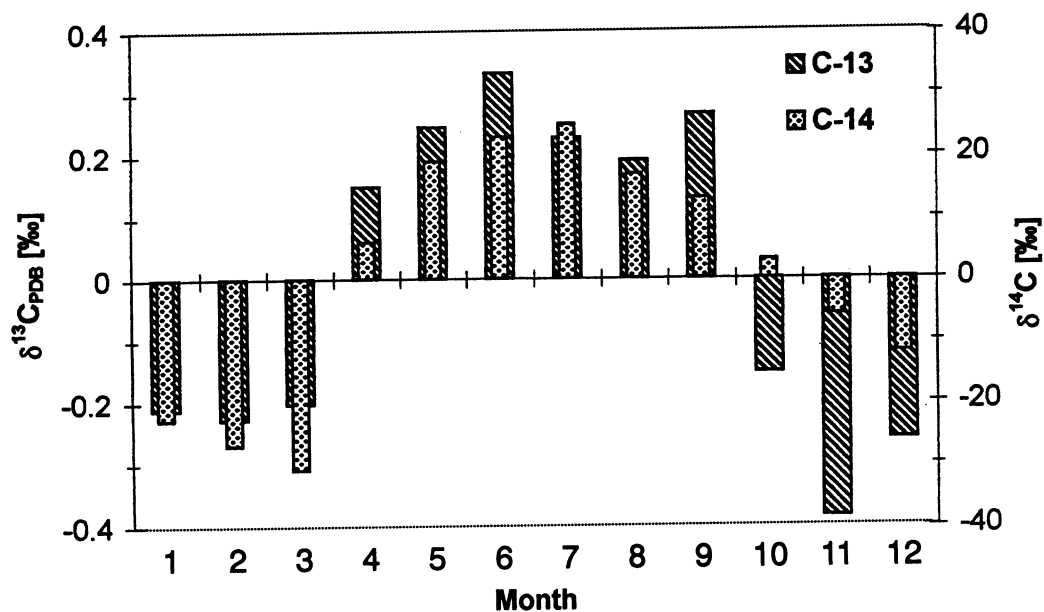
Fig. 2. Monthly mean detrended values of $\delta^{14}C$ and $\delta^{13}C$ averaged for 1983–1994 in atmospheric CO_2 at the Kraków site
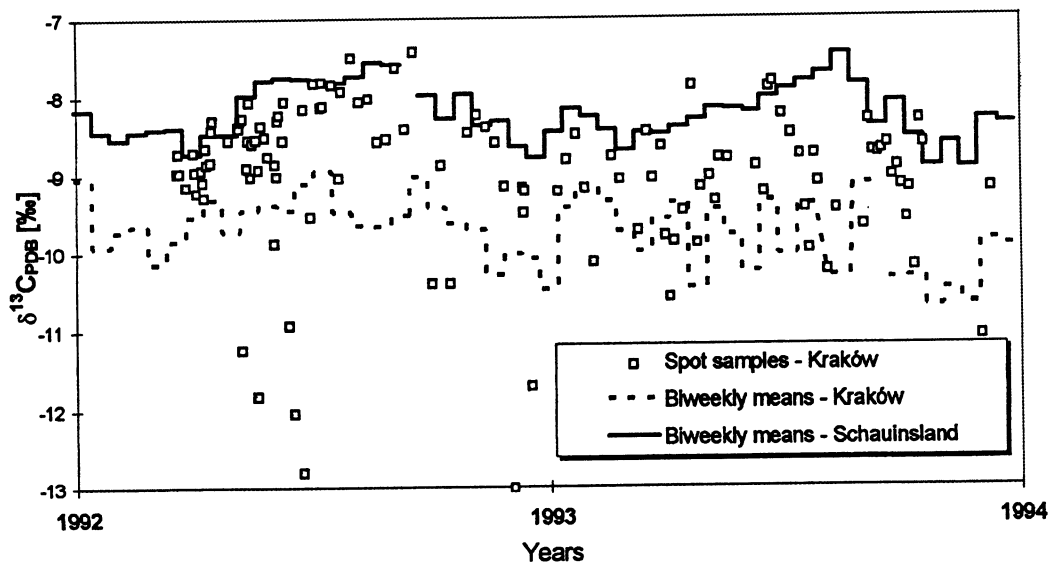

Fig. 3. $\delta^{13}C$ of atmospheric CO_2 at different sampling points (1992–1993). Schauinsland biweekly means after Levin and Kromer (1997).

The well-pronounced seasonality of the isotope signal during the 12-year observation period (minima in winter and maxima in summer) makes it possible to calculate the average seasonal effects. The monthly mean and detrended values of $\delta^{14}C$ and $\delta^{13}C$ (before the average long-term trend was subtracted) are presented in Figure 2. The highest values of $\Delta\delta^{13}C$ and $\Delta\delta^{14}C$ were observed in the

summer months (June, July) reaching +0.33‰, and 24.8‰ above the trend, respectively, while the lowest values of $\Delta\delta^{13}C$ appear in November (–0.39‰) gradually increasing until summer. The observed peak-to-peak difference is *ca.* 0.71‰. For $\Delta\delta^{14}C$, the minimum (–30.5‰) is observed 4 months later than for $\Delta\delta^{13}C$ (in February–March).

We assume that the local atmospheric CO_2 is a mixture of three components: 1) fossil CO_2, which is generated during the burning of fossil fuels, 2) biogenic CO_2, which is released from the biosphere, and 3) primary (background) CO_2 representing the undisturbed regional signal. The known isotopic signatures ($\delta^{14}C$, $\delta^{13}C$) of each component allow for separation of fossil fuel from biogenic and primary CO_2 components.

For the reference value (clean air) of the ^{14}C concentration, we used numeric values of the Schauinsland record with an introduced correction of +6‰ (Levin and Kromer 1997), and for 1983 to June 1994, the background fit from observations for Jungfraujoch (Levin *et al.* 1995), which we assume to be representative of the biogenic and background (atmospheric) component ($\delta^{14}C_b = \delta^{14}C_a$) over continental Europe.

The mass balance equations for carbon, ^{13}C and ^{14}C can be formulated as

$$C = C_f + C_b + C_a \tag{1}$$

$$C\delta^{13}C = C_f\,\delta^{13}C_f + C_b\,\delta^{13}C_b + C_a\,\delta^{13}C_a \tag{2}$$

and

$$(1 + \delta^{14}C)\,C = (1 + \delta^{14}C_f)\,C_f + (1 + \delta^{14}C_b)\,C_b + (1 + \delta^{14}C_a)\,C_a \tag{3}$$

where

    C = atmospheric concentration (volumetric ratio), ppmv
    δ = notation in ‰
    $(1 + \delta^{14}C_f) = 0$, and
    f, b and a = fossil, biogenic and background (atmospheric) components, respectively.

The fossil component (C_f), derived from Equation 3, used a mixture of two components: C_f, and $C_a + C_b$, while $\delta^{14}C_a = \delta^{14}C_b$, and applying for concentration (C) values measured at the Kraków sampling point.

The seasonal fluctuation of the derived fossil component (C_f) is correlated with the heating period in the urban area (Fig. 4). The yearly means of this component (Fig. 4a) show a remarkable decrease from 27.5 ppmv in 1990 to *ca.* 11.5 ppmv in 1994. This decrease is well correlated with the reported consumption of coal in power and heating stations in Poland (Fig. 4b) forming the "long-distance background", and substantial decrease in the local CO_2 emissions (cuts in production and upgrading technology in the neighboring HTS foundry as well as change of heating method in the city, *i.e.*, the shutdown of local, inefficient coal-heating stations, replaced partly by natural gas and electric heating). We note that the reduced input of ^{14}C-free CO_2 to the atmosphere, marked in the $\delta^{14}C$ record, is not pronounced in the $\delta^{13}C$ data. This can be caused by a significant increase of gas burning for heating purposes in the Kraków agglomeration (8% in 1990 to >16% in 1995, according to estimates by Raport z Prac Fazy I (1995)). The $\delta^{13}C$ of methane supplied to the city gas network is *ca.* 54.4‰ (Mirosław *et al.* 1997), which is characteristic for natural gas from the east-European suppliers. A simple "isotopic" calculation (Eq. 2) allows us to estimate the share of CO_2 from natural gas (C_{fg}) in the fossil component (C_f). For comparison, we choose the winters of 1990 and 1994. Assuming that in
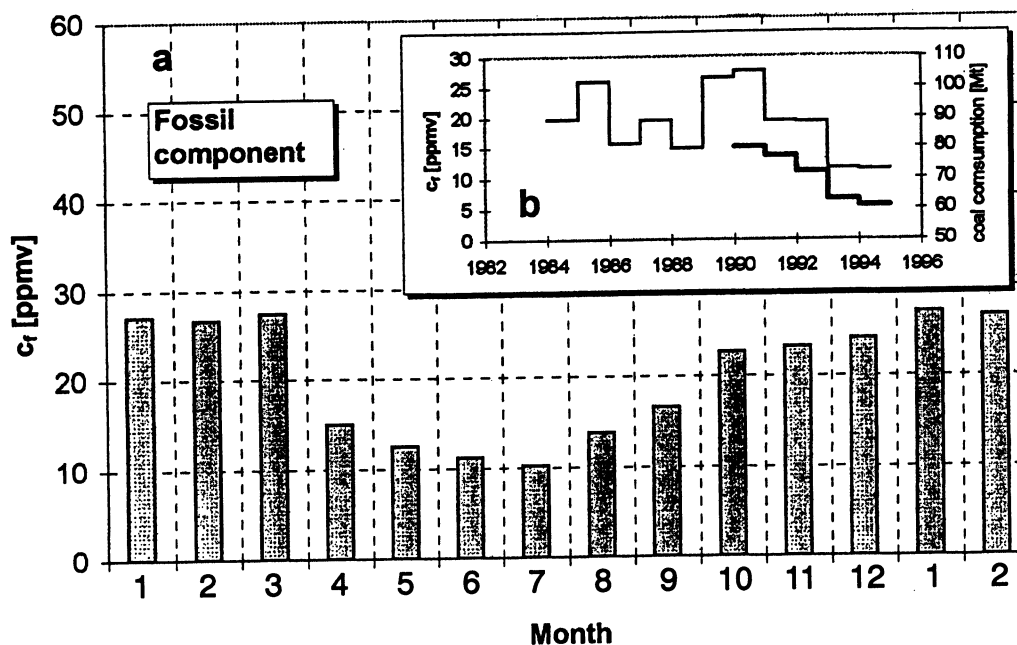
Fig. 4. Monthly means of fossil component C_f, averaged for 1983–1994 in atmospheric CO_2 at the Kraków sampling site (a). Yearly means of the fossil component, C_f (thin solid line), and total tonnage of coal burned in Polish power and heating stations (thick solid line), after Rocznik Statystyczny (1996) (b).

January–March 1990, $C_{fg}/C_f = 0.1$ (10% of CO_2 originated from natural gas), which determined $\delta^{13}C_f = -27.0‰$, while measured parameters were $\delta^{13}C = -10.0$ ‰, $C = 371$ ppmv, and calculated $C_f = 35.2$ ppmv. Four years later, in January–March 1994, respective values were $\delta^{13}C = -9.8‰$, $C = 367$ ppmv, $C_f = 15.2$ ppmv, and estimated $\delta^{13}C_{a+b} = -8.4‰$. Based on this, one can calculate isotopic composition of fossil component in winter 1994 ($\delta^{13}C_f = -42.0‰$). Known values of $\delta^{13}C$ for coal and natural gas ($\delta^{13}C_g = -54.4‰$, $\delta^{13}C_{coal} = -24.0‰$), applied to the balance the equation, point to a *ca.* 59% contribution of CO_2 from natural gas in the fossil component (C_f), expressed as a concentration (C_{fg}), is *ca.* 3.5 ppmv, and 9.0 ppmv for 1990 and 1994, respectively. In comparison, a >50% share of CO_2 from natural gas in exhausted CO_2 is reported for the Netherlands (Meijer *et al.* 1996).

CONCLUSION

^{14}C concentrations ($\delta^{14}C$) in atmospheric CO_2 recorded at the Krakow sampling point are systematically lower than the reference background, which is a result of the fossil fuel effect. The calculated fossil component varies seasonally from *ca.* 27.5 ppmv in winter to *ca.* 10 ppmv in summer. The increase of $\delta^{14}C$ after 1991 is interpreted as a regional effect caused by the reduced consumption of ^{14}C-free fuels. A high contribution of anthropogenic CO_2 is confirmed by generally low $\delta^{13}C$, however, an increased input of CO_2 from the burned gas compensates for the expected trend towards higher values of $\delta^{13}C$.

The observed decrease of the fossil component in 1990–1994 is correlated with the total decrease in the quantity of coal burned in Polish power stations with a strong regional effect in the reduction of "consumption" of coal by the HTS foundry, and the reconstruction of the heating system in the historic city of Kraków. The assessed increased contribution of CO_2 from natural gas in the Kraków

agglomeration in 1994 shows higher values than those reported after examination of the supply. This is probably because some of the industrial uses of gas are not taken into account.

The measurement of isotopic ratios and concentration of atmospheric CO_2 is a powerful tool for identifying sources and sinks in the regions strongly affected by anthropogenic activity. For model calculations and differentiation between effects on a regional and continental scale, a large number of accurate measurements of isotopic ratios is required.

ACKNOWLEDGMENTS

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