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TWO DECADES OF REGULAR OBSERVATIONS OF $^{14}CO_2$ AND $^{13}CO_2$ CONTENT IN ATMOSPHERIC CARBON DIOXIDE IN CENTRAL EUROPE: LONG-TERM CHANGES OF REGIONAL ANTHROPOGENIC FOSSIL CO_2 EMISSIONS

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ABSTRACT. Time series are presented of radiocarbon and ^{13}C contents in atmospheric carbon dioxide over eastern Europe (southern Poland), covering the periods 1983–1994 and 2000–2004. The carbon isotope composition was measured in biweekly composite samples of atmospheric CO_2, collected about 20 m above the local ground level. The data for 2 observational sites are presented: i) city of Kraków (50°04′N, 19°55′E; 220 m asl; for 1983–1994 and 2000–2004); and ii) Kasprowy Wierch, Tatra Mountains (49°14′N, 19°56′E; 1989 m asl; for 2000–2004). The latter site is considered a regional reference station, relatively free of anthropogenic influences. During the period 1983–1994, observations in the Kraków area revealed a gradual decrease of ^{14}C content with a broad minimum around 1991 and a small increase by about 10‰ in the subsequent years. $\delta^{13}C$ also changes with time, showing a decreasing trend from approximately –9.6‰ in 1983, with a slope of –0.02‰/yr. The observed trends for both isotopes coincide well with a substantial reduction of coal consumption in Poland and partial replacement of coal by natural gas, especially in urban regions. After 2000, the $\delta^{13}C$ slightly increases, reaching a mean value of –10‰ in 2004, while $\Delta^{14}C$ is below the reference level by ~3.5‰. Observations at Kasprowy Wierch (regional reference station) also reflect a diminishing input of fossil carbon into the regional atmosphere. The fossil component in atmospheric CO_2, calculated with the aid of ^{14}C data available for the 2 study periods, shows a reduction of anthropogenic input by a factor of 2, which is confirmed by annual statistics of coal consumption.

INTRODUCTION

Carbon isotope composition of atmospheric carbon dioxide (CO_2) constitutes an important source of information on carbon circulation between the atmosphere, biosphere, and oceans. It also helps to quantify anthropogenic disturbances of the carbon cycle. Observations of atmospheric CO_2 were initiated by Keeling in the late 1950s (e.g. Keeling et al. 1984) and are continued currently at numerous sites belonging to s global network of observations (GLOBALVIEW-CO_2 2006). The observed variations of annual accumulation of CO_2 in the atmosphere over the last 3 decades were much greater than the annual variability of fossil emissions. This is due to the fact that observed changes in accumulation of atmospheric CO_2 also reflect the fluctuating balance between ocean and land CO_2 fluxes. Contrary to marine stations, only continental sampling sites are able to directly record signals of biospheric and fossil emissions of CO_2. The European continent, densely populated with numerous large consumers of fossil fuels, which results in anthropogenic CO_2 emissions, plays an important role in the global carbon budget. Without quantification of the fossil CO_2 contribution into the regional atmosphere, sources and sinks of biogenic CO_2 cannot be estimated from the atmospheric CO_2 record. However, observations of CO_2 concentration alone do not provide information on apportionment of biogenic and fossil fuel-related sources of CO_2. In order to perform such apportionment, additional information is required. Such information can be obtained from the radiocarbon signature of carbon stored in atmospheric CO_2. In western Europe, a network of inland stations recording atmospheric CO_2 mixing ratios was established in the early 1970s (e.g. Levin et al. 1995). In the framework of this network, 3 stations (Jungfraujoch, Schauinsland, and Westerland) also perform long-term measurements of carbon isotopes in atmospheric CO_2.

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A number of studies aimed at a better understanding of the role of CO_2 in global warming have demonstrated advantages of using carbon isotope composition for quantifying fossil-fuel emissions on both small and large scales (Tans et al. 1979; de Jong and Mook 1982; Meijer et al. 1996; Randerson et al. 2002; Kuc et al. 2003; Levin et al. 2003). These studies confirmed that ^{14}C is a particularly useful tracer for detecting the fossil carbon and for assessing its contribution to the environment on different spatial and temporal scales.

In Poland, systematic measurements of carbon isotope composition in atmospheric CO_2 have been performed since 1983 by the Department of Environmental Physics, AGH University of Science and Technology, Kraków, Poland. Two sampling sites are currently in operation: the city of Kraków (50°14′N, 19°55′E; 220 m asl) represents a typical urban environment; and since 2000, Kasprowy Wierch (49°14′N, 19°59′E; 1989 m asl; 300 m above the tree line), a high-mountain meteorological observatory that can be regarded as a regional reference site relatively free of local influences. Regular observations of atmospheric CO_2 mixing ratios have also been performed at both sites. They are discussed in detail elsewhere (Chmura L, unpublished data).

DESCRIPTION OF SAMPLING SITES

Kasprowy Wierch

The Kasprowy Wierch station is located at the southern edge of Poland in the High Tatra Mountains (Figure 1). The meteorological observatory housing the station is located on a mountain peak called Kasprowy Wierch (49°14′N, 19°59′E; 1989 m asl; 300 m above the tree line) that is situated at the intersection of 3 main valleys at the border between Poland and the Slovak Republic. The nearest town, Zakopane, is located approximately 900 m below and 6 km north of Kasprowy Wierch. In this small tourist town situated in the valley, relatively large amounts of wood and fossil fuels are combusted during the winter season. The Kasprowy Wierch meteorological observatory is equipped with an electrical heating system and does not use any fossil fuel. During winter, diesel-operated snow cars are used in the nearby valleys to maintain proper conditions for skiing. The intake of outside air is located ~1 m above the roof of the observatory building, about 6 m above the ground level.

The climate of the Kasprowy Wierch area is typical for a continental mountain location, with large diurnal and seasonal variations of temperature, high precipitation rate, frequent changes of atmospheric pressure, and strong winds. The local surface winds are strongly influenced by the morphology of the surrounding area. A westerly circulation dominates the lower atmosphere, with winds from the sector S-SW-W-NW-N contributing more than 75% to the local wind patterns. The average wind speed recorded at Kasprowy Wierch is around 7 m/s. The winter season lasts for about 8 months and ends rapidly after strong foehn circulation in the spring.

Since Kasprowy Wierch is situated within the transition zone between the free troposphere and the planetary boundary layer and is relatively free of local influences, this site is considered a regional reference station for trace gas measurements in the lower atmosphere. Since 1996, regular observations of atmospheric mixing ratios of CO_2 and CH_4 have been performed at this site (Necki et al. 2003).

Kraków

Kraków (50°04′N, 19°55′E; 220 m asl) is the 4th largest city in Poland and is located approximately 100 km north of the Tatra Mountains. With about 1 million inhabitants, rapidly growing car traffic, and significant industrial activities, Kraków represents a typical urban environment. Kraków is located in the Vistula River valley, which is oriented east-west. To the south, the city borders a hilly

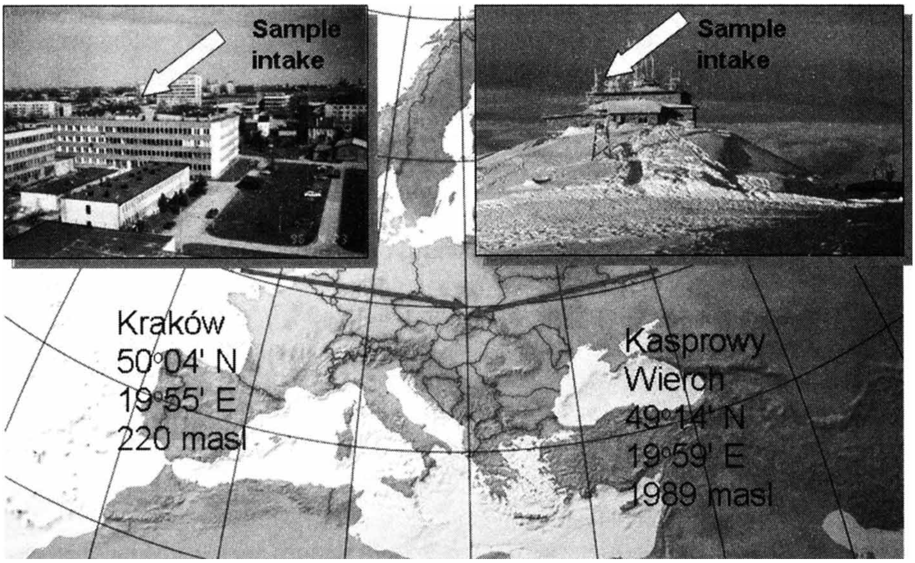

Figure 1 Location of the continental sampling sites in southern Poland: Kasprowy Wierch, a high mountain station at the northern edge of the Tatra Mountains; and Kraków, a large city in the Vistula River valley.

region, while to the north it opens towards a flat upland area. Local sources of fossil CO_2 derived from coal, gas, and oil consumed for communal and transport purposes generate the main flux of anthropogenic CO_2 within the region. In addition, with the prevailing westerly circulation, the Kraków region is under the substantial influence of a large coal mining and industrial center (Upper Silesia) located approximately 60 km west of the city. The sampling site is situated on the university campus (Figure 1) in the western part of the city, bordering recreation and sports grounds. The air intake is placed on the roof of the Faculty building, approximately 20 m above the ground level.

Characteristic features of the local climate are generally weak winds (annual average ~2.7 m/s) and frequent inversions, extending sometimes over several days (particularly during the winter). These factors favor accumulation of gases from surface emissions within the lower atmosphere above the city.

SAMPLING AND MEASUREMENT

Sampling of atmospheric CO_2 for measurements of $^{14}CO_2/^{12}CO_2$ and $^{13}CO_2/^{12}CO_2$ ratios was performed at both sites using the method based on sorption of CO_2 on a molecular sieve (Kuc 1991). Sampled air was pumped with a constant flow rate through a system of 2 traps, one filled with silica gel and the other with a molecular sieve. The total yield of the sampling process is better than 95%. The role of silica gel is to remove a majority of the moisture, while CO_2 is quantitatively absorbed on the molecular sieve. Thermal desorption under vacuum is used to extract the absorbed CO_2 from the molecular sieve. The memory effects of the system are within the quoted uncertainty of ^{14}C analyses (T Kuc, unpublished data).

The typical sampling interval is 2 weeks, during which about 15 m^3 of air is pumped through the system. As a result, an integrated sample of CO_2 (typically ~5 dm^3 STP) representing the 2-week sampling interval is obtained. The ^{14}C content in the collected CO_2 is measured using benzene syn-

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thesis followed by liquid scintillation spectrometry (Florkowski et al. 1975; Kuc 1991). The ^{13}C content of the collected CO_2 is determined using standard mass-spectrometry techniques.

The results of ^{14}C measurements ($\Delta^{14}C$) are reported in per mil (‰) versus the NBS oxalic acid standard, following the generally accepted notation (Stuiver and Polach 1977; Mook and van der Plicht 1999). The NBS standard is corrected for decay since 1950. The stable isotope ratios ($\delta^{13}C$) are reported on the VPDB scale (Coplen 1996). Correction for N_2O has not been applied to the presented time series of $\delta^{13}C$. N_2O is present in the atmosphere and is collected on the molecular sieve together with the CO_2 sample; N_2O cannot be separated cryogenically from CO_2. When introduced to the mass spectrometer together with CO_2, N_2O will contribute to the mass 44, thus influencing the measured $^{13}C/^{12}C$ ratios (Gorczyca and Piasecka 2004). Since 2000, N_2O has been regularly monitored during $\delta^{13}C$ measurements, and the average correction was about +0.072‰ for Kraków and +0.061‰ for CO_2 sampled at Kasprowy Wierch. Typical uncertainties of $\Delta^{14}C$ and $\delta^{13}C$ determinations (1 σ) are on the order of ±8‰ and ±0.1‰, respectively.

RESULTS AND DISCUSSION

The carbon isotope ratios measured over the past 2 decades in Kraków and since 2000 at Kasprowy Wierch are presented in Figures 2 ($\Delta^{14}C$) and 4 ($\delta^{13}C$). Both stations are situated far from the Atlantic coast and are sampling air masses that have been modified above the continent before their arrival to eastern Europe. The extent of this modification by surface CO_2 fluxes of biogenic and anthropogenic origin varies both in space and time. For Kraków (elevation ~200 m asl), this modification is much more pronounced mostly due to the strong influence of local sources and sinks of CO_2. The Kasprowy Wierch site, thanks to its location (elevation 1989 m asl), is often sampling free atmosphere above the planetary boundary layer, thus responding to changes of carbon isotope characteristics of air masses that have occurred on a regional or even continental scale.

For the reference records for $\Delta^{14}C$ and $\delta^{13}C$, we adopted the data available for 2 stations: for $\Delta^{14}C$, Schauinsland, Germany (47°55′N, 7°55′E; 1205 m asl; Levin and Kromer 2004); and for $\delta^{13}C$, Mace Head, Ireland (53°20′N, 9°54′W; 25 m asl; GLOBALVIEW-CO_2 2006). The Schauinsland station is located on top of a mountain in the Black Forest, southern Germany, and represents a continental site that is relatively free of local anthropogenic influences. Nevertheless, a small contribution of anthropogenic emissions has been detected for this station. As seen in Figure 2, Schauinsland's $\Delta^{14}C$ record is below the continental reference (Jungfraujoch, a high-altitude station in the Alps) by 2–6‰ during the summer and 10–15‰ during the winter months (Levin et al. 2003). Nevertheless, the Schauinsland record was chosen as a reference because it covers a longer period than the Jungfraujoch record, which only starts in 1986 and is not available past 2003, and represents similar environmental conditions to those encountered at Kasprowy Wierch and Kraków. The Mace Head station is a typical maritime site providing information on ^{13}C content in atmospheric CO_2 present in air masses entering the European continent from the North Atlantic Ocean.

The $\Delta^{14}C$ record available for Kraków (Figure 2) reveals well-pronounced seasonal oscillations superimposed on the long-term trend, which varies with time. The observed seasonality of the $\Delta^{14}C$ record stems mainly from the seasonal nature of CO_2 emissions associated with enhanced burning of fossil fuels during the winter (heating systems), as well as seasonal changes in the degree of vertical mixing of the lower atmosphere. During winter months, nighttime inversions in Kraków often extend over several days.

A systematic offset of $\Delta^{14}C$ values recorded at Kraków with respect to the reference station (Schauinsland) is observed for the entire available record (1983–2004). The slope of the trend curve

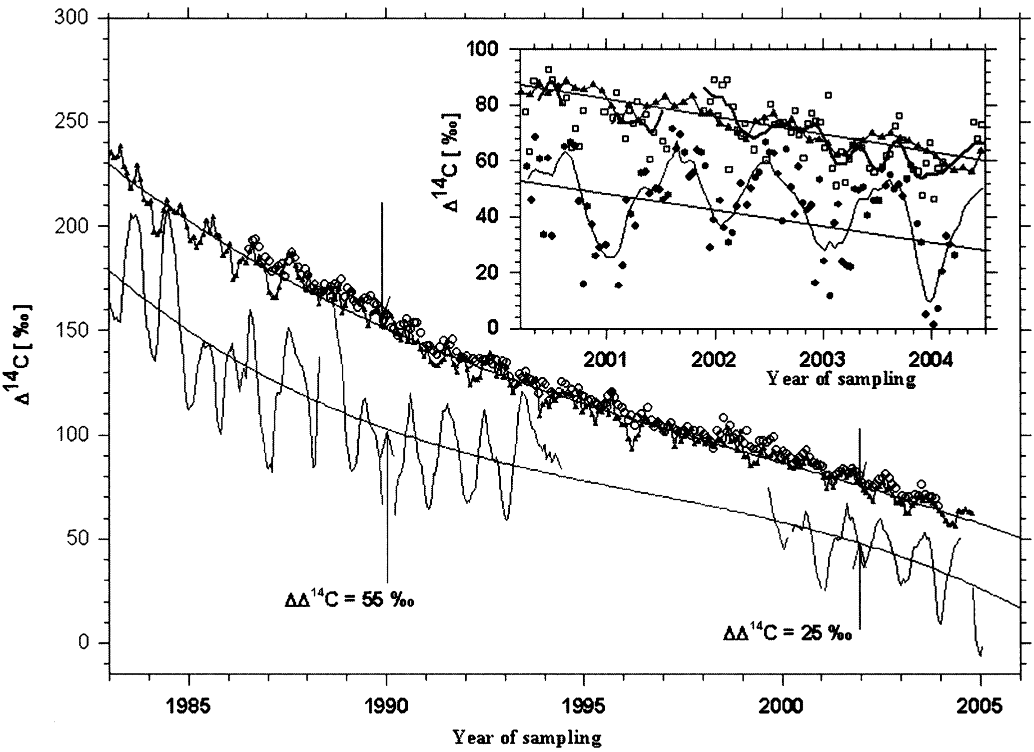

Figure 2 Main panel: smoothed $\Delta^{14}C$ record of atmospheric CO_2 obtained at the Kraków sampling site (lower curve) compared with the reference data for Schauinsland (triangles) and Jungfraujoch (open circles). Insert: the $\Delta^{14}C$ data obtained for Kasprowy Wierch (open squares, bold line), Kraków (black dots, thin line, lowermost), and Schauinsland (triangles, thin line) for the period 2000–2004. The differences between the smoothed Kraków $\Delta^{14}C$ data and the Schauinsland data (for January 1990 and January 2002) are marked by vertical arrows. These differences are labeled as $\Delta\Delta^{14}C$ and are equal to 55‰ and 25‰, respectively.

for the first part of the record (1983–1989) is close to the trend observed at Schauinsland (around 11‰ per year). The difference between the mean $\Delta^{14}C$ values recorded at both sites reaches about 55‰ (Kraków being depleted in ^{14}C with respect to Schauinsland) and is roughly constant for this part of the record. The peak-to-peak amplitude of the seasonal cycle observed at Kraków is much higher than of that recorded at Schauinsland and varies strongly from year to year. Significant changes in the temporal trend of the $\Delta^{14}C$ record are visible for the period from 1989 to 1994. The yearly mean $\Delta^{14}C$ values remain on a roughly constant level at about 90‰ until 1993 and an increase to 100‰ in 1994. The peak-to-peak amplitudes of seasonal $\Delta^{14}C$ changes are reduced (~50‰ compared to 75‰ for 1983–1985) and are more regular during this period. The offset with respect to the reference record decreases gradually until about 30‰, observed in December 1994. The most recent part of the $\Delta^{14}C$ record (from 2000–2004) is even closer to the reference, with the offset not exceeding 25‰ and with smaller amplitudes (~30‰) of the seasonal changes. A more detailed analysis of the $\Delta^{14}C$ record available for this period reveals the following features: i) the upper envelope of the record (summer values) reveals a slightly smaller slope than the reference data; ii) the lower envelope of the record (winter values) reveals an opposite tendency, with the offset growing with time (seasonal amplitudes gradually increasing); and iii) the trend line fitting the yearly means of $\Delta^{14}C$ has the same slope as the reference record, with the offset fluctuating around ~23‰ (Figure 2).

A comparison of $\Delta^{14}C$ records available for the most recent period (2000–2004) for Kasprowy Wierch and Kraków with that available for the reference site (Schauinsland) is shown in the insert of Figure 2. It is apparent that, in spite of a considerably larger spread of individual data points, temporal evolution of $^{14}CO_2$ content observed at Kasprowy Wierch essentially follows the long-term changes of $\Delta^{14}C$ recorded at the reference site (Schauinsland). Seasonal changes of $\Delta^{14}C$ are less visible at Kasprowy Wierch, which could be due to the larger uncertainty of individual $\Delta^{14}C$ determinations at this station and/or the cumulative influence of the regional continental biosphere and anthropogenic emissions along main routes of air masses moving from west to east.

The Kraków urban area has been under significant anthropogenic stress for the past several decades due to both local emissions as well as the influence of the heavily industrialized Silesia region. Thus, one may expect that this anthropogenic load will be reflected in the isotopic characteristics of CO_2 in the local atmosphere. Assuming that atmospheric CO_2 consists of 3 components (regional background, biospheric, and fossil fuel-derived CO_2), one can establish balance equations for both $^{12}CO_2$ and $^{14}CO_2$ molecules in air (Levin et al. 1989, 2003; Kuc et al. 1998):

$$C_{mix} = C_{bg} + C_b + C_f \quad (1)$$

$$C_{mix}(\Delta^{14}C_{mix} + 1000) = C_{bg}(\Delta^{14}C_{bg} + 1000) + C_b(\Delta^{14}C_b + 1000) + C_f(\Delta^{14}C_f + 1000) \quad (2)$$

where C_{mix} is the measured CO_2 mixing ratio; while C_{bg}, C_b, and C_f represent 3 components (background, biospheric, and fossil, respectively). Assuming that $\Delta^{14}C_b = \Delta^{14}C_{bg}$ (CO_2 flux from the biosphere originates predominantly from autotrophic respiration) and $\Delta^{14}C_{bg} = -1000$ (fossil CO_2 is free of ^{14}C), one obtains the following expression for the fossil fuel-derived component:

$$C_f = C_{mix}\frac{\Delta^{14}C_{bg} - \Delta^{14}C_{mix}}{\Delta^{14}C_{bg} + 1000} \quad (3)$$

Although CO_2 mixing ratios have been measured in Kraków since 2003, no continuous record is available for this site. Therefore, we adopted the background mixing ratios from GLOBALVIEW-CO_2 (2006) for the latitude of Kraków (50°N), with the seasonal amplitudes modified according the continuous CO_2 record available for Kasprowy Wierch. The calculations of C_f have been performed on a monthly basis for the entire $\Delta^{14}C$ record available for Kraków and were then averaged for 2 periods: 1983–1994 and 2000–2004. The results are presented in Figure 3. The insert in Figure 3 illustrates the temporal evolution of annual average C_f values between 1983 and 2004, superimposed on the statistics of annual consumption of coal in Poland during this period. The estimated uncertainty of the average annual C_f values shown in Figure 3 is about 20%.

It is apparent from Figure 3 that major changes have occurred during the last 2 decades in the local atmosphere of Kraków with respect to the load with fossil fuel-derived CO_2. The average yearly load decreased from approximately 21 ppm in 1988–1989 to 10–12 ppm in the past several years. This drop correlates well with the decrease in the consumption of coal, from about 160 Mt in 1985 (not shown in Figure 3), to 120 Mt in 1990, and to 84 Mt in 2004 (Central Statistical Office 2003, 2004, 2005). The drop in coal consumption is linked with the dramatic transformation of the Polish economy in the 1990s, leading to the introduction of more energy-efficient technologies and the implementation energy-saving programs in industry and the public sector. Also, the seasonality of the fossil component has changed dramatically. The average monthly C_f values for the period 1983–1994 vary between 26.9 ppm in December and 9.4 ppm in July, while during the period 2000–2004 they dropped to about 14 ppm and 6.7 ppm, respectively. However, it has to be noted that C_f values

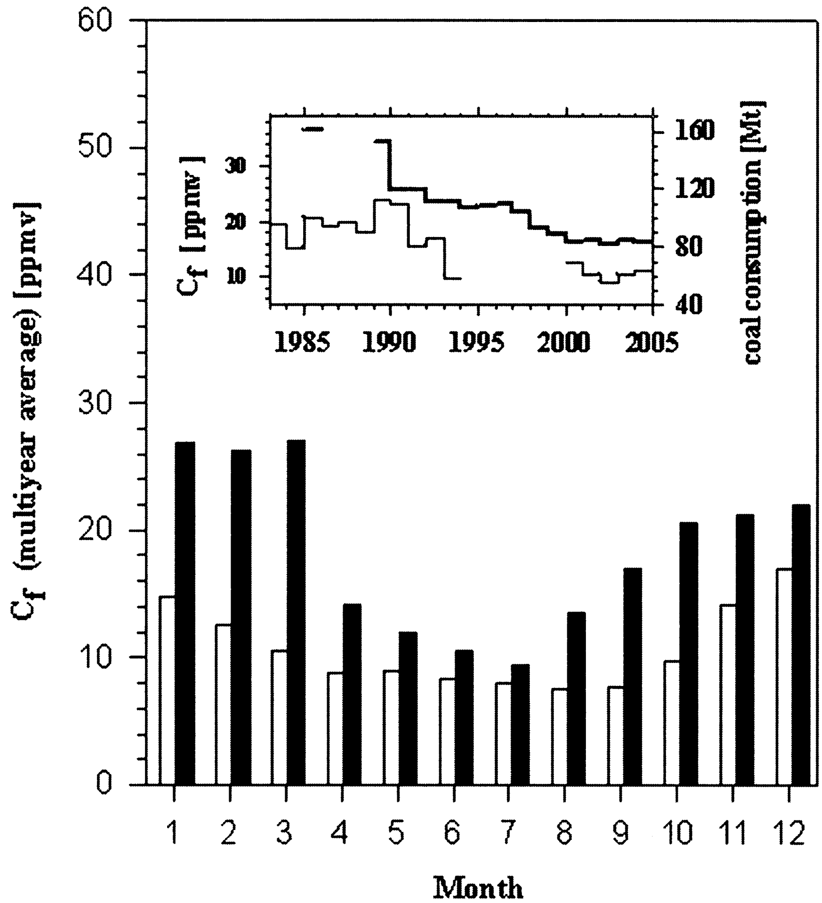

Figure 3 Main panel: seasonal variations of the fossil-fuel CO_2 component in the local atmosphere of the Kraków area, C_f, calculated as average monthly means for 2 periods: 1983–1994 (black bars) and 2000–2004 (open bars)—see text for details. Insert: changes of the yearly mean C_f values in Kraków atmosphere during the period 1983–2004 (thin line, left-hand scale) superimposed on the yearly mean consumption of coal in Poland during this period (thick line, right-hand scale).

presented in Figure 3 have been derived for the background mixing ratios from GLOBALVIEW-CO_2 (2006), with the amplitude of seasonal changes modified to match the seasonality of CO_2 mixing ratios observed at Kasprowy Wierch. The CO_2 mixing ratios available for Kraków since 2003 (covering ~30% of the time) suggest that the seasonal offset between the background curve amounts to about 20 ppm in summer and about 40 ppm in winter, which leads to ~10% higher C_f values when compared to those reported in Figure 3. In the 1980s and 1990s, this offset could be significantly higher. Thus, the reported C_f values should be considered only as a lower limit.

Major changes in the amount and structure of fossil CO_2 emissions that have occurred over the past 2 decades in Poland and in Kraków left their mark also on the measured $^{13}CO_2/^{12}CO_2$ ratios. Figure 4 summarizes the available $\delta^{13}C$ data. The $\delta^{13}C$ records available for the Kraków and Kasprowy Wierch stations for the period 2000–2004 are compared with the marine reference $\delta^{13}C$ record (Mace Head, Ireland) in the insert of Figure 4.

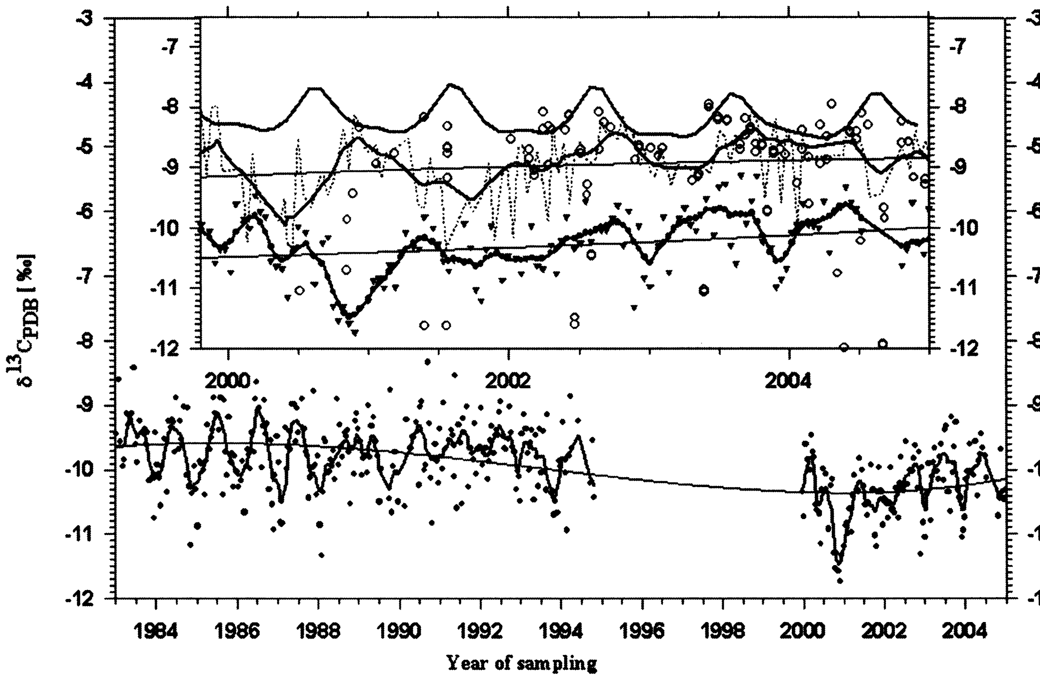

Figure 4 Main panel: smoothed $\delta^{13}C$ record of atmospheric CO_2 at Kraków sampling site (dots indicate data points). Insert: comparison of $\delta^{13}C$ records available for the period 2000–2004 for 3 sites representing different environments: i) city of Kraków, a typical urban environment (lowest curve, triangles); ii) Kasprowy Wierch, a high mountain site, continental area (middle curve, thin dotted line connects measurement points); and iii) Mace Head, an oceanic, coastal station (upper curve). Data points for Kraków and Kasprowy Wierch represent 2-week integrated samples. Open circles represent spot samples taken twice a month at Kasprowy Wierch.

The reduced input of ^{14}C-free CO_2 into the local atmosphere after 1989 should have been accompanied by an increase of $\delta^{13}C$ of atmospheric CO_2, which is not clearly seen in Figure 4. This expected increase should result from the fact that $\delta^{13}C$ values of CO_2 in an undisturbed marine atmosphere are around –8‰ (cf. Mace Head record shown in the insert of Figure 4), while $\delta^{13}C$ values for coal and oil range from about –20‰ to about –30‰ (Mook 2000). Instead of the expected increase, a distinct reduction of $\delta^{13}C$ values is apparent in the Kraków $\delta^{13}C$ record between 1990 and 2000. The most probable reason for such a shift is a significant decrease of the $\delta^{13}C$ signature of the locally released CO_2 due to the growing share of CO_2 originating from the burning of natural gas (a gradual change from coal to gas in local heating systems). The $\delta^{13}C$ value of methane supplied to the gas network in southern Poland fluctuates around –54‰ (Miroslaw 1997). The low $\delta^{13}C$ signature of the local CO_2 emissions has been confirmed by measurements of CO_2 and $^{13}CO_2/^{12}CO_2$ mixing ratios carried out on spot samples collected in Kraków during 2000. A 2-component mixing approach yields the characteristic $\delta^{13}C$ signature of CO_2 source mix (about –40‰) during the winter (Kuc et al. 2003).

During the most recent period (2000–2004), a parallel, slight increase in the recorded $\delta^{13}C$ values at both Kraków and Kasprowy Wierch is observed (cf. insert in Figure 4). This trend might reflect gradual "cleaning" of the regional atmosphere due to reduced CO_2 emissions related to fossil-fuel burning. However, as the spread of individual data points is relatively large, the significance of this trend remains to be demonstrated. The offset between $\delta^{13}C$ records available for Kraków and Kasprowy Wierch remains roughly constant (~1.2‰) during the discussed time period. The $\delta^{13}C$

record for Kasprowy Wierch gradually approaches the Mace Head reference curve. The average offset between those 2 stations diminishes from about 1.2‰ for the period 2000–2001 to approximately 0.8‰ during 2002–2004. Seasonal fluctuations of $\delta^{13}C$ are less regular and shifted in phase with respect to the Mace Head record. The $\delta^{13}C$ values obtained for spot samples taken twice a month at Kasprowy Wierch (midnight sampling) scatter around the smoothed curve representing 2-week integrated sampling intervals.

CONCLUSION

Long-term observations of carbon isotope composition of atmospheric CO_2 at 2 continental sites located in eastern Europe in contrasting environments allowed some new insights into the dynamics of carbon cycling and the role of anthropogenic emissions. Despite their relative proximity, the 2 sites represent entirely different settings: i) a high-altitude mountainous area relatively free of anthropogenic influences; and ii) a typical urban environment with numerous local sources of CO_2 under the additional influence of a large, heavily industrialized area. The isotope records obtained for both sites revealed some similarities, but also substantial differences.

The $^{14}CO_2/^{12}CO_2$ ratios measured at Kraków since 1983 testify to major changes since 1989 in the economy of the region. The ^{14}C signature of atmospheric CO_2 reflects significant changes in anthropogenic CO_2 fluxes released into the atmosphere both on local and regional scales. The contribution of fossil fuel-derived CO_2 in the total CO_2 load of the lower atmosphere in Kraków decreased from approximately 21 ppm in 1989 to around 10–12 ppm in the last few years. This change is linked with the major reduction in coal consumption in Poland, from about 160 Mt in 1985 to 84 Mt in 2004. During the period immediately following the political change in Poland (1989–1992), consumption of oil and natural gas also decreased considerably.

The carbon isotope signature of atmospheric CO_2 measured at Kraków allowed us to trace not only the changes in the load of local atmosphere with fossil fuel-derived CO_2, but also to gain some insight into the structure of those emissions. The gradual replacement within the city of heating systems based on the burning of coal by more energy-efficient systems relying on natural gas has been imprinted in the temporal evolution of the measured $^{13}CO_2/^{12}CO_2$ ratios. This was possible due to the fact that natural gas in the city gas network has an isotopic signature distinctly lower than CO_2 being emitted as a result of burning of coal and oil.

The Kasprowy Wierch station confirmed its role as a suitable regional reference site for carbon isotopes. The $^{14}CO_2/^{12}CO_2$ ratios recorded at this station during the past 5 yr are indistinguishable from the analogous data obtained for Schauinsland station, located in southern Germany. As far as $^{13}CO_2/^{12}CO_2$ ratios are concerned, the Kasprowy Wierch data are gradually approaching the marine reference $\delta^{13}C$ curve, pointing to a gradual "cleaning" of the regional atmosphere.

The presented data clearly demonstrate the strength and usefulness of carbon isotopic composition of atmospheric CO_2 as a specific tool for identification and quantification of surface CO_2 fluxes of fossil-fuel origin. Systematic observations of carbon isotope signatures of atmospheric CO_2 allow one to trace long-term changes of the anthropogenic load of the lower atmosphere with respect to this important greenhouse gas.

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