CARBON ISOTOPE COMPOSITION OF ATMOSPHERIC CARBON DIOXIDE IN SOUTHERN POLAND: IMPRINT OF ANTHROPOGENIC CO₂ EMISSIONS IN REGIONAL BIOSPHERE

Anna Pazdur^{1,2} • Tadeusz Kuc³ • Sławomira Pawełczyk¹ • Natalia Piotrowska¹ • Barbara Sensuła¹ • Kazimierz Rozanski³

ABSTRACT. Southern Poland is home to numerous large mining and energy industry facilities, which consume relatively great amounts of fossil fuels. Temporal and spatial distribution of CO₂ emissions to the atmosphere were estimated on the basis of ¹³C and ¹⁴C isotope measurements in atmospheric CO₂ and in α -cellulose from pine tree rings. The Suess effect was evaluated in the atmospheric CO₂ from the High Tatra Mountains (Kasprowy Wierch) and the urban area (Kraków), as well as in tree rings from Niepołomice Forest near Kraków. Two different models were used to estimate the emission component recorded in tree ring δ^{13} C on the background of climatic changes.

INTRODUCTION

An abrupt increase in atmospheric carbon dioxide concentration over the last century, far exceeding natural variations, is unequivocally attributed to human activities in fast-developing countries in the Northern Hemisphere (Keeling et al. 2010; Conway and Tans 2011; NOAA 2011). The observed anthropogenic impact on the global carbon cycle, mainly related to fossil fuel and biomass burning, land-use changes, and various industrial activities (Marland et al. 2002) also caused changes in the isotopic composition of carbon not only in the atmosphere, but also in other reservoirs such as the biosphere and oceans. Identification and quantification of sources and sinks of carbon, and their temporal and spatial variability on both global and regional scales, is a prerequisite for a better understanding of the dynamics of the carbon cycle and its response to ever-increasing human impact (IPCC 2001; Levin et al. 2010).

This article presents investigations of carbon isotopic composition in samples of atmospheric CO₂, and carbon in wood material collected in the Kraków area and nearby Niepołomice Forest. Both locations are exposed to anthropogenic stress typical for heavily urbanized areas and areas in close proximity to large steel plants. In the collected samples representing the last 2 decades, the carbon isotope signature is studied with respect to local emissions of anthropogenic CO₂. Observed fluctuations of δ^{13} C content in α -cellulose and glucose extracted from tree rings covering the time period 1900–2000 are interpreted on the grounds of local climatic and habitat parameters, using simple mathematical models for quantification.

By measuring the ¹⁴C and ¹³C concentrations, we can determine the decrease in the concentration of these isotopes in modern atmospheric CO₂. Furthermore, the magnitude of emission to the atmosphere of CO₂ not containing the isotope ¹⁴C can be estimated on this basis. Such emissions in southern Poland originate from fossil fuel combustion—petroleum, natural gas, and black coal. Modeling is presented below of ¹⁴C results (Kuc and Zimnoch 1998; Zimnoch et al. 2012) for the southern Poland sites of Kraków, Niepołomice Forest, and Kasprowy Wierch.

²Corresponding author. Email: anna.pazdur@polsl.pl.

³AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059 Kraków, Poland.

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¹Silesian University of Technology, Institute of Physics, GADAM Centre of Excellence, Krzywoustego 2, 44-100 Gliwice, Poland.

Annual tree rings are another sensitive bioindicator of CO_2 emissions. Accelerator mass spectrometry (AMS) measurements of ¹⁴C concentrations in tree-ring material provide information about annual ¹⁴C changes. Trees, treated as an archive of changes in conjunction with data about the stable isotope composition of carbon, can be used for monitoring the environment as sensitive bioindicators on a local or global scale. Regular investigations of the isotopic composition of carbon in trees have been carried out at the GADAM Centre for urban areas of both Poland and worldwide (Rakowski et al. 2001, 2005, 2008; Pazdur et al. 2007). This method can be applied to the study of the emission of CO_2 to the atmosphere and its spatial and temporal distribution connected with the production of energy by power plants based on fossil fuel combustion for the area of southern Poland. Modeling of CO_2 emission using both ¹⁴C and ¹³C carbon isotopes measured in pine tree rings from Niepołomice Forest on the background of climatic changes will be presented.

STUDY AREA

Kasprowy Wierch

The Kasprowy Wierch monitoring station is located in the High Tatra Mountains of southern Poland (Figure 1). The meteorological observatory that houses the monitoring station is located on top of the mountain peak Kasprowy Wierch (49°14'N, 19°59'E, 1989 m asl, 300 m above the tree line). Kasprowy Wierch is situated at the intersection of 3 main valleys, on the border between Poland and the Slovak Republic. The nearest town, Zakopane, is located ~900 m below and 6 km north of Kasprowy Wierch. It is a small tourist town and major ski station on the northern side of the Tatra Mountains. During the winter, relatively large amounts of wood and fossil fuels are combusted in the valley. The Kasprowy Wierch 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.



Figure 1 Map of Poland showing the investigated sites: Kasprowy Wierch, Kraków, and Niepołomice Forest.

The climate of the Kasprowy Wierch area is typical for a continental mountain location, with relatively large diurnal and seasonal temperature variations, high precipitation rate, frequent changes in atmospheric pressure, and strong winds. The winds blow predominantly N-S, with an average speed

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of ~7 ms⁻¹. The winter season usually lasts for 8 months and ends quickly due to strong foehn-type circulation. Regular observations of atmospheric CO_2 concentrations started at Kasprowy Wierch in 1994, as a joint project of the AGH University of Science and Technology, Kraków, Poland, and the University of Heidelberg, Germany. Continuous measurements of CO_2 mixing ratios using gas counting (GC) were initiated in 1996. The intake of outside air is located ~1 m above the roof of the observatory and ~6 m above the local ground. The data gathered at Kasprowy Wierch station until 2000 were summarized by Necki et al. (2003). Zimnoch et al. (2012) discussed the records of atmospheric CO_2 mixing ratios and their ¹⁴C content available for this station for the period 2005–2010. 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 can be considered a regional reference station for trace gas measurements in the lower atmosphere.

Kraków

Kraków (50°04'N, 19°55'E, 220 m asl), the largest city in southern Poland, is located ~100 km north of Kasprowy Wierch. With more than 800k inhabitants, rapidly growing automobile traffic, and significant industrial activities, it represents a typical urban environment. Moreover, with the prevailing westerly winds along Vistula River valley, the Kraków region is under the substantial influence of a large coal mining and industrial center (Upper Silesia) located ~60 km west of the city. Characteristic features of the local climate are generally weak winds (annual average ~2.7 ms⁻¹) and frequent inversions, extending sometimes over several days (particularly during winter). These factors favor accumulation of surface gaseous emissions within the lower atmosphere above the city. The sampling site for atmospheric CO_2 measurements was situated at the university campus located in the western part of the city, bordering recreation and sports grounds. The air intake was mounted on the roof of the faculty building, ~20 m above the local ground level.

Niepołomice Forest

Niepołomice Forest is located in southern Poland (49°59′–50°07′N; 20°13′–20°28′E), ~20 km east of Kraków. Niepołomice covers ~110 km² but is only a small part of the primeval forest extending from Kraków to Sandomierz, ~300 km to the east. The area of the Niepołomice Forest is home to geological and geomorphologic variety as well as diverse ecosystems. Climatic conditions (temperature, precipitation, humidity) and human activities in the past determine the species of trees. In this mixed forest complex, the following species dominate: pine (*Pinus sylvestris*); oak (*Quercus robur* and *Quercus petraea*); and black alder (*Alnus glutinosa*). The vegetative period lasts for ~218 days from the beginning of April until October (Szarek-Łukaszewska et al. 2002). Heavy industry located in the vicinity of Niepołomice Forest and its intensified production in the 1960s is thought to have resulted in reduced widths of the annual tree rings observed since the late 1970s (Szychowska-Krapiec and Krapiec 2002; Szczepanek et al. 2006).

SAMPLING AND METHODS

Atmospheric CO₂

Sampling for measurements of ¹³C and ¹⁴C content in atmospheric CO₂ was performed at the Kraków and Kasprowy Wierch sites using the method based on sorption of CO₂ using a molecular sieve (Kuc 1991). Sampled air was pumped with a constant flow rate through a system of 2 traps mounted in series and filled with molecular sieves, preceded by a container with silica gel. The total yield of the sampling process was better than 98%. The role of the silica gel was to remove most of the atmospheric moisture, while CO₂ was quantitatively absorbed on the molecular sieve. Thermal

desorption under vacuum was used to extract the absorbed CO_2 from the molecular sieve. The memory effects of the system were within the quoted uncertainty of ¹⁴C analyses. ¹⁴C content in the collected CO_2 samples was measured using benzene synthesis followed by liquid scintillation spectrometry (Florkowski et al. 1975), while $\delta^{13}C$ content was measured using the conventional isotope ratio mass spectrometry (IRMS) technique.

¹⁴C concentration in the analyzed samples of atmospheric CO₂ is expressed as normalized, per mil deviation (Δ^{14} C) from the international ¹⁴C standard (Stuiver and Polach 1977; Mook and van der Plicht 1999). The δ^{13} C content in these samples is expressed as per mil deviation (δ^{13} C) from the internationally accepted standard V-PDB (Coplen 1996). Typical uncertainty of the reported atmospheric Δ^{14} CO₂ and δ^{13} CO₂ values (1 σ level) is in the order of 7 and 0.1‰, respectively.

Tree Rings

The α -cellulose samples used in the present study were collected from annual tree rings of pine and latewood of oak from trees sampled in the Niepołomice Forest under the FP5 ISONET project (EVK2-CT-2002-0014, 400 yr of Annual Reconstructions of European Climate Variability using a High Resolution Isotopic Network). Sampled trees were selected from the dominant species at the study site—Scots pine (*Pinus silvestris* L.) and oak (*Quercus robur* L.). In order to obtain representative samples, the wood material of annual tree rings taken from 4 trees was homogenized. The α -cellulose was extracted from cores, and sometimes from slices of trees of variable age, which were correlated and dated using dendrochronological methods. Within the ISONET project, the 400-yrlong time series of dendrochronological and stable isotope (C, O, H) data sets were obtained for the purpose of climate reconstruction in the past, covering the period of AD 1600–2002.

Isotopic records for the analyzed period were presented by Pazdur et al. (2007). In this work, the youngest data series have been used, covering the period of 1900–2002, for the modeling of climatic and CO₂ emission influences on the δ^{13} C. The α -cellulose samples were extracted from consecutive tree rings of pine and latewood of oak applying Green's (1963; Pazdur et al. 2005) method in the following steps: (1) removal of lignin with sodium chlorite and acetic acid; (2) processing of the holocellulose to α -cellulose in NaOH solution; (3) bleaching with HCl; and (4) neutralizing and drying. The reactions were performed in ultrasonic baths accelerating separation of the single cellulose fibers from the wood samples and increasing penetration of the reagents. Glucose was obtained by hydrolysis of α -cellulose using H₂SO₄ at conditions described by Chambat et al. (1997), based on the Saeman et al. (1954) protocol. The quantitative and qualitative analyses of hydrolysates, carried out at CERMAV-CNRS (Grenoble, France) using a Hewlett Packard 5890 gas chromatograph with a SP2380 column and a Hewlett Packard HP3395 integrator, were thoroughly discussed by Sensula et al. (2011). Measurements of ¹³C content were performed in the Gliwice Mass Spectrometry Laboratory using an IsoPrime system coupled to the Eurovector elemental analyzer (1935-2000 record of δ^{13} C in α -cellulose and glucose), and in UFZ-Umweltforschungszentrum Leipzig-Halle (Germany, 1900–2002 record). The results obtained of carbon and oxygen stable isotopes composition in α -cellulose and glucose samples were previously discussed (Sensuła et al. 2011).

Graphite targets for ¹⁴C AMS measurement were prepared at the Gliwice Radiocarbon Laboratory from the α -cellulose samples extracted from Niepołomice Forest pine tree rings in the following steps: (1) the α -cellulose was combusted in evacuated quartz tubes with CuO rods and Ag wool; (2) the obtained CO₂ was purified using dry ice/alcohol and liquid nitrogen traps; and (3) finally graphitized was done with an Fe catalyst (Piotrowska 2013). AMS measurements were conducted at the Center for Chronological Research (Nagoya University, Japan) using the HVEE 2.5MV AMS facility (Nakamura et al. 2000).

Climatic Data

Records of temperature, precipitation, and sunshine from the Kraków local meteorological station (50°07'N, 19°58'E) were used for estimating the emission component based on δ^{13} C measurements in annual pine tree rings and oak latewood from the Niepołomice Forest on the background of climatic changes. The Kraków station is the nearest unit conducting such measurements from the Niepołomice Forest area. The annual mean temperature is ~8.6 °C (for the last 100 yr), and the annual sum of precipitation is ~700 mm (Szarek-Łukaszewska et al. 2002; Szczepanek et al. 2006). The systematic meteorological data set used in the present work covers all of the longest series of δ^{13} C measurements, i.e. years 1900–2002.

¹⁴C AND ¹³C ISOTOPES IN ATMOSPHERIC CO₂ AND TREE RINGS

Radiocarbon in Atmospheric CO₂ and Tree Rings

Figure 2 shows long-term variations of ¹⁴C content in atmospheric CO₂ collected at Kraków during 1983–2004. Annual and growing-season (April–August) means of Δ^{14} CO₂ at Kraków for the period 1983–2004 are given in the figure. (For 1996–1999, no data are available.) The annual and growing-season averages were calculated using the Δ^{14} CO₂ results from biweekly cumulative samples of atmospheric CO₂. Time series of Δ^{14} CO₂ recorded at Kraków station are compared with analogous data available for the Kasprowy Wierch site for the period 2000–2004. Atmospheric Δ^{14} CO₂ data shown in Figure 2 are compared with the ¹⁴C content of cellulose extracted from annual tree rings of *P. silvestris* from Niepołomice Forest, ~15 km east of Kraków. Figure 2 also contains the regional reference Δ^{14} CO₂ curve for Jungfraujoch, a high-altitude mountain station located in the Swiss Alps and covering the period 1986–2004 (Levin et al. 2008).



Figure 2 Changes of ¹⁴C content in atmospheric CO₂ as observed in Kraków, southern Poland, during the period 1983–2004, compared with ¹⁴C content of tree-ring cellulose of *P. silvestris* growing in Niepołomice Forest, ~15 km east of Kraków. European background values of Δ^{14} C in atmospheric CO₂ are also shown, recorded at the high-altitude Jungfraujoch station (Levin et al. 2008).

A distinct offset of $\Delta^{14}CO_2$ values observed at Kraków station with respect to the European reference background curve is attributed to local emissions of CO₂ originating mostly from burning of

fossil fuels within the Kraków agglomeration (Kuc et al. 2007). During the 1980s, the average offset was equal to 55‰ for the annual averages and ~30‰ for the growing-season means. During the 1990s and early 2000s, the offset was gradually reduced to ~30‰ and 20‰, for annual and growing-season means, respectively. Although the available $\Delta^{14}CO_2$ record for Kasprowy Wierch station is relatively short, it reveals already a much lower offset with respect to the regional reference, reaching only ~4–6‰. This distinctly smaller offset observed at Kasprowy Wierch when compared to Kraków station, stems from the remote, mountain location of the station and the lack of strong sources of fossil-fuel-derived CO₂ in the immediate vicinity of the station.

Although the ¹⁴C level recorded in the cellulose extracted from annual rings of *P. silvestris* is distinctly higher than that recorded in the urban atmosphere of Kraków, it is still lower when compared to the Jungfraujoch reference curve. The difference varies with time, being largest for the period 1988–1990 (~20‰). Interestingly, also atmospheric $\Delta^{14}CO_2$ curves shown in Figure 2 reveal a distinct minimum during 1989–1990, indicating increased load of regional atmosphere with fossil-fuelderived CO₂. The year 1989 marks the beginning of major economic and social changes in eastern Europe and the associated reduction of CO₂ emissions associated with burning of fossil fuels. For the period 1997–1998, the ¹⁴C content in tree-ring cellulose increases, reaching a local maximum in 1998 that is indistinguishable from the regional background value for this year. Reasons for this anomalously high ¹⁴C content for the 1988 cellulose sample remain unclear. Unfortunately, atmospheric $\Delta^{14}CO_2$ data are not available for this period. Also unclear is the origin of anomalously low ¹⁴C content recorded in 2001 when the ¹⁴C level measured in wood cellulose was close to that recorded in the urban atmosphere of Kraków during the growing season.

Figure 3 shows the Δ^{14} CO₂ values for the growing season (April–August) plotted against Δ^{14} C of wood cellulose. Despite the relatively large fluctuations in ¹⁴C levels recorded in wood cellulose of *P. silvestris* and in atmospheric CO₂, both records reveal a high degree of similarity (*r* = 93.5%).



Figure 3 Correlation between Δ^{14} C in wood cellulose (Niepołomice) and Δ^{14} CO₂ in Kraków agglomeration (KRK Summer: April–August), 1983–2004.

The significantly higher ¹⁴C levels recorded in *Pinus silvestris* α -cellulose compared to mean Δ^{14} CO₂ values for the growing season recorded in the urban atmosphere of Kraków can be viewed from 2 perspectives. First, they may indeed reflect a significantly lower load of the local atmosphere in Niepołomice Forest with the fossil-fuel-derived CO₂, when compared to the urban environment of Kraków, despite the relatively short distance between both sampling sites. Second, the fossil-fuel-

derived CO₂ component in the local atmosphere of Niepołomice Forest can be partly masked by soil CO₂ emissions originating from heterotrophic respiration of organic matter that was formed during the periods of high levels of ¹⁴C in the atmosphere associated with thermonuclear tests. Systematic ¹⁴C measurements of soil CO₂ flux performed in the forest environment for 1998–2001 suggest that indeed Δ^{14} C values of the CO₂ emitted from the forest soil were ~50‰ higher than current atmospheric background values.

¹³C Content in Atmospheric CO₂

Although the ¹³C isotope signature of fossil-fuel-derived CO₂ is similar to that of biogenic CO₂, its impact on the local atmosphere is also clearly visible in the atmospheric δ^{13} CO₂ record. Figure 4 shows the long-term evolution of δ^{13} CO₂ in the urban atmosphere of Kraków, compared with the δ^{13} CO₂ records for Kasprowy Wierch and for Mace Head station (Ireland), which represents a marine background CO₂ entering the European continent. The δ^{13} C values for biweekly cumulative samples of CO₂ collected at both Kraków and Kasprowy Wierch are presented. The Mace Head δ^{13} CO₂ record shown in Figure 4 (NOAA 2011) shows distinct seasonal fluctuations, with a peak-to-peak amplitude of ~1‰, and long-term decreasing trend of about -0.03‰ per decade. The mean value for 1998–2003 is about -8.0‰. The Kasprowy Wierch site reveals significantly higher seasonal fluctuations of δ^{13} CO₂ (peak-to-peak amplitude of 1.6‰), and a lower mean value (~-9.2‰). Summer maximum of δ^{13} CO₂ at Mace Head is not replicated in the Kasprowy Wierch record, where the highest δ^{13} CO₂ values are observed in December.



Figure 4 The $\delta^{13}CO_2$ record obtained for the urban atmosphere of Kraków (1984–2004) and the mountain station Kasprowy Wierch (1988–2004). The linear trend of decreasing summer $\delta^{13}C$ (growing season) in Kraków is also plotted. Also shown is the $\delta^{13}CO_2$ record for Mace Head station (Ireland) representing marine background CO_2 entering the European continent (NOAA 2011).

The ¹³C signature of carbon dioxide in the urban atmosphere of Kraków shows much higher irregularities, most probably linked with the varying impact of local CO₂ sources. The apparent offset of the δ^{13} CO₂ record for Kraków with respect to Kasprowy Wierch is about 1.2‰ (Figure 4). This shift is mainly attributed to local emissions of CO₂ mostly due to burning of fossil fuels. The mean δ^{13} CO₂ values for the growing season reveal a decreasing trend of ~1‰ over the period 1984–2001.

This might reflect a gradual transition from coal to natural gas as a major fossil-fuel type used for heating purposes within metropolitan Kraków, which occurred during this time period. δ^{13} C values of natural gas supplied for communal use in Kraków and neighboring areas range from -50.7% to -54.4% (Zimnoch et al. 2012). The more recent record of δ^{13} CO₂ in Kraków (not shown here) reveals fluctuations of this parameter around -10%. The Kasprowy Wierch δ^{13} C record especially in recent years approaches values reported for the "clean" reference sites (Levin and Kromer 1997; NOAA 2011).

The δ^{13} CO₂ record both for Kraków and Kasprowy Wierch reveals a distinct seasonality. In Kraków, low δ^{13} CO₂ values are usually recorded during winter, when local CO₂ emissions due to burning of fossil fuels in the city (heating plus car traffic) are most intense. At Kasprowy Wierch, less negative δ^{13} C values are generally recorded during winter, when advection of biospheric CO₂ from the valleys beneath the station is cut off and free tropospheric air is "seen" by the station more frequently. The Mace Head δ^{13} CO₂ record reveals maximum values in August and minimums in April, reflecting seasonal changes in the exchange of CO₂ between the surface ocean and atmosphere.

FOSSIL-FUEL CO₂ IN KRAKÓW ATMOSPHERE AND WOOD CELLULOSE BASED ON ¹⁴C

The data presented in Figure 2 may serve as a starting point for assessing the contribution of fossil-fuel-derived CO_2 both in the local atmosphere and in wood cellulose. This assessment can be based on isotope and mass balance equations leading to the following formula describing the fraction F of fossil-fuel-derived CO_2 (C_{foss}) in the total CO_2 load (C_{meas}) observed in the local atmosphere (e.g. Meijer et al. 1996; Kuc and Zimnoch 1998; Levin et al. 2003; Pazdur et al. 2007; Zimnoch et al. 2012):

$$F = \frac{C_{foss}}{C_{meas}} = \frac{\Delta^{14} C_{bg} - \Delta^{14} C_{meas}}{\Delta^{14} C_{bg} + 1000}$$
(1)

where $\Delta^{14}C_{meas}$ is the $\Delta^{14}CO_2$ value measured in the local atmosphere while $\Delta^{14}C_{bg}$ is the $\Delta^{14}CO_2$ value of the regional background. Equation 1 is valid under 2 assumptions: $\Delta^{14}C_{foss} = -1000\%$, meaning that fossil fuel CO₂ is devoid of ¹⁴C; and $\Delta^{14}C_{bio} = \Delta^{14}C_{bg}$, meaning that the ¹⁴C signature of biogenic CO₂ component is equal to that of regional background CO₂.

Equation 1 can be also used to formally derive the contribution of fossil fuel carbon in the wood cellulose formed in the local atmosphere with the specific load of CO_2 consisting of regional background (C_{bg}), biogenic (C_{bio}), and fossil fuel (C_{foss}) components. It is important to note that the biogenic component represents a net result over the considered period of time of the processes adding CO_2 to the atmosphere (autotrophic and heterotrophic respiration) and removing it from the atmospheric reservoir (photosynthesis).

Equation 1 was used to calculate the fossil fuel CO_2 fraction in the urban atmosphere of Kraków, both for annual averages and the growing-season mean shown in Figure 2. The results are summarized in Table 1, which contains also the apparent fossil fuel fraction of carbon in the wood cellulose of pine from Niepołomice Forest. The derived fossil fuel fraction in atmospheric CO_2 shows a decreasing tendency for Kraków agglomeration from >5% in 1987–1990 to ~2.5% in 2002–2004 for the annual mean of ¹⁴C content, and from ~4% to 1.5% for the same periods for the growing-season mean $\Delta^{14}CO_2$ values. Contrary to the atmospheric fossil fuel fraction, in wood cellulose no apparent trend of the F parameter during 1987–2002 could be observed. The values scatter around 1%. This

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relatively small value of the F parameter and lack of long-term trend can stem from the fact that the assumption that $\Delta^{14}C_{bio} = \Delta^{14}C_{bg}$ might not be valid for the forest environment, as discussed above.

	Δ^{14} C content (‰)			Fossil fuel fraction F (%)		
	Kraków	Kraków	Wood	Kraków	Kraków	Wood
Year	(annual)	(Apr–Aug)	cellulose	(annual)	(AprAug.)	cellulose
1983	172	188	217	_	_	
1984	167	192	205			
1985	126	148	197			
1986	138	154	188			
1987	119	125	174	5.3	4.8	0.6
1988	110	137	157	5.3	3.1	1.3
1989	87	112	152	6.6	4.4	1.0
1990	76	100	136	6.6	4.5	1.4
1991	90	108	133	4.6	3.0	0.9
1992	83	96	129	4.6	3.5	0.5
1993	95	106	122	2.9	1.9	0.5
1994	87	91	111	3.1	2.7	1.0
1995			105			0.9
1996			95			1.2
1997			95			0.8
1998			102			-0.3
1999			83			1.1
2000	46	59	82	4.0	2.7	0.6
2001	50	57	62	3.0	2.4	1.9
2002	47	55	69	2.7	2.0	0.7
2003	45	54	_	2.4	1.6	
2004	45	53		1.7	1.0	

Table 1 Apparent fossil fuel fraction in local atmospheric carbon dioxide derived from 14 C content in atmospheric CO₂ and wood cellulose.

MODELING CLIMATIC AND FOSSIL FUEL EMISSION IN TREE RINGS BASED ON ¹³C DATA

Climate and CO₂ Emission Model 1

Values of δ^{13} C in tree rings are controlled by environmental factors that determine stomatal conductance and the rate of photosynthesis. For carbon, McCarroll and Pawellek (2001) and Gagen et al. (2007) found that photosynthetic rate is controlled primarily by photon flux (sunshine) and temperature, whereas stomatal conductance is controlled by air humidity and soil moisture. It should be noted that not only the climatic factors affect the value of δ^{13} C, but also factors related to human activities such as CO₂ emission. The correlation between isotopic data for pine and oak from Niepołomice Forest and climatic factors was investigated by Szczepanek et al. (2006).

For the modeling and fossil fuel emission estimation, the $\delta^{13}C$ series were used from annual tree rings of pine (whole wood) and latewood for oak for 1900–2002. This period is covered by the data set of temperature, precipitation, and sunshine from the Kraków meteorological station (see above). For the estimation of CO₂ emission component in the total amount of CO₂ absorbed in the photosynthesis process, relationships between $\delta^{13}C$ in pine α -cellulose from Niepołomice Forest and sunshine, temperature, and precipitation were determined based on meteorological data for Kraków for March–June in the case of sunshine, June–August for temperature, and May–August precipitation

data. For this period 1900–2002, the highest correlation coefficients between $\delta^{13}C$ and meteorological data are observed (Szczepanek et al. 2006). Considering the impact of anthropogenic effects on $\delta^{13}C$ values, the period 1951–2000 was excluded. On the contrary, climate signals in $\delta^{13}C$ of oak are strongest for 1966–2000. In this case, a relationship between $\delta^{13}C$ and sunshine, temperature, and precipitation were determined using Kraków meteorological data from July–August in each case.

Analyzing the impacts of subsequent factors on δ^{13} C, the following partial differential equation supplemented by sunshine can be written from the formula given by Pawełczyk and Pazdur (2004). Assuming δ^{13} C as a function of time, climatic, and anthropogenic factors:

$$\delta^{13}C = f(y,t,p,s,e,\rho) \tag{2}$$

where y = time, t = temperature, p = precipitation, s = sunshine, e = emission of CO₂, and r = additional factors, for example: pollutants emission, "potential for growth," carbon flux from biosphere to atmosphere or error connected to the assumptions, the equation can be written:

$$\frac{\partial \delta^{13}C(y,s,t,p,e,\rho)}{\partial y} = \frac{\partial \delta^{13}C}{\partial t} \cdot \frac{\partial t(y)}{\partial y} + \frac{\partial \delta^{13}C}{\partial p} \cdot \frac{\partial p(y)}{\partial y} + \frac{\partial \delta^{13}C}{\partial s} \cdot \frac{\partial s(y)}{\partial y} + \frac{\partial \delta^{13}C}{\partial e} \cdot \frac{\partial e(y)}{\partial y} + \frac{\partial \rho(y)}{\partial y}$$
(3)

For uncorrected δ^{13} C, the constant gradients of δ^{13} C with respect to temperature, precipitation, sunshine, and CO₂ emission were assumed in the analysis using pine and oak α -cellulose. The gradients were calculated with the linear regression method (Table 2).

Table 2 Constant gradients of δ^{13} C with to respect temperature (in (‰/°C), precipitation (in ‰/mm), sunshine (in ‰/number of sunshine hours), and CO₂ emission (in ‰/tons carbon) determined from a simple linear regression model.

	$\frac{\partial \delta^{13} C}{\partial t}$	$\frac{\partial \delta^{13} C}{\partial p}$	$\frac{\partial \delta^{13} C}{\partial s}$	$\frac{\partial \delta^{13}C}{\partial e}$
Species	(‰/°C)	(‰/mm)	(‰/nr of sunshine hr)	(‰/ tons carbon)
Pine	0.292	-0.0019	0.013	-0.0000217
Oak	0.181	-0.0042	0.010	-0.0000039

Integrating Equation 3 with respect to time, the individual components of δ^{13} C originating from those factors were obtained. Defining the following notation as it is given in Table 3, Equation 3 can be written as:

$$\delta^{13}C(y) = \delta 1(y) + \delta 2(y) + \delta 3(y) + \delta 4(y) + R \tag{4}$$

In the above, *R* stands for other factors, noted as *r* in Equations 2 and 3 together with errors due to the assumptions made. Figure 5 presents the fluctuations of $\Delta\delta$ for all components from Equation 4.

The correlation coefficient between measured $\delta^{13}C$ for pine and estimated $\delta^{13}C$ on the basis of components: $\delta l(y)$, $\delta 2(y)$, $\delta 3(y)$, and $\delta 4(y)$ is 0.71. In the case of oak, this correlation is relatively weak (r = 0.15). This may indicate that there are probably other factors affecting the value of $\delta^{13}C$ in oak α -cellulose. However, the relationship between $\delta^{13}C$ and CO₂ emission was determined following the estimations of Boden et al. (2011). CO₂ emission concerns the entire year and whole area of



Poland. Local factors have the strongest impact on the δ^{13} C values, and a similar conclusion should be also true for CO₂ emission.

Figure 5 Measured δ^{13} C (red lines) and estimated δ^{13} C based on modeled components of δ^{13} C due to different factors in time (y): A – components for pine; B – components for oak. Components 1, 2, 3, and 4 correspond to relevant climatic parameters: temperature, precipitation, sunshine, and CO₂ emission from their average values in the analyzed period of 1900–2002.

Table 3 Components of δ^{13} C for pine and oak. Values of individual components in a given year (*y*) are calculated as the product of relevant gradients presented in Table 2 and values of temperature, precipitation, sunshine, and emission of carbon.

Component	Pine	Oak
$\delta l(y)$ Temperature	$0.292\%/^{\circ}\mathrm{C} \cdot t(y)$	$0.181\%/^{\circ}\mathrm{C} \cdot t(y)$
$\delta^{2}(y)$ Precipitation	-0.0019‰/mm · $p(y)$	-0.0042‰/mm · $p(y)$
$\delta 3(y)$ Sunshine	0.013‰/number of sunshine hours $\cdot s(y)$	0.013‰/number of sunshine hours $\cdot s(y)$
∂4(y) Emission	-0.0000217%/tons carbon · $e(y)$	-0.0000039 %/tons carbon $\cdot e(y)$

A strong decline from about -22.5 to about -25.5‰, and therefore ~ 3 ‰, is observed for δ^{13} C values measured in α -cellulose of pine annual tree rings during 1965–1970, and lower levels of δ values in the following years. This phenomena may be due to the relatively high proportion of the CO₂ emission component assimilated during photosynthesis, since those years fall into a period of rapid increase of CO₂ emissions from fossil fuel burning, visible in the data reported by Boden et al. (2011) on a global scale, as well as for the Polish territory. It was also a period of intense production

of steel in the Sendzimir steel factory, located in the Nowa Huta (Kraków district), ~15 km from the Niepołomice Forest. However, other unidentified factors cannot be excluded (e.g. the strictly local ecological conditions).

Assuming that only temperature, precipitation, sunshine, and CO₂ from fossil fuel burning contribute to δ^{13} C, the CO₂ emission can be evaluated as presented in Figure 6. This CO₂ emission was compared with CO₂ emission evaluated for Poland by Boden et al. (2011). Emission estimated on the basis of δ^{13} C from pine α -cellulose shows a similar trend as evaluated by Boden et al. A significant increase in emissions can be observed in the second half of the 20th century. More problematic is the CO₂ emission evaluated on the basis of δ^{13} C from oak α -cellulose. An increasing trend of CO₂ emission is also visible, but the time resolution of CO₂ changes is less visible. Pine is an evergreen tree and, therefore, may for a longer time in the year collect information about the surrounding environment than oak. In addition, the pine species is more sensitive to contamination than oak.



Figure 6 Comparison between CO₂ emission (in thousand metric tons of carbon) estimated on the basis of measured δ^{13} C and evaluated by Boden et al. (2011) for the whole of Poland: A – comparison for pine; B – comparison for oak.

Climate and CO₂ Emission Multiple Regression Model 2

This model attempts to assess the CO₂ emission component based on multiple regression analyses of the δ^{13} C records. The δ^{13} C was measured in α -cellulose and glucose derived from it, from the same samples of annual tree rings of pine from Niepołomice Forest for which the measured Δ^{14} C values were used to estimate the Suess effect (see above) and δ^{13} C values in the first model. The same data set of meteorological data was also used. However, the input isotope records are restricted to the years 1935–2000, i.e. the period of time for which glucose samples were available from the pioneer isotopic analysis of this saccharide in α -cellulose of tree rings (Sensuła et al. 2011).

Changes in the temperature (T), precipitation (P), and hours of sunshine (S) have an influence on ${}^{13}C$ content in the α -cellulose and glucose from pine annual rings. In order to follow the model 1 data set, this analysis was performed using the same climatic data for the March–June for sunshine, June–August for temperature, and May–August for precipitation data. To describe the variation of the carbon stable isotopic composition of glucose and in annual tree rings of pine caused by climate changes and human activities, we used a model based on multiple regression:

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$$\delta = b_T T + b_P P + S + b_E E_{\frac{1}{CO_2}} + R$$
(5)

where δ^{13} C values have not been directly corrected for changes in the isotopic ratio of atmospheric CO₂ in the time according to McCarroll et al. (2009), but we used the inverse CO₂ emission in Poland (E_{1/CO2}) according to Keeling et al. (2010) as an additional variable. The E_{1/CO2} values were taken from Boden et al. (2011).

The values of individual components are calculated according to Equation 5 as the product of relevant coefficients presented in Table 4 and values of temperature, precipitation, and sunshine. This model uses $E_{1/CO2}$ as an emission of carbon factor and *R* as any additional factors connected with pine physiology. The modeling results are shown in Figure 7 and Table 4.



Figure 7 Time records of $\delta^{13}C$ measurements and modeling results for α -cellulose and glucose from annual rings of pine.

Period				b _s (‰/nr of hr	b _{E 1/CO2}	
(AD)	Material	$b_T (\%/^{o}C)$	b _P (‰/mm)	of sunshine)	(‰ · kg of CO ₂)	R (‰)
1900-2000	α -cellulose	0.15 ± 0.12	0.0046 ± 0.0042	0.0146 ± 0.0039	$(0.5 \pm 2.5) \cdot 10^9$	-29.1 ± 2.3
1935-2000	α -cellulose	-0.05 ± 0.21	0.0044 ± 0.0072	0.0153 ± 0.0068	$(11.5 \pm 3.2) \cdot 10^{10}$	-26.6 ± 4.0
1935-2000	Glucose	0.55 ± 0.23	0.0109 ± 0.0078	0.0039 ± 0.0074	$(10.6 \pm 3.5) \cdot 10^{10}$	-34.5 ± 4.4

Eighty percent of the data were used to train the system and 20% of the data were then tested using STATISTICA 10.0 (StatSoft, Hamburg, Germany). The correlation coefficients between the measured and modeled ¹³C composition of the α -cellulose is equal to 0.67 and of the glucose to 0.47. The concentration of atmospheric CO₂ also influences δ^{13} C. This is particularly evident in the period of time since 1975–2000, when a significant rise in CO₂ emissions related to human activities took place. The measured values of δ^{13} C in saccharides show much higher dynamics of ¹³C variations in glucose than in α -cellulose. However, longer periodic trends in ¹³C measured and modeled values in both the saccharides are similar.

Comparison of Model 1 and 2 Results

The summarized comparison of measured and modeled $\delta^{13}C$ values, obtained using models 1 and 2, is presented in Figure 8. The comparison was made for pine tree rings, since the emission component for oak in the period 1900–2000 is negligible, being nearly constant (see Figure 6B). The input data sets used in both models are the same; therefore, the differences of the obtained $\delta^{13}C$ values result from the different statistical approaches and algorithms applied. In particular, the trends of $\delta^{13}C$ changes calculated for 1900–2000 are similar, but model 2 provides output of much higher variability than both the measured and model 1 $\delta^{13}C$ values.



Figure 8 Comparison of δ^{13} C time records: measured data and modeling results: δ^{13} C measured: (a) for α -cellulose samples for the period AD 1900–2002 (repeated for better readability); (b) for α -cellulose modeled using model 1 for the period AD 1900–2002; (c) for α -cellulose modeled using model 2 for the period AD 1900–2002; (d) for α -cellulose modeled using model 2 for the period AD 1935–2000; (e) for glucose modeled using Model 2 for the period AD 1935–2000.

It is also evident that none of the models is capable of reproducing the rapid $\delta^{13}C$ decrease that has been recorded in pine α -cellulose, measured for the period of only 4 yr (1968–1972). Neither the analysis performed for the shorter time period nor for glucose samples (1935–2000) is found to be able to model this phenomena. It is therefore expected that the decrease is not caused by climatic factors, nor by the emission component influence on the final $\delta^{13}C$ values.

CONCLUSIONS

This work focused on comparing isotopic signals in 3 different ecosystems, all exposed to considerable CO₂ emissions of fossil fuel origin. The trend of ¹⁴C concentration in sampled wood material (tree rings) covering 2000–2004 is similar to the trend observed at the Kasprowy Wierch station, recognized as a regional reference and only ~4–6‰ lower than that measured at Jungfraujoch. We can thus conclude that intensive emissions of anthropogenic CO₂ deprived of ¹⁴C in neighboring steel work are not manifested in Niepołomice wood material. The lack of fossil fuel imprint can be explained by higher ¹⁴C content in CO₂ generated by decomposing organic matter in forest environment, still affected by the bomb peak, thus masking anthropogenic stress.

 CO_2 sampled in Kraków shows a systematic lower ¹⁴C content than the reference value and estimated yearly mean contribution of anthropogenic CO_2 shows a decreasing tendency from ~6% in 1987 to ~1.7% in 2004. For the summer period, these values are 4.8% and 1.0%, respectively. Burning of fossil fuels is also manifested in lower $\delta^{13}C$ values recorded in atmospheric CO_2 . The $\delta^{13}C$ record for the Kasprowy Wierch regional reference is ~1‰ more negative than for Mace Head with extremes shifted by 5 months, reflecting biogenic activity on areas far from direct oceanic influence.

The results based on climate model 1 indicate that the presence of the emission component is clearly visible in the δ^{13} C values measured in the α -cellulose of annual pine tree rings, and less clearly recorded in the latewood of oak. The most intensive assimilation of CO₂ for the oak takes place during the spring-summer period (April–August). This may indicate a significant influence of local emissions in the autumn-winter season related to household heating. The model 1 can also estimate the trends of climate parameters and CO₂ emission component in time, which is in agreement with the trend of changes in the amount of fossil carbon introduced into the atmosphere.

The δ^{13} C dependency on climatic and CO₂ emission components is also evident in climate model 2 (multiple regression model), both in the time record of δ^{13} C values measured in α -cellulose, as well as in the glucose derived from it. However, the variability of modeled δ^{13} C obtained by model 1 is closer to the measured δ^{13} C variability. Moreover, the model 1 algorithm allows for quantitative estimation of the CO₂ emission.

The influence of climatic and CO₂ emission factors on the δ^{13} C of tree-ring α -cellulose is straightforwardly proven by both models. However, the model output data set may also help to evaluate the presence of other factors influencing the δ^{13} C, which may have a local character and can cause pronounced changes in stable carbon isotope composition, such as the rapid δ^{13} C decrease in Niepołomice pine tree rings in 1968–1972.

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