CARBON ISOTOPIC COMPOSITION OF TREE RINGS AS A TOOL FOR BIOMONITORING CO_2 LEVEL

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ABSTRACT. Carbon isotopes are widely used as indicators in the study of atmospheric CO_2 variability in space and time. Preliminary results are part of a project investigating ^{13}C and ^{14}C concentration changes during the last 150 yr in Poland, both in industrial and ecologically clean regions, using annual tree rings (*Pinus sylvestris*, *Populus nigra*). The results describe the local Suess effect recorded in the industrial Kraków and Upper Silesia regions compared to changes of background radiocarbon concentration caused by global human activity in a "clean region," Augustów Wilderness. The $\delta^{13}C$ record also shows the influence of the local Suess effect.

INTRODUCTION

$^{14}C/^{12}C$ ($\Delta^{14}C$) and $^{13}C/^{12}C$ ($\delta^{13}C$) ratios in tree rings can reflect corresponding atmospheric CO_2 concentration during their formation and can be used to reconstruct changes in factors influencing these parameters. In particular, $\Delta^{14}C$ and $\delta^{13}C$ could be used as proxies when CO_2 concentrations are unavailable. The carbon isotopic composition of plant material depends on the isotopic composition of CO_2 assimilated during the photosynthesis process. For this reason, $\delta^{13}C$ and $\Delta^{14}C$ determined for plant material can be used as isotopic composition indicators as well as indicators of CO_2 emission caused by fossil-fuel burning and human activity. Many other factors, in addition to isotopic composition of atmospheric CO_2, influence $\delta^{13}C$ and $\Delta^{14}C$. Although the carbon atoms of plant material come from atmospheric CO_2, the $\delta^{13}C$ value is not the same as that of atmospheric CO_2. Diffusion via stomata and carboxylation discriminate against heavier isotopes. Environmental variables, such as temperature, precipitation, humidity, light intensity, and changes in soil moisture, control the degree of fractionation and, thus, $\delta^{13}C$ values. $\Delta^{14}C$ correlates with sun activity and terrestrial geomagnetic variations.

Human activity is another reason for changes in the environment's carbon composition. Changes can have either a global range, which can affect all of nature or a specified reservoir, or a local range covering only a part of reservoirs neighboring the source that caused the changes. Human activity can lead to an increase as well as decrease of ^{14}C concentration in the environment. Anthropogenic changes of radiocarbon concentration are caused by:

- Suess effect;
- Rapid increase of ^{14}C concentration caused by nuclear weapon tests in the atmosphere;
- Production of ^{14}C connected with nuclear reactors and nuclear fuel reprocessing plant activity;
- Release and production of ^{14}C isotope during a nuclear system failure.

Increase of mining and burning of fossil fuels in industrial areas since the 19th century caused the emission of CO_2 to the atmosphere and changes of carbon isotopic composition in both the atmosphere and other carbon reservoirs. Fossil-fuel burning results in the emission of CO_2 to the atmosphere lacking ^{14}C. This decreases the atmospheric ^{14}C concentration and is known as the Suess effect (Awsiuk and Pazdur 1986; Damon et al. 1989; Levin et al. 1989; Levin and Hesshaimer 2000; Rakowski et al. 2001). An increase of ^{14}C concentration in the atmosphere, as a result of nuclear weapon tests in the stratosphere and at the earth surface after the 1950s, made it impossible to eval-

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uate the Suess effect directly from measurements of the concentration in the atmosphere and biosphere (Nydal and Lövseth 1983). Such an evaluation is only possible when assuming a mathematical model describing carbon exchange between reservoirs (Oeschger et al. 1975; Siegenthaler and Oeschger 1987).

It can be assumed that lower values of $\delta^{13}C$ in organic material are connected with lower values of ^{13}C concentration in the atmosphere. The depression of $\delta^{13}C$ results from ^{13}C-depleted emission from fossil fuels. In particular, several investigators have tried using $^{13}C/^{12}C$ in tree rings to establish an atmospheric record of this ratio. Nevertheless, many factors may disturb atmospheric CO_2 isotope abundance reconstruction from tree rings, including the choice of a wood constituent for analysis, the effect of respired CO_2, and the influence of climatic factors (Schleser et al. 1999; Tans and Mook 1980).

Marland et al. (2001) estimated fossil-fuel emissions released in successive years from 1751 to 1998. Results of these estimations were used for comparison of values of $\delta^{13}C$ and $\Delta^{14}C$ with estimated CO_2 emission.

Systematic direct observation of Mauna Loa from 1958 and the analysis of air inclusion in Antarctic ice cores shows a continuous increase of CO_2 concentration in the air. We can state that for the period 1000–1800, the CO_2 concentration was at a steady level of 280 ppm, and from 1800–2000, it increased about 80 ppm (Keeling et al. 1989; Levin and Hesshaimer 2000).

The increase in atmospheric CO_2 concentration has been elegantly demonstrated through ^{14}C analyses of tree rings from the last 2 centuries. The first investigation of contemporary tree samples (Suess 1955) proved that their ^{14}C activity was lower than the activity of samples from the middle 19th century. On the basis of $\Delta^{14}C$ determined for tree-ring samples, a rapid decrease of about $\Delta^{14}C = 20‰$ from 1890 to 1950 was observed by Stuiver and Quay (1981).

The $\Delta^{14}C$ depletion in the first half of the 20th century has been shown to be larger in a more polluted area (De Jong and Mook 1982). In such areas, extra CO_2 from the burning of fossil fuels is clearly detectable as $\Delta^{14}C$ depletion relative to background levels. The determination of a local decrease of ^{14}C concentration in the air surrounding urban and industrial areas is important in investigations of the degree of atmosphere contamination, air mass migration, and spread of the contamination (Levin and Hesshaimer 2000).

Representative investigations of local Suess effect were carried out by Levin et al. (1989) in Central Europe, i.e., in Heidelberg, Westerland, Schauinsland, and Jungfraujoch. Levin et al. (1995) used $\Delta^{14}C$ observations to estimate the fossil-fuel contribution in atmospheric CO_2 concentration. Results of those measurements clearly demonstrate decreasing CO_2 from fossil-fuel burning with the increase of distance from the polluted area.

In Poland, investigations of local changes of ^{14}C concentration were performed by Kuc and Florkowski. They observed the depletion of ^{14}C concentration in samples of tree leaves from Kraków. Measurements of atmospheric CO_2 revealed maximum values in December and minimum values in April and May (Kuc 1986).

Investigations of changes of ^{14}C concentration in the boundary of the Upper Silesia region were carried out by Awsiuk and Pazdur (1986). They aimed to determine the range of the Suess effect. The local Suess effect on this area was investigated, in turn, by Rakowski et al. (2001) and Pazdur et al. (1998).

The increase of ^{14}C concentration in the atmosphere as a result of nuclear weapon tests in the stratosphere and on the earth's surface made it impossible to determine the Suess effect directly from mea-

surements of the ^{14}C concentration in the atmosphere and biosphere. However, it is possible to determine the local Suess effect in polluted areas. In this case, ^{14}C concentration in atmospheric CO_2 acquired at sites far from an industrial area can be considered as the ^{14}C of so-called "clean air."

RESEARCH AREA AND TIME RANGE

Investigations were carried out for 3 different areas in Poland (Figure 1). The Upper Silesia region is in the basins of Upper Wisła and Odra in southern Poland. This is the most industrialized area in Poland. Its main natural resources are deposits of coal. Other industrial activities in this area are associated with chemical processing of coal and development of heavy industry utilizing coal as the main source of energy. Spatial distribution of the air pollution is diversified. The largest concentration of pollution in the Upper Silesia region was noted in Zabrze, Ruda Śląska, Bytom, Chorzów, and Gliwice. Due to the prevailing west-south winds, the pollution partly comes from Zagłębie Ostrawsko—Karwińskie in the northern Czech Republic. The towns of Upper Silesia form a specific urban and industrial area between Mysłowice in the east and Gliwice in the west. Sampling sites were at the boundary of Ruda Śląska and Chorzów, but the distance between those places was no more than 5 km. Therefore, they can be considered as 1 site, the center of the Upper Silesia industrial area. Our investigation of Upper Silesia covers the years 1965–1995.

Figure 1 Map of Poland with location of sample collection sites

The second area where investigations were performed was Kraków (50°03′N, 19°03′E). It is one of the biggest Polish cities located in southern Poland and strongly industrialized. Our investigation covers the years 1964–2000.

The third region is Augustów (53°51′N, 22°58′E). It is an ecologically clean region (now a sanctuary) in northeast Poland. Augustów is a town located on the Netta River at the west edge of Augustów Wilderness. The region is the biggest forest complex in Europe. Our investigation covers the years 1861–1968. A minimal impact of anthropogenic effects (mainly the Suess effect) on carbon isotopic composition in tree rings was expected there. The aim of this research was to evaluate the human impact on the environment in this area.

MATERIALS AND METHODS

For investigations of the Upper Silesia region, tree trunks were collected from forests outside of local towns. Annual tree rings of pine (*Pinus sylvestris*), the dominant conifer in Polish forests, constituted the material for isotopic analysis. The choice of tree species was imposed by necessity to unify experimental material, as well as by the fact that pines are commonly used in isotopic studies around the world. An important argument supporting the use of pine for ^{14}C measurements is the fact that pine has a significantly longer vegetation period than deciduous trees. This allows tracking changes of ^{14}C concentration over a longer period. In order to compare changes of ^{14}C concentration in tree rings of deciduous and coniferous trees, the concentration of ^{14}C in tree rings of poplar (*Populus nigra*) was also determined.

In case of the Kraków area, a trunk of pine *(Pinus sylvestris)* was used. That pine grew in the central part of the city.

The investigations performed for Augustów Wilderness were also based on a pine (*Pinus sylvestris*). That tree grew in Augustów in a forest near Necko Lake.

Meteorological data used in the investigation was obtained from meteorological observatories in Warsaw (52°12′N, 21°10′E) and Kaunas (54°88′N, 23°88′E). There is no meteorological data for Augustów, but we did use data from the nearest city. From the cities mentioned above, Kaunas is the nearest one, but the meteorological data set only begins in 1922.

Preparation of samples involved separation of tree rings from the trunk cross-section along edges of the rings. This mechanical operation was performed by cutting the material with a chisel. Samples were cut from individual rings into very small slivers with a scalpel. Then, they were subject to a chemical pretreatment. Wood slivers were refluxed in a Soxhlet apparatus with a 2:1 benzene ethylene mixture to remove resin.

After mechanical processing and resin extraction in the Soxhlet apparatus, the wood samples were converted to Li_2C_2 by combustion with lithium, then to C_2H_2 by adding water, and finally to C_6H_6 in a catalyst process. The detailed procedure is described by Pawlyta et al. (1998). Measurements of Δ^{14}C were made with the liquid scintillation method using Quantulus 1220.

Values of δ^{13}C were determined for wholewood and latewood α-cellulose. In the case of several samples from Kraków, δ^{13}C was determined for earlywood because it was a part of climatic study. The technique for extraction of α-cellulose based upon the sodium chlorite oxidation method of Green (1963) utilizes an ultrasonic bath and small Soxhlet thimbles to prepare α-cellulose from latewood. This technique yields a material with sufficient homogeneity required for isotopic composition measurements (Loader et al. 1997).

The diagram of α-cellulose extraction from latewood samples can be briefly presented as follows (Robertson and Waterhouse 1998):

$$\text{wood} \xrightarrow[\text{CH}_3\text{COOH}]{\text{NaClO}_2} \text{holocellulose} \xrightarrow{\text{NaOH}} \text{α-cellulose}$$
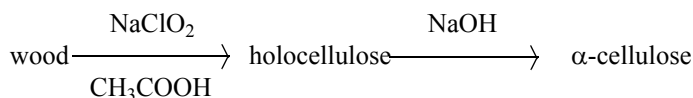
For $\delta^{13}C$ wholewood, earlywood and α-cellulose were combusted and the CO_2 cryogenically purified. Isotope ratios were measured using a mass spectrometer and expressed in the conventional δ notation as deviation in permil from the international standard, Vienna PDB (Loader et al. 1997).

RESULTS AND DISCUSSION

Comparison of $\delta^{13}C$ and $\Delta^{14}C$ Results from Different Sites

Data from Kraków are presented in Table 1 and data from Augustów are presented in Table 2. Results of ^{14}C concentration measurements in tree rings from Chorzów and Ruda Śląska are presented by Rakowski et al. (2001).

Table 1 Results of carbon isotopic composition measurements in tree rings (*Pinus sylvestris*) and in atmospheric CO_2 from Kraków (from Kuc and Zimnoch 1998).

Year	$\delta^{13}C$ (±0.1) (‰)	$\Delta^{14}C$ (‰) tree rings	pMC (%)	^{14}S (%)	$\Delta^{14}C$ (‰) atmospheric CO_2
1964	−24.34[*a]	708.91 ± 27.95	170.89 ± 2.79	−8.34 ± 1.55	—
1966	−24.55[*]	763.86 ± 24.83	176.39 ± 2.48	4.03 ± 1.47	—
1968	−24.94	536.76 ± 27.38	153.68 ± 2.74	−3.48 ± 1.72	—
1970	−25.42	511.04 ± 21.84	151.10 ± 2.18	−2.30 ± 1.42	—
1972	−24.87	423.14 ± 21.18	142.31 ± 2.12	−3.94 ± 1.43	—
1974	−24.42	367.55 ± 19.91	136.76 ± 1.99	−3.66 ± 1.41	—
1975	−24.97[*]	250.66 ± 20.33	125.07 ± 2.03	−9.89 ± 1.47	—
1977	−24.51	235.34 ± 19.80	123.53 ± 1.98	−7.72 ± 1.48	—
1979	−25.29	208.89 ± 19.94	120.89 ± 1.99	−7.40 ± 1.53	—
1981	−25.49	178.20 ± 19.18	117.82 ± 1.92	−7.32 ± 1.51	—
1983	−23.05[*]	159.54 ± 20.50	115.95 ± 2.05	−6.08 ± 1.66	225.28 ± 12
1985	−28.04	186.08 ± 18.01	118.61 ± 1.80	−1.52 ± 1.50	175.57 ± 11
1987	−23.20	175.22 ± 18.26	117.52 ± 1.83	−0.37 ± 1.55	163.33 ± 10
1988	−23.88[*]	153.89 ± 17.47	115.39 ± 1.75	−1.50 ± 1.50	197.00 ± 10
1989	−23.79[*]	71.29 ± 17.84	107.13 ± 1.78	−7.63 ± 1.54	151.14 ± 10
1990	−23.54	49.49 ± 17.65	104.95 ± 1.77	−9.13 ± 1.53	144.00 ± 10
1991	−23.12	51.38 ± 18.48	105.14 ± 1.85	−7.64 ± 1.63	—
1997	−25.12	24.19 ± 19.26	102.42 ± 1.93	−6.46 ± 1.76	—
1998	−25.89	−2.67 ± 20.08	99.73 ± 2.01	−8.50 ± 1.85	—
1999	−25.60	−13.38 ± 24.11	98.66 ± 2.41	−9.31 ± 2.22	—
2000	−27.07	17.21 ± 19.15	101.72 ± 1.92	−5.81 ± 1.78	—

[a]* = values of $\delta^{13}C$ determined for earlywood.

$\Delta^{14}C$ in the Environment and the Impact of CO_2 Emission

Figure 2 presents annual changes of $\Delta^{14}C$ in tree rings from Augustów, Ruda Śląska, Chorzów, and Kraków, and changes of ^{14}C concentration in the "clean air." Data concerning the concentration in the clean air are taken from the work by Levin and Kromer (1997). They constitute a record of changes of ^{14}C concentration in the atmospheric CO_2 from Schauinsland (48°N, 8°E, 1205 m asl, Black Forest, southern Germany). For the calculation, average values of $\Delta^{14}C$ determined from May

to August for Schauinsland were used. Those changes can be described by the expression $\Delta^{14}C = 417\exp(-0.0625 \times t)$ (‰), where *t* is time (in yr) counted from 1974.

Table 2 Results of carbon isotopic composition measurements for wholewood and latewood α-cellulose of tree rings (*Pinus sylvestris*) from Augustów.

Year	$\Delta^{14}C$ (‰)	$\delta^{13}C$ for wholewood (±0.1) (‰)	$\delta^{13}C$ for latewood α-cellulose (±0.05) (‰)
1861	−30.41 ± 7.64	−27.02	—
1862	−3.50 ± 6.30	−26.91	—
1863	5.57 ± 6.57	−25.39	—
1864	6.26 ± 6.99	−27.19	—
1865	12.33 ± 6.42	−27.62	—
1866	−9.04 ± 6.39	−27.01	—
1867	−10.42 ± 6.71	−26.59	—
1868	−13.78 ± 7.07	−26.32	—
1869	−4.38 ± 6.73	−26.03	—
1870	6.47 ± 6.79	−27.19	—
1871	−28.02 ± 6.76	−26.82	—
1872	−3.43 ± 5.04	−26.29	—
1873	−42.27 ± 6.25	−26.89	—
1874	0.93 ± 7.42	−26.81	—
1875	−21.00 ± 6.00	−26.13	—
1876	8.16 ± 6.90	−25.32	—
1877	−15.89 ± 6,01	−25.9	—
1878	−10.58 ± 7.24	−25.78	—
1879	−10.64 ± 6.33	−26.60	—
1880	−8.67 ± 6.47	−26.58	—
1881	−1.60 ± 7.37	−26.72	—
1882	−9.55 ± 5.74	−26.21	—
1883	−12.21 ± 9.59	−25.70	—
1884	−20.20 ± 8.92	−25.01	—
1885	−22.87 ± 8.29	−24.90	—
1886	−23.09 ± 9.70	−26.60	—
1887	−12.09 ± 4.24	−25.03	—
1888	−13.90 ± 7.39	−25.91	—
1889	−9.47 ± 6.83	−25.73	—
1890	2.67 ± 6.24	−25.99	—
1891	7.74 ± 6.08	−25.41	—
1892	−0.76 ± 6.51	−25.74	—
1893	2.53 ± 6.61	−26.10	—
1894	−0.54 ± 7.05	−25.32	—
1895	−7.86 ± 7.14	−25.00	—
1896	2.81 ± 6.71	−25.59	—
1897	−6.40 ± 6.44	−25.33	—
1898	−10.42 ± 9.07	−25.00	—
1899	18.10 ± 6.19	−25.66	−25.43
1900	9.62 ± 5.47	−25.06	−24.00
1901	12.44 ± 5.85	−25.76	−24.83
1902	8.23 ± 5.85	−27.26	−25.77
1903	−21.33 ± 5.83	−25.66	−24.80
1904	−3.67 ± 10.91	−25.96	−24.92

Table 2 Results of carbon isotopic composition measurements for wholewood and latewood
α-cellulose of tree rings (*Pinus sylvestris*) from Augustów. *(Continued)*

Year	$\Delta^{14}C$ (‰)	$\delta^{13}C$ for wholewood (±0.1) (‰)	$\delta^{13}C$ for latewood α-cellulose (±0.05) (‰)
1905	−0.52 ± 9.42	−25.76	−24.46
1906	5.09 ± 6.44	−25.56	−25.50
1907	−9.16 ± 9.44	−25.76	−25.39
1908	−8.12 ± 5.76	−25.16	−25.20
1909	−23.28 ± 12.44	−25.86	−25.95
1910	−38.50 ± 5.94	−25.86	−24.30
1911	−35.81 ± 7.77	−24.68	−24.62
1912	11.10 ± 6.63	−25.36	−24.36
1913	−41.70 ± 12.41	−25.16	−25.09
1914	−10.90 ± 7.83	−25.96	−24.58
1915	−26.53 ± 8.63	−25.76	−25.78
1916	−0.56 ± 5.60	−26.26	−24.53
1917	31.71 ± 6.81	−25.16	−24.48
1918	−14.72 ± 6.12	−24.96	−25.75
1919	−1.55 ± 6.35	−25.16	−25.02
1920	−4.95 ± 6.03	−23.96	−23.51
1921	−33.11 ± 7.04	−25.36	−24.94
1922	−27.84 ± 7.22	−25.16	−24.68
1923	−4.20 ± 7.13	−25.76	−25.66
1924	32.82 ± 10.78	−25.36	−25.35
1925	33.13 ± 9.76	−25.16	−24.81
1926	34.99 ± 5.44	−25.06	−24.93
1927	18.06 ± 9.56	−24.26	−24.13
1928	12.21 ± 8.76	−25.06	−24.39
1929	38.90 ± 11.99	−25.46	−23.85
1930	5.29 ± 10.19	−24.46	−24.84
1931	25.20 ± 9.90	−25.66	−24.54
1932	36.01 ± 5.88	−25.58	−22.91
1933	21.83 ± 10.40	−26.20	−24.51
1934	−47.33 ± 11.12	−25.82	−25.74
1935	−7.04 ± 10.31	−25.67	−25.56
1936	26.46 ± 6.66	−25.47	−24.22
1937	−84.75 ± 10.39	−26.17	−24.17
1938	4.31 ± 10.16	−26.51	−24.28
1939	−58.72 ± 9.66	−26.76	−22.90
1940	−43.04 ± 11.55	−25.38	−25.82
1941	−20.13 ± 11.35	−25.75	−24.75
1942	−15.61 ± 8.52	−26.05	−24.30
1943	−18.41 ± 5.14	−25.87	−24.94
1944	−26.22 ± 11.99	−27.57	−23.14
1945	−15.85 ± 10.96	−25.51	−25.04
1946	−51.00 ± 12.44	−24.90	−24.12
1947	−14.43 ± 12.35	−26.36	−23.94
1948	−8.50 ± 8.94	−25.22	−24.12
1949	−6.78 ± 10.94	−25.54	−26.18
1950	2.97 ± 11.76	−25.73	−24.85

Table 2 Results of carbon isotopic composition measurements for wholewood and latewood α-cellulose of tree rings (*Pinus sylvestris*) from Augustów. *(Continued)*

Year	$\Delta^{14}C$ (‰)	$\delta^{13}C$ for wholewood (±0.1) (‰)	$\delta^{13}C$ for latewood α-cellulose (±0.05) (‰)
1951	–4.53 ± 9.22	–26.55	–25.99
1952	–9.18 ± 8.56	–26.18	–25.69
1953	–23.42 ± 15.00	–25.39	–24.81
1954	–50.45 ± 11.90	–25.31	–25.53
1955	–26.76 ± 11.09	–25.97	–25.96
1956	2.35 ± 9.32	–26.36	–26.15
1957	10.19 ± 11.47	–26.77	–26.16
1958	129.11 ± 10.37	–26.24	–25.80
1959	247.83 ± 10.87	–27.07	–25.97
1960	209.69 ± 13.23	–27.04	–25.80
1961	264.44 ± 13.74	–28.60	–25.98
1962	459.20 ± 9.21	–25.92	–25.91
1963	—	–27.23	–24.04
1964	—	–27.09	–25.60
1965	—	–26.74	–23.82
1966	—	–26.37	–24.94
1967	—	–25.95	–24.06
1968	—	–26.83	–24.24

We can assume that relations describing changes of this value for data for Chorzów, Ruda Śląska, and Kraków reveal a similar character. The equations take the form of $\Delta^{14}C = exp(–B \times t)$ for Ruda Śląska (*Pinus sylvestris*), parameter A = (680 ± 40)‰ and B = (6.77 ± 0.50) × 10⁻² 1/yr, and for Chorzów (*Populus nigra*) A = (675 ± 70)‰ and B = (5.91 ± 0.45)‰ 10⁻² 1/yr, where t is time (in yr) counted from 1965; for Kraków (*Pinus sylvestris*), parameter A = (198 ± 16)‰ and B = (9.70 ± 0.80) × 10⁻² 1/yr, and for atmospheric CO_2 for Kraków A = (156 ± 48)‰ and B = (7.60 ± 0.24) × 10⁻² 1/yr, where t is time (in yr) counted from 1964. Time constants of $\Delta^{14}C$ changes are, respectively:

- 14.8 for tree rings from Rudza Śląska,
- 16.9 for tree rings from Chorzów,
- 10.3 for tree rings from Kraków,
- 13.2 for atmospheric CO_2 from Kraków,
- 15.4 for atmospheric CO_2 from Schauinsland.

A local Suess effect can be described by the following value (Florkowski and Kuc 1979):

$$^{14}S = \frac{\Delta^{14}C - \Delta^{14}C_{backgr}}{1000 + \Delta^{14}C_{backgr}} \times 100 \%$$

(1),

where $\Delta^{14}C$ is the ^{14}C concentration in the sample examined and $\Delta^{14}C_{backgr}$ is the ^{14}C concentration in the clean air.

Figure 3 presents annual changes of ^{14}S determined on the basis of measurements for samples from Chorzów, Ruda Śląska, and Kraków. A decrease of ^{14}C concentration in Kraków caused by emission of ^{14}C-free CO_2 from fossil-fuel burning can be observed. The average value of the Suess effect in Kraków is −5.4 ± 1.6% for 1964–2000. For comparison, the average value of ^{14}S determined for Ruda Śląska is −4.05 ± 1.3% for 1965–1995, and for Chorzów is −1.43 ± 0.9% for 1966–1992.
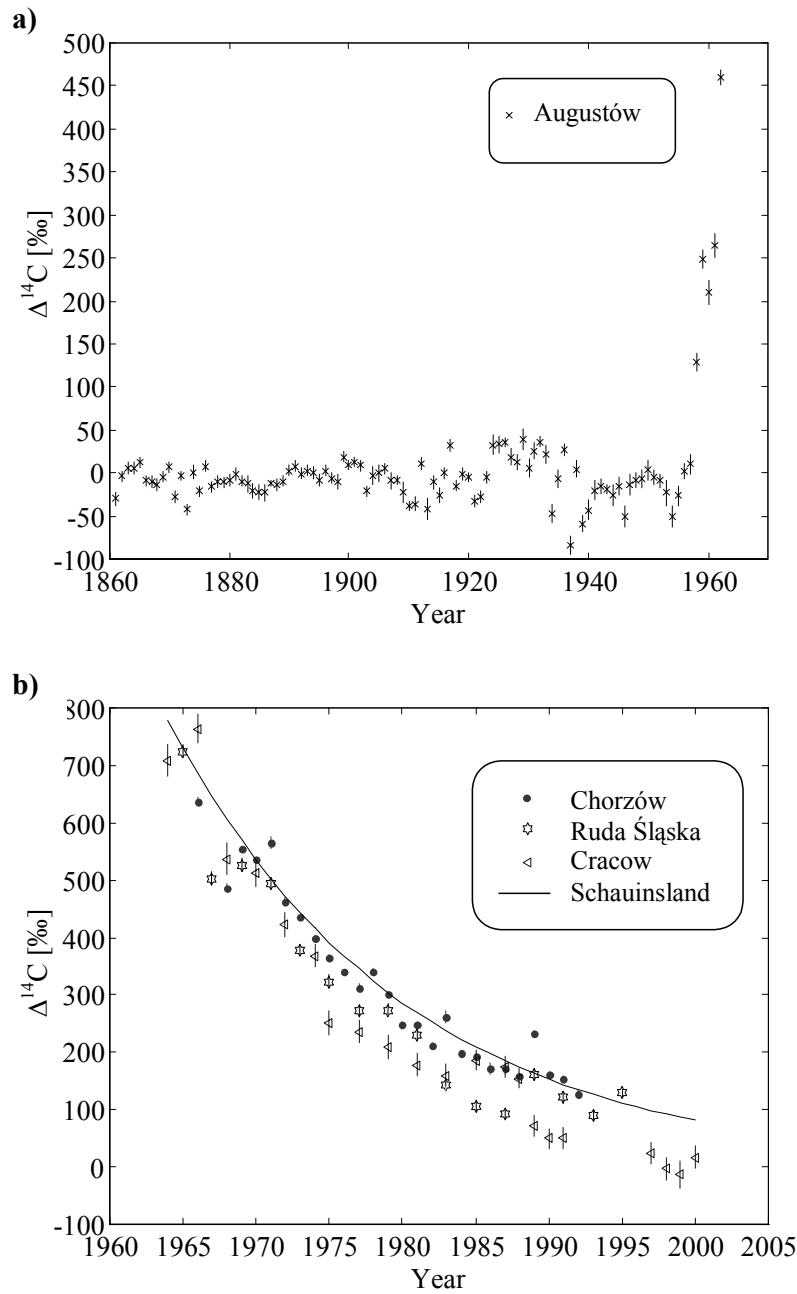
Figure 2 (a) Annual changes of $\Delta^{14}C$ in tree rings from Augustów; (b) Ruda Śląska, Chorzów (from Rakowski et al. 2001), and Kraków.

The values of [14]S determined for Ruda Śląska are much lower than corresponding values determined for Chorzów for the same years. The discrepancies result from differences in species of the examined trees. Annual tree rings of pine were used as the samples from Ruda Śląska because the vegetative period in our climatic zone is much longer than that for deciduous trees. Annual tree rings of deciduous poplar were used to determine changes of carbon isotopic composition for Chorzów.
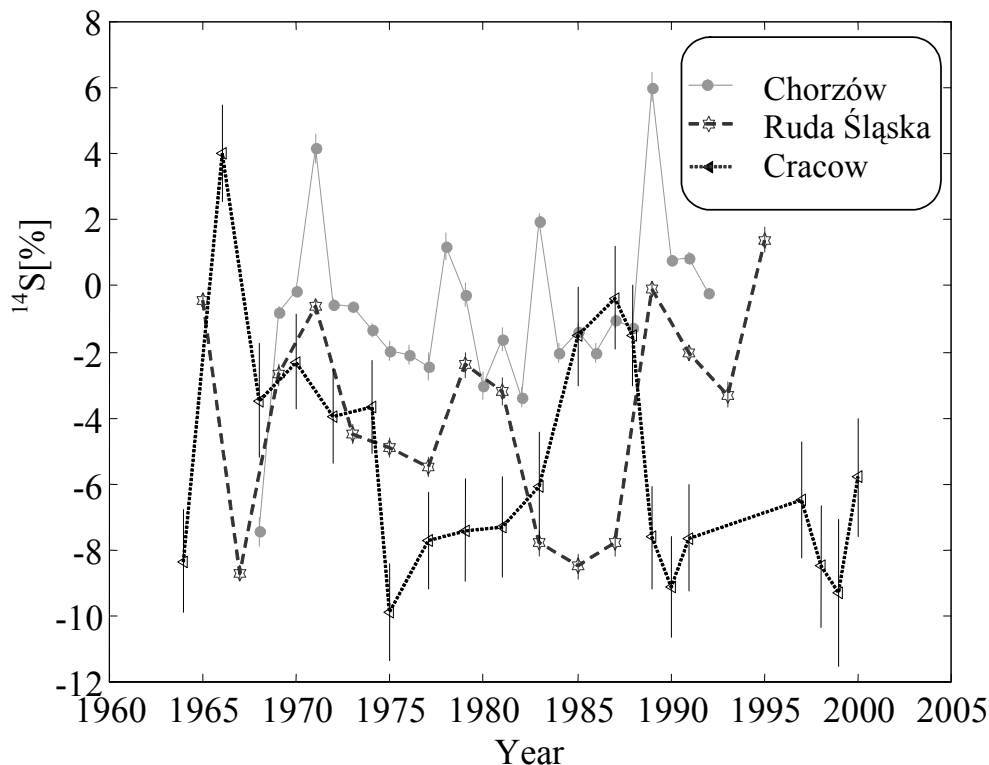
Figure 3 Changes of [14]S in tree rings from Ruda Śląska, Chorzów, and Kraków

Coniferous trees, contrary to deciduous trees, begin the assimilation cycle earlier, which allows registration of decreased ^{14}C concentration due to seasonal changes of CO_2 emission originating from fossil-fuel burning.

The value of CO_2 concentration in the atmosphere is a sum of 2 components. Natural changes of CO_2 concentration in the atmosphere and changes due to the global Suess effect are described by C_{backgr}, referred to as the natural component (background concentration). Changes of the concentration due to a local Suess effect are expressed by C_{fossil}, referred to as the emission component (fossil-fuel concentration, Levin et al. 1989). In order to determine the emission component, the following formula is used:

$$C_{fossil} = C_{backgr} \times \left[\left(\frac{{}^{14}C_{backgr} - {}^{14}C}{{}^{14}C_{backgr}} \right) \times 100\% \right] \qquad (2),$$

where C_{backgr} is the CO_2 concentration in the clean air in (ppmv), ${}^{14}C_{backgr}$ is the ^{14}C concentration in clean air in (pMC), and ${}^{14}C$ is the ^{14}C concentration for the examined region in (pMC).

Values of CO_2 concentration and ^{14}C concentration in the clean air were taken from measurements done in Schauinsland (Levin et. al. 1995; Levin and Kromer 1997). Figure 4 present values of C_{fossil} for tree rings from Kraków, Ruda Śląska, and Chorzów. Negative values of C_{fossil} are not presented in this figure. Such values are contrary to the assumption about ^{14}C concentration in the clean air.
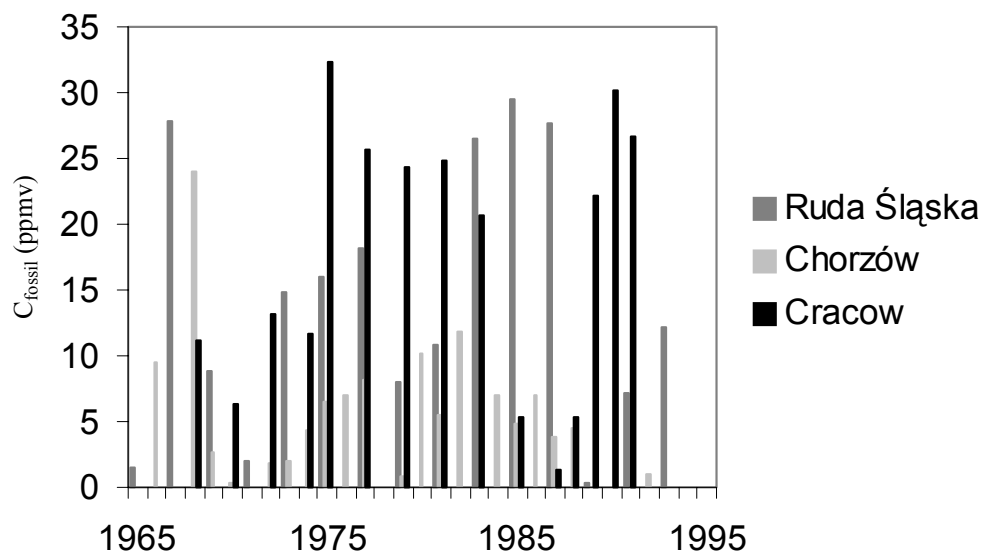
Figure 4 Changes of component value C_{fossil} for Ruda Śląska, Chorzów, and Kraków

A comparison between Δ^{14}C determined for tree rings and for atmospheric CO_2 from Kraków is presented in Figure 5. The values for atmospheric CO_2 from Kraków were determined on the basis of the average value of Δ^{14}C for the period from May to August in 1983–1990 (Kuc and Zimnoch 1998). It can be observed that values of Δ^{14}C in tree rings are lower that in atmospheric CO_2. It is very difficult to explain this effect. It might be connected with natural processes occurring during assimilation of CO_2 by trees. A systematic error between laboratories, however, cannot be excluded.

Δ^{14}C and δ^{13}C in a "Clean" Environment in North Poland

Impact of Fossil-Fuel Burning on the Values of Δ^{14}C

Emission of CO_2 from fossil-fuel burning is the reason for ^{14}C concentration depletion. Therefore, ^{14}C concentration was compared with emission of CO_2 for Poland for 1861–1955 as estimated by Marland et al. (2001). Results of that comparison are presented in Figure 6. The correlation coefficient between Δ^{14}C and average CO_2 emission for 1851–1955 is –0.23 (n = 95, p<0.01). Analyzing trends of changes reveals that from 1910, an anticorrelation between Δ^{14}C and average CO_2 emission exists. The correlation coefficient for 1910–1955 is –0.33 (n = 50, p<0.02).

Generally, the relationship between Δ^{14}C and CO_2 emission can be described as follows:

$$\Delta^{14}C = a \times e + b \tag{3},$$

where e is CO_2 emission in Poland in tons/yr as estimated by Marland et al. (2001).

Table 3 contains values of parameters a and b, correlation coefficients (r), numbers of samples (n), and significance levels (p) for different periods.

Impact of Anthropogenic Effect on δ^{13}C Values in Wholewood of Tree Rings

In the case of the trunk from Augustów, the observed decrease of δ^{13}C values is not absolutely connected with physiological processes occurring in the plant, but it can be anthropogenic. The reason for the decrease can be found in changes of carbon isotopic composition of atmospheric CO_2 for that
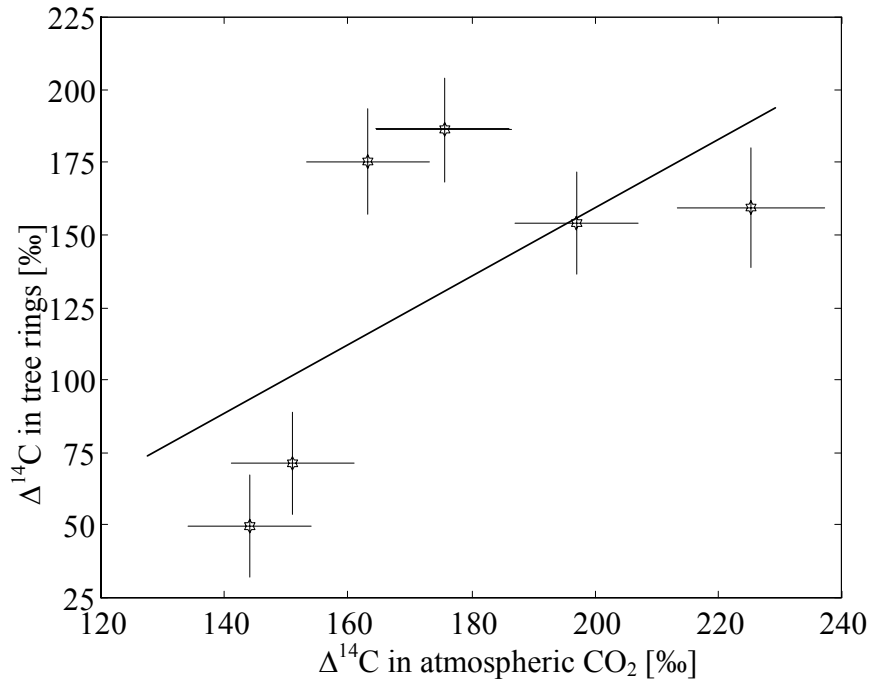
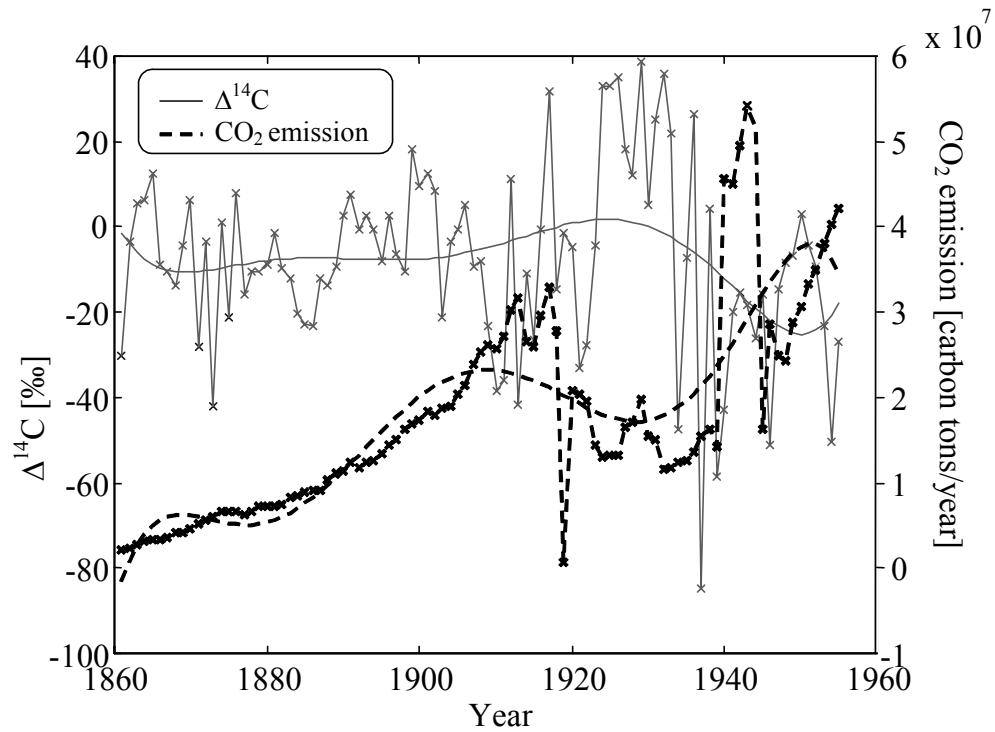Figure 5   Comparison between Δ^{14}C determined for tree rings and for atmospheric CO_2 from Kraków

Figure 6   Comparison values of tree ring Δ^{14}C with estimated CO_2 emission in Poland for years 1861–1955 (Marland et al. 2001)

Table 3 Relationship between Δ^{14}C in Augustów tree rings and average CO$_2$ emission estimated for Poland for different periods.

Years	a	b	r	n	p
1861–1955	-4×10^{-7}	-0.691	-0.23	95	<0.01
1910–1955	-8×10^{-7}	9.965	-0.33	50	<0.02

period. Development of local industry began in the 1950s. It was a source of CO$_2$ emission from fossil-fuel burning. Such an increase in CO$_2$ emission throughout Poland since 1949 is evident. Depletion observed after 1950 can be caused by both a local and regional scale increase of CO$_2$ emission.

Figure 7 presents comparison between δ^{13}C in wholewood and CO$_2$ estimated by Marland et al. (2001) for Poland for 1861–1968. Data correlated with CO$_2$ emission cover the entire year, but wood used for the investigating was formed during a vegetation period. The tree used materials stored in a period before the growth. Analysis by linear regression shows that the average sequence of δ^{13}C exhibits a higher correlation than Δ^{14}C with CO$_2$ emission, $r = -0.24$.
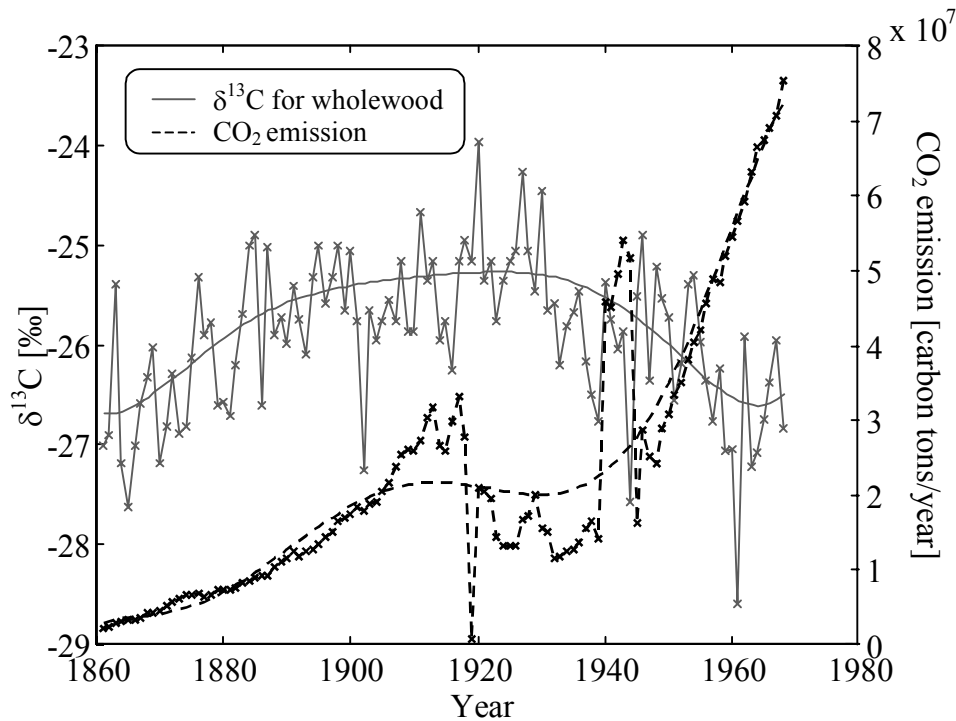

Figure 7 Comparison between δ^{13}C in Augustów tree rings (wholewood) and emission of CO$_2$ estimated for Poland for 1861–1968 (Marland et al. 2001).

If values (1861–1889) related to the preliminary stage of growth—"juvenile effect" or "canopy effect" (Sheu et al. 1997)—are eliminated from the curve of δ^{13}C values, then the correlation coefficient between δ^{13}C and CO$_2$ emission is greatly improved, $r = -54$ ($n = 79$, $p<0.001$).

The relationship between δ^{13}C values of wholewood and CO$_2$ emission estimated by Marland et al. (2001) can be written as follows:

$$\delta^{13}C = a \times e + b \tag{4},$$

where e is the CO_2 emission in Poland expressed in carbon tons/yr.

Parameters a and b, correlation coefficients (r), numbers of samples (n), and significance levels (p) for different periods are listed in Table 4.

Table 4 Relationship between Augustów $\delta^{13}C$ and CO_2 emission for different periods.

Years	a	b	r	n	p
1861–1968	-9×10^{-9}	-25.724	-0.20	108	<0.02
1890–1968	-2×10^{-8}	-25.116	-0.54	79	<0.001

Impact of Anthropogenic Effect on $\delta^{13}C$ Values in Latewood α-Cellulose

Figure 8 presents a comparison between $\delta^{13}C$ in latewood α-cellulose and CO_2 emission in Poland estimated by Marland et al. (2001) for 1899–1968. A quantitative comparison in this case is complicated because the entire year data is available and CO_2 emission changes seasonally. Higher CO_2 emission is generally connected with the winter time. However, in the case of the investigated material, the strongest impact was probably the local effect due to the development of local industry. If local factories were the main source of CO_2 emission, it can be supposed that this kind of source was not seasonal.
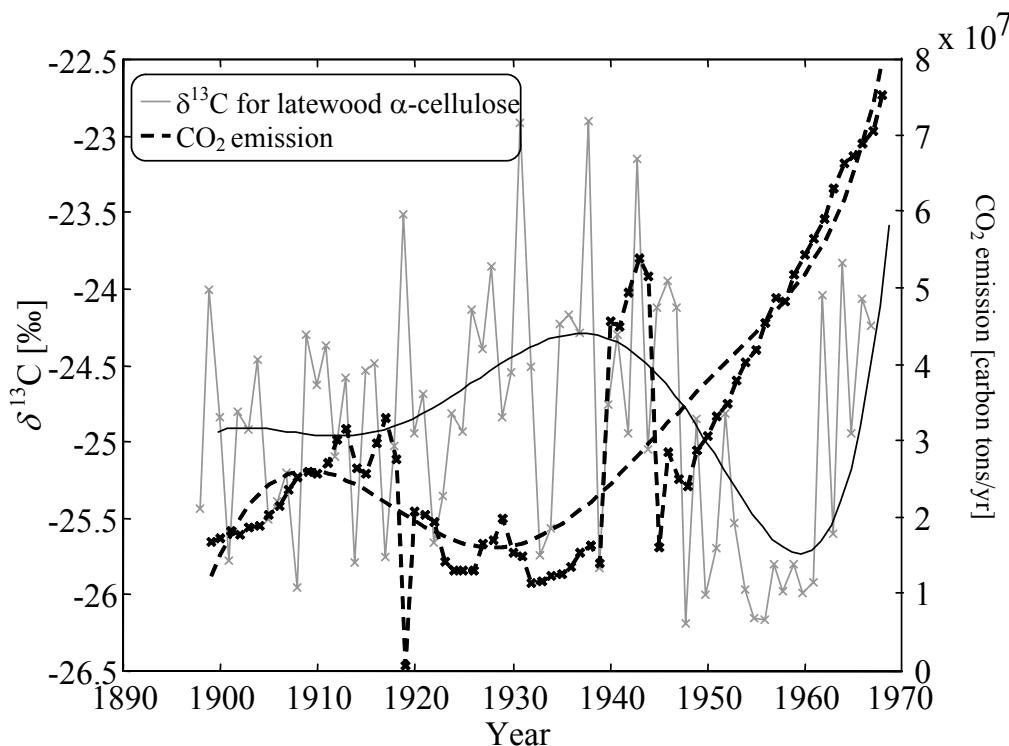

Figure 8 Comparison between $\delta^{13}C$ in latewood α-cellulose of Augustów tree rings and emission of CO_2 estimated for Poland for years 1899–1968.

Values of $\delta^{13}C$ have increased since 1963. Such a behavior can result from the lower hydraulic conductance in vascular systems (Switsur et al. 1996). Considering the impact of anthropogenic and physiological effects on $\delta^{13}C$ values, the period 1963–1968 was ruled out. In this case, the correlation coefficient is -0.36 ($n = 64$, $p<0.005$).

Comparing trends in Figure 8, it can be noticed that from 1910 a clear anticorrelation between $\delta^{13}C$ and CO_2 emission exists. The correlation coefficient for 1910–1962 is –0.40 ($n = 53$, $p < 0.005$).

On the basis of Equation 4, a relationship between $\delta^{13}C$ in latewood α-cellulose and CO_2 emission estimated for Poland can be described. Parameters a and b, correlation coefficients (r), numbers of samples (n), and significance levels (p) for different periods are listed in Table 5.

Table 5 Relationship between $\delta^{13}C$ in Augustów α-cellulose and CO_2 emission for different periods.

Years	a	b	r	n	p
1899–1968	-7×10^{-9}	–24.685	–0.15	70	<0.3
1899–1962	-2×10^{-8}	–24.357	–0.36	64	<0.005
1910–1962	-2×10^{-8}	–24.232	–0.40	53	<0.005

ESTIMATION OF CO$_2$ CONCENTRATION IN THE ATMOSPHERE ON THE BASIS OF Δ^{13}C IN LATEWOOD α-CELLULOSE

Values of $\delta^{13}C$ in latewood α-cellulose depend on many factors. By analyzing the impacts of subsequent factors on $\delta^{13}C$, the following partial differential equation can be written:

$$\delta^{13}C = f(y, t, p, e, \rho) \tag{5},$$

$$\frac{\partial \delta^{13}C(y, t, p, e, \rho)}{\partial y} = \frac{\partial \delta^{13}C}{\partial t} \times \frac{\partial \delta^{13}C}{\partial y} + \frac{\partial \delta^{13}C}{\partial p} \times \frac{\partial p(y)}{\partial y} + \frac{\partial \delta^{13}C}{\partial e} \times \frac{\partial pe(y)}{\partial y} + \frac{\partial p(y)}{\partial y} \tag{6},$$

where y is the year, $\frac{\partial \delta^{13}C}{\partial y}$ is the partial derivative of $\delta^{13}C$ with respect to time (in yr),

$\frac{\partial \delta^{13}C}{\partial t}$ is the partial derivative of $\delta^{13}C$ with respect to temperature,

$\frac{\partial \delta^{13}C}{\partial p}$ is the partial derivative of $\delta^{13}C$ with respect to precipitation,

$\frac{\partial \delta^{13}C}{\partial e}$ is the partial derivative of $\delta^{13}C$ with respect to CO_2 emission,

$\frac{\partial t}{\partial y}$ is the change of temperature in time,

$\frac{\partial p}{\partial y}$ is the change of precipitation in time,

$\frac{\partial e}{\partial y}$ is the change of CO_2 in time,

$\frac{\partial \rho}{\partial y}$ is the change of $\delta^{13}C$ in time under the influence of additional factors, for example, "potential for growth," carbon flux from biosphere to atmosphere, or an error connected with establishment.

In the analysis using latewood $\delta^{13}C$, constant gradients of $\delta^{13}C$ with respect to temperature, precipitation, and CO_2 emission were assumed.

With the linear regression method, they were found to be:
$\frac{\partial \delta^{13}C}{\partial t} = 0.51‰ / °C$, $\frac{\partial \delta^{13}C}{\partial p} = -0.00217‰ / mm$, $= \frac{\partial \delta^{13}C}{\partial e} = -2 \times 10^{-8}‰ / $ tons carbon (see also the trends). Integrating Equation 6 with respect to time, individual components of $\delta^{13}C$ originating from those factors were obtained (see Figure 9). Defining the following notation:

$$\delta 1(y) = 0.51‰ / °C \times t(y) \tag{7},$$

$$\delta 2(y) = -0.00217‰ / mm \times p(y) \tag{8},$$

$$\delta 3(y) = -2 \times 10^{-8}‰ / tons\ carbon \times e(y) \tag{9},$$

it can be written as

$$\delta^{13}C(y) = \delta 1(y) + \delta 2(y) + \delta 3(y) + R \tag{10}.$$

In the above equations, R stands for other factors, noted as ρ in Equations 5 and 6 together with errors due to the assumptions made. Figure 9 presents all the components from Equation 10.
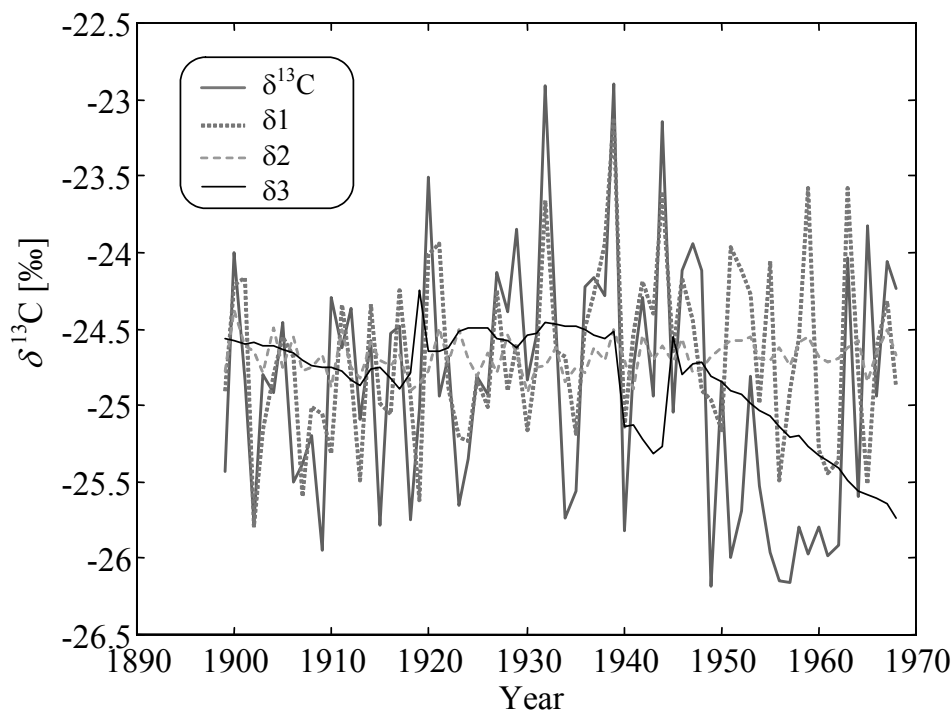

Figure 9 Components of $\delta^{13}C$ due to different factors

The correlation coefficient between $\delta^{13}C$ in latewood α-cellulose and average temperature in July and August (meteorological data for Warsaw) is $r = 0.49$ ($n = 70$, p <0.001).

Considering the impact of anthropogenic and physiological effects on $\delta^{13}C$ values, the period of 1949–1968 was ruled out. In such a case, the correlation coefficient is 0.71, which indicates the significance level is better than 0.001‰.

Because there is no meteorological data for Augustów, values of $\delta^{13}C$ were also compared with average temperatures recorded in Kaunas (for 1922–1968). Correlation coefficients between values of $\delta^{13}C$ in latewood α-cellulose and average temperature for the period of July–August noted in Kaunas are comparable to that obtained for the case of meteorological data for Warsaw ($r = 0.45$, $n = 47$, $p<0.02$). The correlation coefficient for 1922–1948 between $\delta^{13}C$ and the average temperature noted in Kaunas is 0.63 ($n = 27$, $p<0.001$). A simple way to relate $\delta^{13}C$ variations to temperature

is by a coefficient that means carbon isotopes shift per unit temperature change. By analyzing spatial distribution of temperature, it can be noted that δ^{13}C changes with temperature appear in the range 0.42 – 0.51‰ / °C.

Generally, the relationship between δ^{13}C in latewood α-cellulose and the average temperature for the period of July–September can be described as follows:

$$\delta^{13}C = a \times t + b \tag{11},$$

where t is average temperature (in °C) for the period of July–September.

Table 6 contains values of parameters a and b, correlation coefficients (r), number of samples (n), and significance levels (p).

Table 6 Relationship between δ^{13}C in latewood α-cellulose and average temperature in July–August for different periods.

Meteorological data	Years	a [‰ / °C]	b	r	n	p
Warsaw	1899–1968	0.36	–31.4	0.49	70	<0.001
	1899– 1948 and 1963–1968	0.44	–32.73	0.65	56	<0.001
	1899–1948	0.51	–34.01	0.71	50	<0.001
Kaunas	1922–1968	0.33	–30.66	0.45	47	<0.002
	1922–1948	0.42	–31.97	0.63	27	<0.001

In the case of precipitation, the correlation coefficient between δ^{13}C in latewood α-cellulose and precipitation in July and August is –0.33 ($n = 27$, p<0.1). The poor correlation is due to the distance between the meteorological observatory and Augustów.

A relationship between δ^{13}C, temperature, and precipitation was determined on the basis of meteorological data for Warsaw and for Kaunas for July and August (the time when latewood is formed). However, the relationship between δ^{13}C and CO$_2$ emission was determined on the basis of estimations by Marland et al. (2001). CO$_2$ emission concerns the entire year and whole area of Poland. Local factors had the strongest impact on δ^{13}C values. It is believed that a similar conclusion can be drawn for CO$_2$ emission. Therefore, the contribution of CO$_2$ was excluded (see Figure 10).

Assuming that only temperature, precipitation, and CO$_2$ from fossil-fuel burning contribute to δ^{13}C, the CO$_2$ emission can be evaluated as presented in Figure 11. This CO$_2$ emission data was compared with CO$_2$ emission evaluated for Poland by Marland et al. (see Figure 11). The comparison can only be done in terms of quality (a general behavior) but not quantity. It is impossible to determine values of local emission and the trend can only be compared.

CONCLUSION

Carbon isotopic composition in tree rings reflects corresponding atmospheric CO$_2$ concentration during their formation. A decrease of ^{14}C concentration caused by the emission of ^{14}C-depleted CO$_2$ from fossil-fuel burning was observed in Kraków, Chorzów, and Ruda Śląska. The local Suess effect on the polluted area (Upper Silesia and Kraków) was determined.

An anticorrelation exists between Δ^{14}C and average CO$_2$ emission in tree rings from the ecologically clean Augustów Wilderness region. Assuming that only temperature, precipitation, and CO$_2$ from
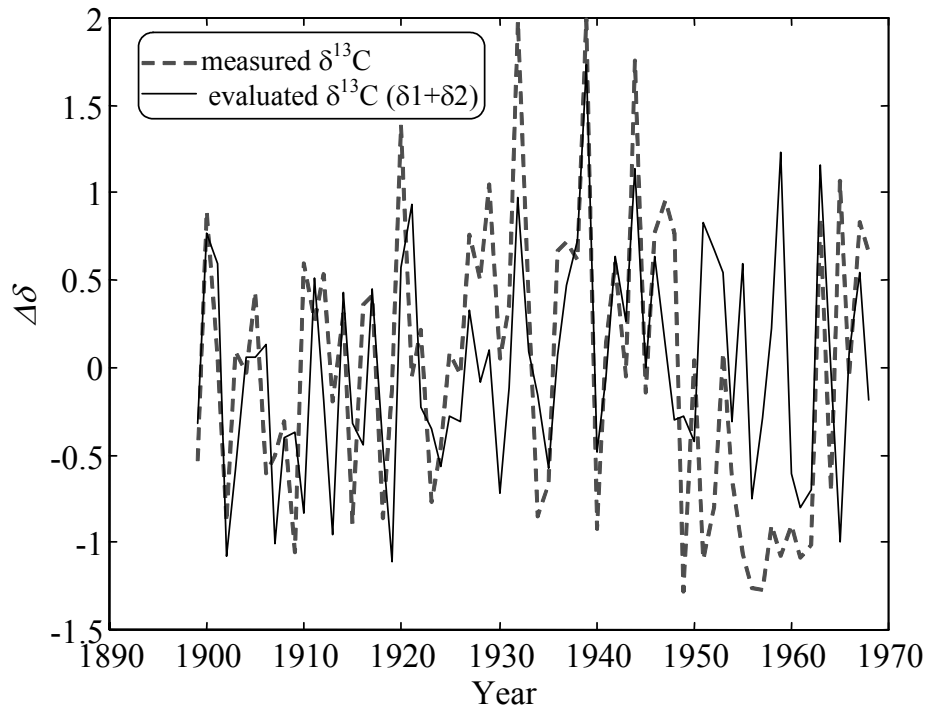
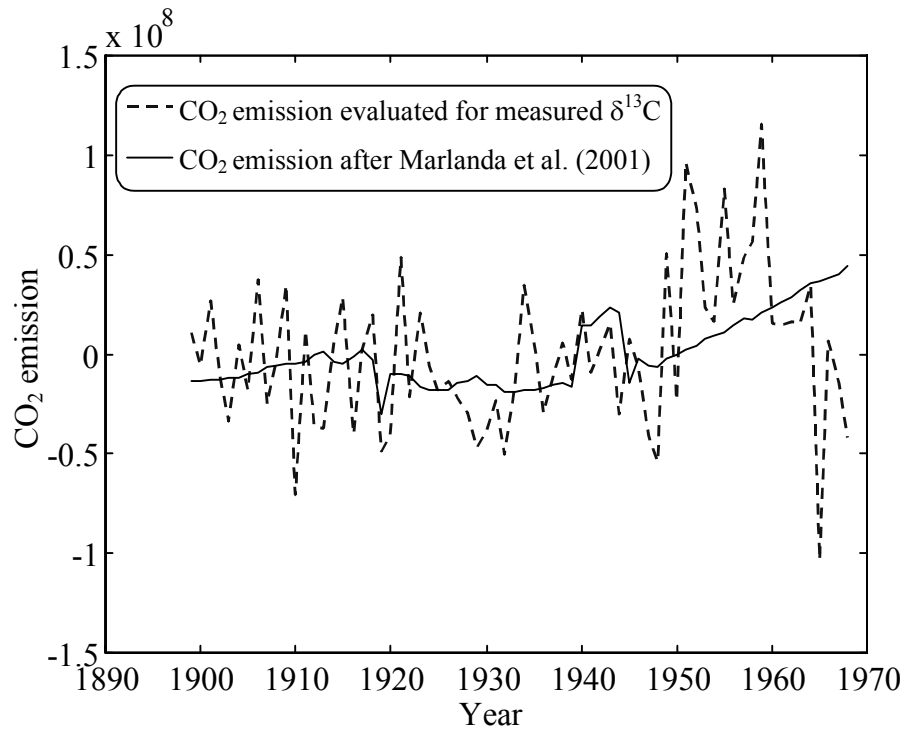Figure 10 Fluctuating measured and evaluated (δ1 + δ2) $\delta^{13}C$

Figure 11 Comparison of evaluated CO_2 emission with that given by Marland et al. (2001)

fossil-fuel burning contributed to δ^{13}C, the CO$_2$ emission was evaluated. That CO$_2$ emission data was compared with CO$_2$ emission evaluated by Marland et al. (2001). The comparison was done only in terms of quality but not quantity.

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