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RADIOCARBON CONCENTRATION IN URBAN AREA

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Abstract: Radiocarbon concentration has decreased in recent years due to the exchange of $^{14}CO_2$ between the atmosphere and the oceans, but also due to $^{12}CO_2$ emission from burning fossil fuels. This second phenomenon known as Suess effect can be observed in the highly industrialized and/or urban areas. New data of radiocarbon concentration in tree rings from Nagoya (Central Japan) and Kraków (Poland), which covered last 20 years, were obtained recently. These data were used to find the relationship between the radiocarbon concentrations in atmosphere and biosphere. Additionally, data of radiocarbon concentration in atmospheric CO_2 in Kraków were compared with those derived from annual tree rings, to calculate the time of CO_2 uptake for pine trees in this region. These data show that radiocarbon concentration of the CO_2 in "urban air" is systematically lower than that in "clean air". Data of radiocarbon concentration were fitted by exponential and linear functions to calculate the time of exchange and predict the future level. Using data of carbon dioxide and radiocarbon concentration from Schauinsland fossil component C_f in carbon dioxide concentration level was calculated in Nagoya and Kraków.

1. INTRODUCTION

Carbon dioxide concentration in atmosphere at present has exceeded a value of 370 ppm (GLOBALVIEW-CO_2, 2003) mostly due to emission from fossil fuels such as coal, petroleum, natural gas, etc. Increased carbon dioxide concentration caused changes in the isotopic composition of carbon not only in the atmosphere, but also in other reservoirs like biosphere and oceans. Decreasing of radiocarbon concentration has been observed (Suess, 1955; Stuiver and Quay, 1981) in wood samples since the middle of 19th century when the Industrial Revolution begun. In the 1950s and 1960s artificial radiocarbon was produced in the atmosphere during nuclear weapon tests, reaching a maximum in 1963 when the level of the concentration was two times higher than natural radiocarbon concentration (Nydal and Lövseth, 1996). Since 1963 when the test ban treaty was enforced, the radiocarbon concentration decreased due to CO_2 exchange, mainly against the ocean carbon reservoir and the input of "dead" carbon from fossil fuels. In 1990s, the concentration was still 10% higher than the natural level in "clean air" (McNeely, 1994; Levin and Kromer, 1997). Significantly lower levels of radiocarbon concentration were observed around urban and/or industrial areas (Rakowski *et al.,* 2001; Muraki *et al.,* 2001) as the result of intense emission of carbon dioxide from industrial facilities, vehicles, and common sources. Atmospheric carbon dioxide level and radiocarbon concentration are constantly monitored, either by direct measurement (Levin and Kromer,1997; NOAA, 2001; Kuc *et al.*, 1998;), or by use of bioindicators (McNeely, 1994; Krajcar Bronic *et al.*, 1998; Muraki *et al.*, 1998 and 2001), by several laboratories around the world. The magnitude of this effect on ^{14}C concentration is dependent on the distance from the sources of CO_2 emissions (Awsiuk and Pazdur, 1986).

To investigate the secular changes in ^{14}C concentration in the urban area of Nagoya city, Japan, and Kraków city, Southern Poland, and to estimate the CO_2 contribution by a local consumption of fossil fuels, we have analyzed carbon isotope composition of atmospheric CO_2 and annual rings of pine trees.

2. STUDY AREA

Nagoya (35°57'N, 136°58'E) is located in Aichi Prefecture, central Japan, and with a population of over two million is the fourth largest city in Japan (**Fig 1a**). Along with pollution related to urban infrastructure and vehicles, local industrial facilities in Nagoya and the surrounding area are the main source of carbon dioxide emissions. The sampling was done on the main campus of Nagoya University and in an area 8 km east of the city centre. Samples of annual growth rings in pine trees (*Pinus densiflora*) were taken using a hollow drill.

Kraków (50°3'N, 19°54'E) is a city of one million people, located about 100 km to the north of the Tatra Mountains in southern Poland (**Fig 1b**). Air pollution related to the urban infrastructure, industrial facilities, and a large steel factory (Huta im. Tadeusza Sendzimira) have elevated carbon dioxide levels in the local atmosphere (Kuc *et al.,* 2003). Since 1983, the Department of Environmental Physics, University of Science and Technology in Kraków, has monitored carbon isotope compositions in tropospheric CO_2 (Florkowski *et al.,* 1975; Kuc, 1991; Kuc and Zimnoch, 1998). Samples of atmospheric CO_2 were taken at biweekly intervals from the Faculty building roof on the university campus, 25 m above ground level. Annual tree rings were also taken from pine trees (*Pinus sylvestris*) growing near the university.

3. SAMPLES AND METHOD

Two kinds of material were used in this study, namely, CO_2 separated directly from the air collected in bi-weekly intervals and representing an integrated value over the sampling period, and tree rings obtained from trunks of pine trees (*Pinus silvestris* and *Pinus densiflora*).

Atmospheric CO_2 Samples

Samples of atmospheric CO_2 were taken applying the method of selective sorption in a capillary sorbent, as described in Florkowski *et al.* (1975), Kuc (1991) and Kuc and Zimnoch (1998). Radiocarbon measurements were performed with a liquid scintillation spectrometer (Tri-Carb®, Canberra-Packard), after the conversion of purified CO_2 to benzene using a standard procedure and mixing with a scintillation cocktail (b-PBD + b-MSB, Packard). Stable carbon isotope composition was measured using VG Micromass 602 C and Finningan MAT Delta S mass spectrometers at Kraków University.

Tree-Ring Samples

Samples of annual growth rings of the pine tree were taken as a radial section of a diameter of 5mm, using a hollow drill. To obtain sufficient amount of material for AMS analysis, three core samples were collected from each tree and the annual growth rings were separated. A mixture of early wood and late wood was used to represent a single year sample. Samples were washed in distilled water and prepared using the A-A-A method. The treated residues were combined with cupric oxide and sealed into glass tubes evacuated with a rotary pump. The tubes were then placed in an electric furnace for 2 hours at 850°C. Carbon dioxide produced from the samples was purified in a glass cryogenic vacuum line system, and then reduced to graphite using iron powder as a catalyst (Kitagawa *et al*., 1993). The resulting mixture of graphite and iron powder was dried and pressed into a target holder for AMS ^{14}C measurements with a HVEE tandetron AMS system at the Nagoya University. The stable carbon isotope ratio was measured using a Finningan MAT 252 isotope-ratio mass spectrometer at the Center for Chronological Research, Nagoya University (Nakamura *et al*.,

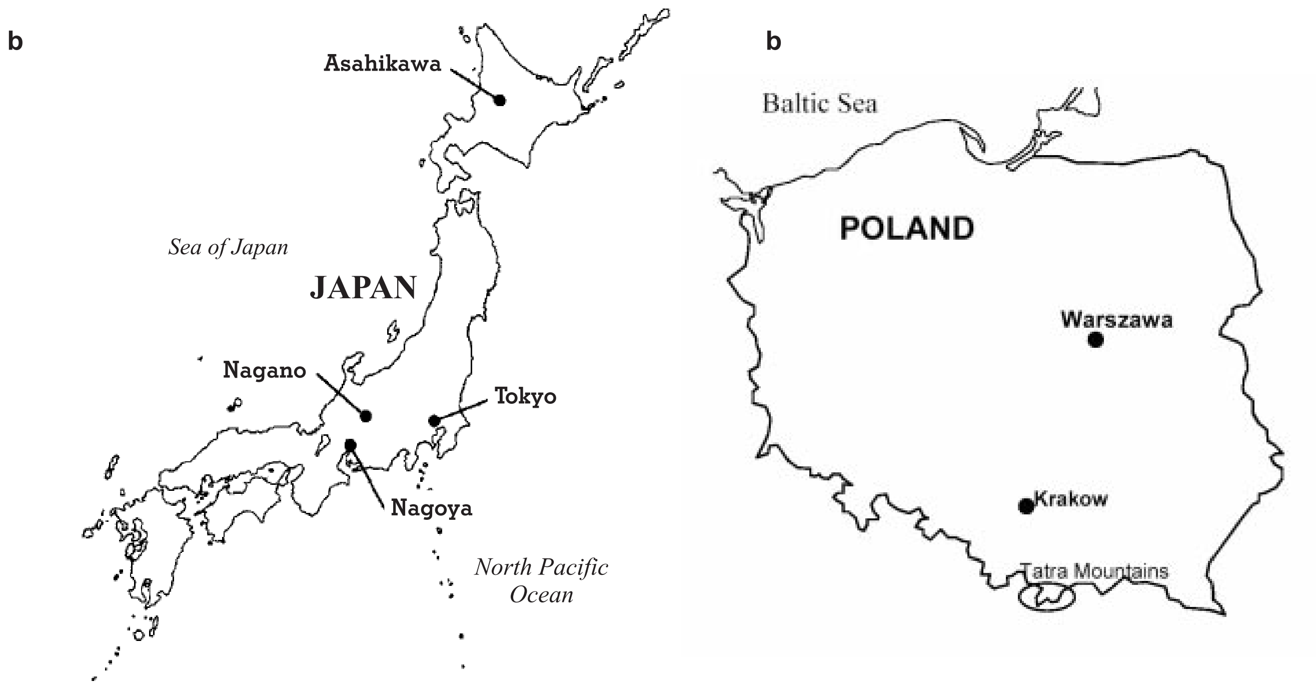

Fig. 1. Maps of Japan (a) (Muraki et al. 2001), and Poland (b) with locations of Nagoya and Kraków.

2000). Radiocarbon contents are reported as $\Delta^{14}C$ in per mil (‰) deviations from the standard sample being 95% activity of NBS oxalic acid (SRM-4990C) (Stuiver and Polach, 1977). The stable carbon isotope ratio is expressed in $\delta^{13}C_{PDB}$ notation on the PDB scale (Craig, 1957).

4. RESULTS AND DISCUSSION

Nagoya

Figure 2a shows the variation of ^{14}C concentrations in tree rings for the 24 years from 1979 to 2002. Data from Schauinsland (Levin and Kromer, 1997) are included to represent yearly average values of ^{14}C concentration in "clean air". Instead of seasonal averages, the yearly average values were used, according to the mild and maritime climate in Nagoya which extends the vegetation period for pine tree to almost the whole year. An exponential function was fitted to the data from Schauinsland to estimate the $\Delta^{14}C$ values for the period 1996-2002 by extrapolation. The results show a gradual decrease in radiocarbon activity over time. A decrease of 8.8‰ per year for the tree ring data was obtained for the period analyzed. Atmospheric $\Delta^{14}C$ data measured at two stations in Croatia (Zagreb and Plitovice) during a similar period yielded decreasing values of 12‰ and 10.6‰ per year respectively (Krajcar-Bronić *et al.,* 1998). For Schauinsland station, decreases of 14.1‰ per year for the period 1983-1985 and 9.7‰ per year for 1985-1989 were obtained (Levin *et al.,* 1992).

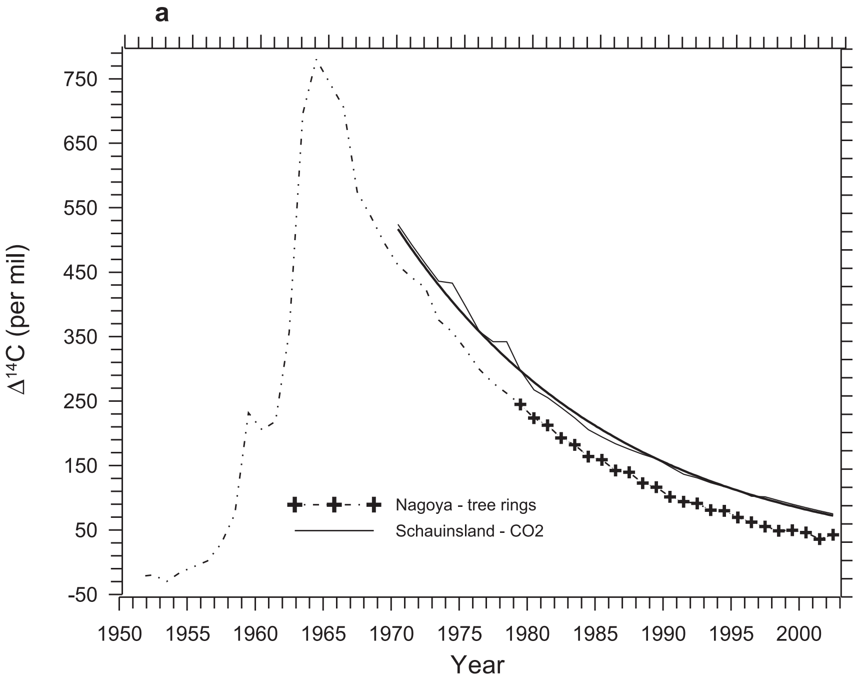

***Fig. 2a**) Radiocarbon concentration in tree rings from Nagoya, central Japan. The solid line represents annual average values of radiocarbon concentration measured in "clean air" at Schauinsland station (Levin and Kromer, 1997). Dotted line presents radiocarbon concentration in Nagoya for the period 1951-1978 (author's unpublished data).*

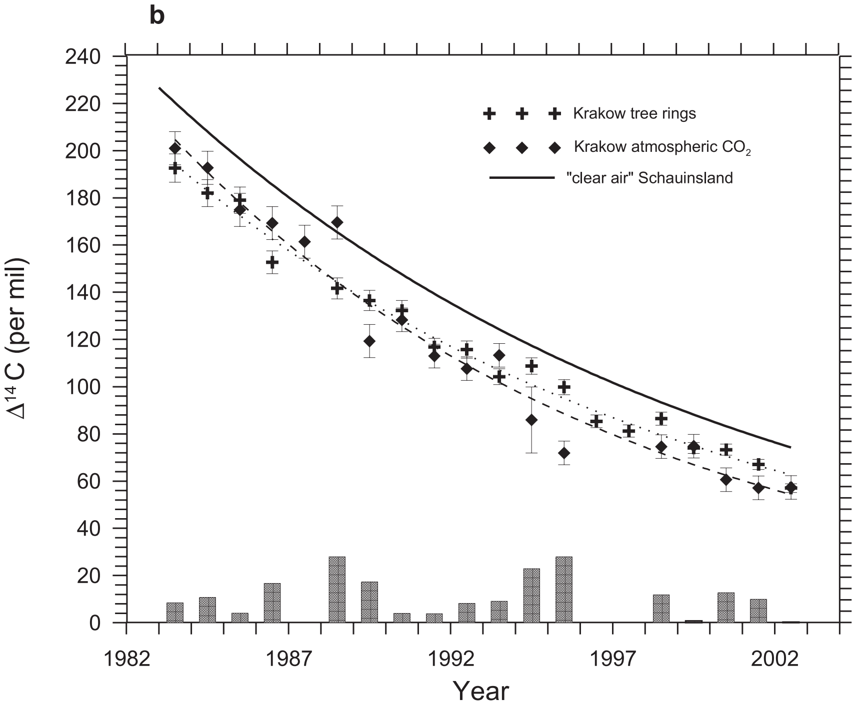

***Fig. 2b**) Radiocarbon concentration in tree rings samples and atmospheric CO_2 collected at Kraków, Southern Poland. To the observed data were fitted exponential functions. Solid line presents radiocarbon concentration in "clean air" at Schauinsland station derived from measurement of atmospheric CO_2 (Levin and Kromer, 1997). All atmospheric data represent mean value for the period of April to September corrected by $\delta^{13}C$=-25‰.*

Radiocarbon concentrations in annual rings of the pine tree from Nagoya are lower than those observed in "clean air" of relevant years from Schauinsland station. This can be attributed to a local Suess effect. The $\Delta^{14}C$ values of 55.4‰, 48.7‰, and 49.5‰ obtained for 1997, 1998, and 1999 annual rings of one pine tree, respectively, are slightly lower than those for the leaves of a tree (*Quercus variabilis*) collected nearby (64.1‰, 54.3‰, and 63.2‰; Muraki *et al*., 2001) for respective years. Possibly, it is due to the differences of CO_2 emission from fossil fuels and due to a different vegetation period of the two kinds of trees used for the experiments. Radiocarbon concentrations of 79‰, 69‰, and 62‰, in tree rings during the years 1994, 1995 and 1996, respectively, are also significantly lower than annual mean values of the $\Delta^{14}C$ in atmospheric CO_2 at Schauinsland (117‰, 111‰, and 102‰; Levin and Kromer, 1997), and in the tree ring year 1995 at Agematsu "clean air" region, Japan (Muraki *et al*., 1998). On the other hand, those data are similar to respective values for atmospheric CO_2 at Zagreb (81‰, 88‰, and 56‰; Krajcar-Bronić *et al.,* 1998), where the decrease of ^{14}C concentration can be also expected due to the Suess effect.

To estimate the long-term changes in the radiocarbon concentration, an exponential function was fitted to the results for tree rings from Nagoya, giving the correlation coefficient R equal 0.99. The function yields an inverse value of the decay constant to be 13.1 yr that is comparable to the estimates of around 16 yr reported in the literature (Levin and Kromer, 1997; Krajcar-Bronić *et al.,* 1998; McNeely, 1994). Additionally, a linear function was fitted to the $\Delta^{14}C$ data for the periods 1979-1983 and 1984-2002, separately, and the $\Delta^{14}C$ value was estimated to decrease at a rate of 15.6‰/yr and 7.1‰/yr, respectively. Atmospheric $\Delta^{14}C$ values measured at two stations in Croatia (Zagreb and Plitovice) during a similar period yielded decreasing rates of 12‰/yr and 10.6‰/yr, respectively (Krajcar-Bronić *et al.,* 1998). Similarly, for the Schauinsland station, decreasing rates were obtained to be 14.1‰/yr and 9.7‰/yr for the periods 1983-1985 and 1985-1989, respectively (Levin *et al*., 1992). The decrease rates of $\Delta^{14}C$ at four different places show similar values for similar periods. This suggests that the process of diluting ^{14}C concentration in the atmospheric CO_2 could have a similar character in different locations and environments. The linear regression predicts that $\Delta^{14}C$ values will be equal to 0‰ in 2006 for Nagoya, comparable with the estimates of 2007 for Schauinsland (Levin and Kromer, 1997), 2004 for Groningen (Meijer *et al*., 1994) and 2000 for Zagreb (Krajcar-Bronić *et al.,* 1998).

Kraków

Figure 2b shows radiocarbon concentrations in tree rings and atmospheric carbon dioxide from Kraków. Data from Schauinsland that represent radiocarbon concentrations in "clean air" are included. To compare the atmospheric data with the results obtained from tree rings, radiocarbon concentration data in atmospheric carbon dioxide were averaged between April and September of each year, which is comparable to the vegetation growth season in Poland, and corrected for carbon stable isotope ratio to $\delta^{13}C$=-25‰ to provide $\Delta^{14}C$ notation (Suiver and Polach, 1977). Data from Schauinsland were treated in the same manner and the radiocarbon concentrations for the period between 1997 and 2002 were calculated from an exponential curve fitted to the observed data. All of the data show a continuous decrease in radiocarbon activity over time. A decrease of 7.1‰/yr for tree ring data and 9.15 ‰/yr for atmospheric radiocarbon concentration was obtained for the analyzed period.

Differences in the $\Delta^{14}C$ values in tree rings and atmospheric carbon dioxide from Kraków are presented in bar form in **Fig. 2b**. Radiocarbon concentrations in atmospheric CO_2 at Kraków show strong peak-to-peak (~56 ‰; Kuc and Zimnoch, 1998) and seasonal fluctuations that cannot be observed in tree ring measurements. Radiocarbon concentrations in both kinds of samples from Kraków are lower than in "clean air" at the Schauinsland station. This can be attributed to a local Suess effect. The $\Delta^{14}C$ values in tree rings (108‰, 99‰, and 85‰ for 1994, 1995 and 1996, respectively) are lower than the yearly mean values in atmospheric CO_2 at Schauinsland (see above; Levin and Kromer, 1997), but higher than those measured in Zagreb (see above; Krajcar-Bronić *et al.,* 1998) for the same period.

Exponential curves were fitted to the Kraków data for the period 1983-2002 to determine long-term changes in radiocarbon concentration in the atmosphere and biosphere. These analyses provide time decay constants of 16.7 yr for tree ring data and 14.3 yr for atmospheric CO_2 data, which agree well with ~16 yr estimates reported in the literature (Levin *et al.,* 1995; McNeely, 1994; Krajcar-Bronić *et al.,* 1998). Decreasing ratios calculated from the exponential and linear data-fitting gave values of 7.1‰/yr and 6.75‰/yr for tree ring data and 7.75‰/yr and 6.29‰/yr for atmospheric CO_2 data. The linear data-fitting predicts 2010 (tree rings) and 2007 (atmospheric CO_2) as the years that $\Delta^{14}C$ values will equal 0‰, which is comparable with reported data (see above).

Fossil fuel component

Radiocarbon concentrations in the atmosphere over large cities depend on emissions of CO_2 from fossil fuels. Concentrations of CO_2 can be divided into three components: a background component (C_a); a biogenic component (C_b); and a fossil fuel component related to the anthropogenic emission of CO_2 (C_f). Mathematical equations that are widely described in (Kuc and Zimnoch, 1998 and Rakowski *et al*., 2001) can be used to describe the relationships between each component and carbon isotopic composition. They were used to estimate the fossil fuel component. The value of the fossil fuel component varied seasonally from *ca.* 27.5 ppmv in winter to *ca.* 10 ppmv in summer in the period 1983-1994 (Kuc and Zimnoch, 1998). These variations correlate with differences in fossil fuel consumption between seasons. The fossil fuel component of the CO_2 concentration in the atmosphere was calculated using data obtained experimentally, along with additional data that represent yearly average values of $\Delta^{14}C$ and CO_2 concentration in "clean

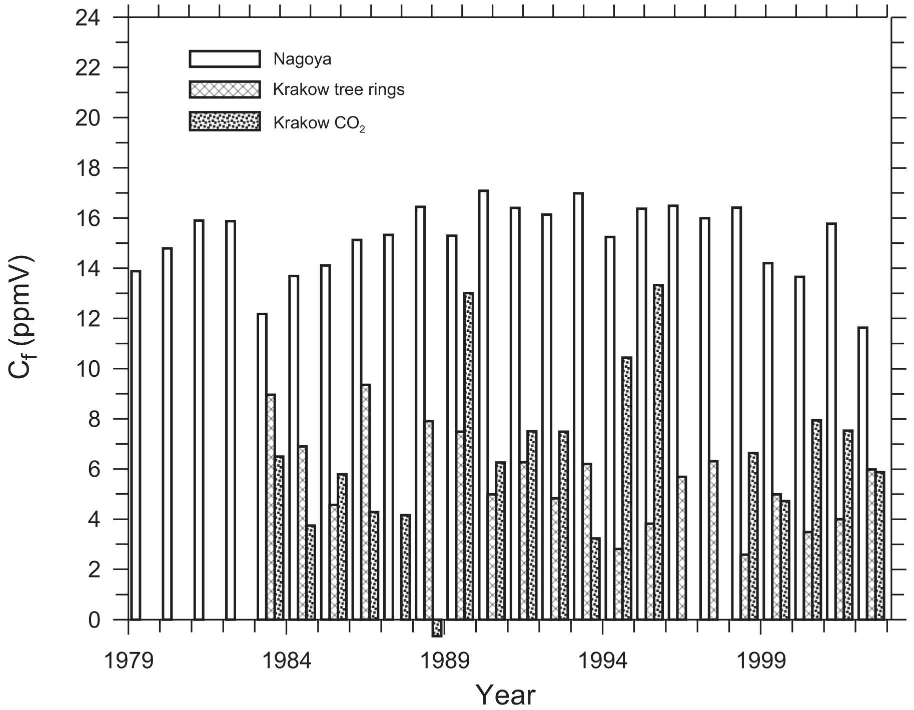

Fig. 3. Values of fossil component C_f calculated using data from tree rings from Nagoya and Kraków and atmospheric CO_2 at the Kraków sampling sites. Data from Nagoya represent annual average value and data from Kraków represent average value for period April to September in every year.

air" at Schauinsland station (GLOBALVIEW-CO_2. 2003; Levin and Kromer, 1997), which includes both, background and biogenic components. Calculated results are shown in **Fig. 3**.

The yearly average value of fossil fuel component in Nagoya for the analyzed period was 15.2 ppmv which falls between the approximate seasonal values of 27.5 ppmv (winter) and 10 ppmv (summer) calculated for the period 1983-1994 in the urban area of Kraków (Kuc and Zimnoch, 1998). Values of 5.9 ppmv and 6.5 ppmv were obtained from tree ring data and atmospheric CO_2 from Kraków respectively. These represent the April to September average for the period 1983-2003 and are both lower than the summer value obtained by Kuc and Zimnoch (1998). This could be a consequence of using different data of carbon dioxide concentration. The error of estimation for the anthropogenic emission of CO_2 (C_f) is around ±8 % or less of the total value.

5. CONCLUSIONS

Radiocarbon concentrations in tree rings from Nagoya and Kraków and in samples of atmospheric carbon dioxide measured at Kraków for the last 20 years are systematically lower than those measured in "clean air", because of anthropogenic CO_2 emission from fossil fuel use. Data were fitted with exponential and linear functions giving more consistent values of decrease rates and decay constants. A linear function fitted to the data was used to predict the time at which "natural" level of radiocarbon ($\Delta\,^{14}C = 0$ ‰) would be reached. From the data it was also possible to calculate the fossil fuel component from the total concentration of carbon dioxide.

Those results show that from the isotopic information recorded in tree rings it is possible to reconstruct radiocarbon concentration in the past, and data like this can also be used for analytical calculation. This method provides a valuable environmental monitor. To obtain a better agreement between two kinds of data, the time of uptake of CO_2 for pine tree in this region should be calculated separately for every year.

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