



RADIOCARBON METHOD IN MONITORING OF FOSSIL FUEL EMISSION

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Received 28 February 2011

Accepted 25 May 2011

Abstract: The traditional radiocarbon method widely used in archaeology and geology for chronological purposes can also be used in environmental studies. Combustion of fossil fuels like coal, natural gas, petroleum, etc., in industrial and/or heavily urbanized areas, has increased the concentration of carbon dioxide in the atmosphere. The addition of fossil carbon caused changes of carbon isotopic composition, in particular, a definite decrease of ^{14}C concentration in atmospheric CO_2 and other carbon reservoirs (ocean and terrestrial biosphere), known as the Suess effect. Tree rings, leaves, as well as other annual growing plants reflected the changes of radiocarbon concentration in the atmosphere due to processes of photosynthesis and assimilation of carbon from the air. By measuring radiocarbon concentration directly in atmospheric CO_2 samples and/or biospheric material growing in industrial and/or highly urbanized areas where high emission of dead carbon is expected, it is possible to estimate the total emission of dead CO_2 . Based on equations of mass balance for CO_2 concentration, stable isotopic composition of carbon and radiocarbon concentration it is possible to calculate CO_2 concentration associated with fossil fuel emission into the atmosphere. The procedure uses differences between the radiocarbon concentration and stable isotope composition of carbon observed in clean areas and industrial or/and highly urbanized areas.

Keywords: Radiocarbon, Suess effect, stable isotopes of carbon, AMS.

1. INTRODUCTION

The increase of combustion of fossil fuels like coal, natural gas, petroleum etc. in industrial areas, causes the emission of carbon dioxide to the atmosphere. Isotopic composition of fossil carbon is slightly different from modern carbon, mostly because the former does not contain radiocarbon whose half-life is much shorter than the formation period of fossil fuels.

First investigations of contemporary tree samples (Suess, 1955) proved that their radiocarbon activity was lower than in samples from the middle of the 19th century. Atmospheric $\Delta^{14}\text{C}$ has decreased by about 20.0‰

between years 1890 and 1950 from which 17.3‰ is attributed to the Suess effect and the remainder is thought to be caused by variation in the cosmic ray production of radiocarbon (Stuiver and Quay, 1981). 95% of the total carbon dioxide from burning of fossil fuels is released in the Northern hemisphere (NH). However, because of air-mass mixing between Northern (NH) and Southern (SH) hemispheres, the Suess effect has a global character.

Precise investigations in atmospheric concentration of carbon dioxide have been performed at Mauna Loa Observatory in Hawaii (Keeling and Whorf, 1994) since 1956. Data from the three Antarctic cores DE08, DE08-2 and DSS (Etheridge *et al.*, 1996) and direct measurement from Mauna Loa (Keeling and Whorf, 1994) were used to reconstruct the past atmospheric carbon dioxide concen-

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tration from 1000 to 1992. The results show that concentration of this gas in the atmosphere maintained constant level of about 280 ppmV between years 1000 and 1880. These results were also used to estimate the amount of carbon in the atmosphere before the Suess effect. The total amount of carbon in the atmosphere before 1880 had a value of $N_0 = 615 \text{ GtC}$ (Keeling *et al.*, 1989). Between 1880 and 1990, the concentration of carbon dioxide in the atmosphere has increased by about 90 ppmV. In present time, the total concentration of this gas is about 370 ppmV and is higher than that observed at any time within the last 400,000 years (Petit *et al.*, 1999). The increasing rate of carbon dioxide concentration in the atmosphere is proportional to the emission rate of carbon dioxide from fossil fuel consumption. In less than two centuries, 280 Gt of carbon has been added to atmosphere from burning of fossil fuels (Marland *et al.*, 1999).

In the late 1950s and early 1960s radiocarbon concentration in the atmosphere rapidly increased due to nuclear bomb tests. The excess radiocarbon from nuclear detonations was mostly injected into the northern stratosphere and through mid- to high- latitude tropopause gap returned to the northern troposphere. As a result of this process in 1963 the level of radiocarbon concentration in Northern hemisphere (NH) was about 100% higher than pre-bomb concentrations. Maximum level of radiocarbon concentration in Southern hemisphere (SH) was lower (only 70% of natural concentration) than in NH and was observed in 1965 (Nydal and Lövseth, 1996). Since the test ban treaty was enforced in 1963, the radiocarbon concentration in the atmosphere slowly decreased, due to carbon exchange between the carbon reservoirs (mainly ocean and biosphere). As bomb radiocarbon reached a global equilibrium in the late 1960s (Telgades, 1971), there have not been large differences between radiocarbon concentrations between the NH and SH from 1970 onwards (Hua and Barbetti, 2004). The large pulse of artificial radiocarbon injected to the atmosphere gave us a powerful tool for studying the carbon cycle and transfer processes between the carbon reservoirs (Nydal, 1968, Oeschger *et al.*, 1975, Levin and Hessheimer, 2000).

Data of CO_2 and radiocarbon concentration level are constantly collected in clean and polluted areas, either directly for atmospheric air (Levin *et al.*, 1994, 1999, 2003, Levin and Kromer, 1997, 2004, Schmidt *et al.*, 2003, GLOBALVIEW- CO_2 , 2008 Kuc *et al.*, 2003), or for plants (McNeely, 1994, Muraki *et al.*, 1998, 2001, Rakowski *et al.*, 2001, 2004a, b, 2005, 2008, 2010, Rakowski, 2010) by several laboratories around the world. To estimate the local decrease of radiocarbon concentration due to the Suess effect and CO_2 emission mathematical equations can be used that include a relationship between carbon isotope composition and CO_2 concentration from fossil fuel combustion and the decreasing trend of radiocarbon content over time (Levin *et al.*, 2003). The method, which was used for calculation of

CO_2 concentration from fossil fuel use, will be presented in detail in this paper.

2. SAMPLES AND METHOD

Samples were taken from annual growth rings in pine trees using hollow drills. To obtain sufficient material for AMS analysis, three core samples were taken from each tree and annual growth rings were separated. Each core taken was 25-30 cm long and had 0.5 cm in diameter. Samples were washed in distilled water and prepared with the widely used A-A-A method. Some of the samples were treated to extract α -cellulose from early and late wood ring using a method described in Green (1963) and Pazdur *et al.* (2005).

Pre-treated residues of samples 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. Water produced during combustion was removed via a trap containing a mixture of methanol and liquid nitrogen at 170K. SO_x compounds were removed with an n-pentane trap cooled to 77K by liquid nitrogen. Purified CO_2 was then condensed in glass tubes using liquid nitrogen.

The prepared carbon dioxide samples were reduced to graphite using iron powder as a catalyst (Kitagawa *et al.*, 1993). The iron powder was prepared in a vacuum line containing hydrogen and heated for about 1 hour at 450°C . The line was evacuated and carbon dioxide was condensed with the iron powder using liquid nitrogen. Hydrogen was then added and the glass tube was sealed. Reduction was done in an electric furnace at 850°C for 6 hours.

The resulting mixture of graphite and iron powder was dried and pressed into a target holder for AMS ^{14}C measurements with a HVEE 3.0 MV Tandem AMS system at Nagoya University (Nakamura *et al.*, 2000). Each target was measured for 30 min in each of three analyses. The $^{12}\text{C}^{3+}$ and $^{13}\text{C}^{3+}$ currents were kept at 190 and 200 nA, respectively. Typical counting rate for NBS HOxII standard samples is about 60 cpm. The stable carbon isotope ratio was measured using a Finnigan MAT 252 isotope-ratio Mass Spectrometer at the Center for Chronological Research, Nagoya University (Nakamura *et al.*, 2000). Radiocarbon contents are reported as $\Delta^{14}\text{C}$ in per mil (‰) deviations from the standard sample, 0.7459 activity of NBS oxalic acid (SRM-4990C) (Stuiver and Polach, 1977) and the stable carbon isotope ratio is expressed in $\delta^{13}\text{C}_{\text{VPDB}}$ (Craig, 1957). For age correction and correction for isotopic composition formulas presented in Mook and Plicht (1999) were used:

$$\Delta^{14}\text{C} = \left(\frac{A_{\text{SN}} e^{\lambda(y-x)}}{A_{\text{abs}}} - 1 \right) \cdot 1000 \text{‰}, \quad (2.1)$$

$$A_{\text{abs}} = 0.7459 A_{\text{Ox}} \left(1 - \frac{2(25 + \delta^{13}\text{C})}{1000} \right) e^{\lambda(y-1950)}, \quad (2.2)$$

where

A_{SN} : radiocarbon activities in the sample,

A_{abs} : absolute activities of oxalic acid standard (HoX-II) whose $\delta^{13}\text{C}$ was normalized to -25‰ and corrected for radioactive decay from 1950 to the measurement year (y),

A_{Ox} : measured activities for oxalic acid standard,

x: year of growing,

y: year of measurement,

λ : decay constant for radiocarbon.

3. RESULTS AND DISCUSSION

Kraków – NH zone 1

Kraków (50°3'N, 19°54'E) is a city of about one million people, located about 100 km to the north of the Tatra Mountains in southern Poland (Fig. 1). Air pollution related to the urban infrastructure, industrial facilities, and a large steel factory (Steel factory – Huta im. Tadeusza Sendzimir) have caused elevated carbon dioxide levels in the local atmosphere (Kuc *et al.*, 2003). Annual tree rings samples from pine tree (*Pinus sylvestris*) growing near the university were taken, using a hollow drill.

Since 1983, the Department of Environmental Physics, University of Science and Technology in Kraków has monitored carbon isotope compositions in tropospheric CO_2 (Kuc and Zimnoch 1998). Samples of atmospheric CO_2 were taken at biweekly intervals from the Faculty building roof on the university campus, 25m above ground level (T. Kuc, personal communication). Data of

radiocarbon concentration in atmospheric CO_2 for the city of Kraków were corrected for isotopic composition of carbon ($\delta^{13}\text{C} = -25\text{‰}$) to provide $\Delta^{14}\text{C}$ notification, and were used to estimate the growing period of pine tree in southern Poland. The estimated growing period for Scots pine (*Pinus sylvestris*) in southern Poland is from early April to late September (see Fig. 2), and was determined by comparing the concentration of radiocarbon in annual tree rings with the average concentration of radiocarbon in atmospheric CO_2 calculated for different periods.

To calculate the differences in radiocarbon concentration levels between “clean air” and urban area of Kraków, data from Schauinsland (Germany) were used (Levin and Kromer, 2004). All data show a continuous decrease in radiocarbon activity over time. An average year to year decrease of $7.3 \pm 1.8\text{‰}$ per year for tree ring data and $9.2 \pm 3.3\text{‰}$ per year for atmospheric radiocarbon concentration were obtained for the analyzed period.

Differences in $\Delta^{14}\text{C}$ values in tree rings and atmospheric carbon dioxide from Kraków are presented in Fig. 2. 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 those in “clean air” at the Schauinsland station. This can be attributed to a local Suess effect. To compare, the $\Delta^{14}\text{C}$ values found in tree rings were $108.7 \pm 3.5\text{‰}$, $99.8 \pm 3.6\text{‰}$ and $85.3 \pm 3.5\text{‰}$ for years 1994, 1995 and 1996, respectively. These values are lower than the yearly mean values in atmospheric CO_2 at Schauinsland (117‰, 111‰ and 102‰; Levin and Kromer, 2004), but higher than those measured in Zagreb (annual average – 81‰, 88‰ and 56‰; Krajcar-Bronić *et al.*, 1998) for the same

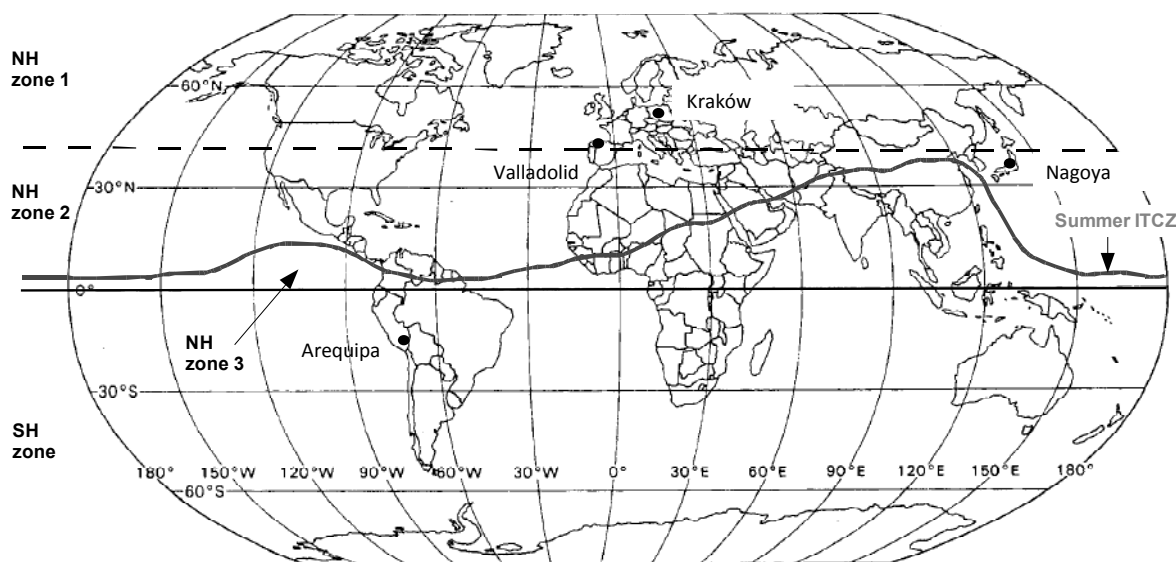


Fig. 1. Location of sample collection sites on the World map showing the areas covered by NH zones 1, 2, 3, and SH zone. The position of the summer ITCZ (Intertropical Convergence Zone) adopted from Linacre and Greet (1997). After Hua and Barbetti (2004).

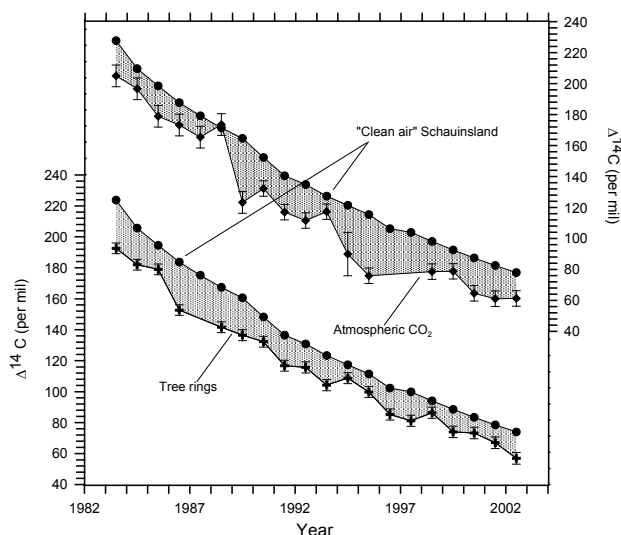


Fig. 2. Radiocarbon concentration in atmospheric CO_2 (Kuc *et al.*, 2003) and tree rings (*Pinus sylvestris*) samples collected at Kraków, Southern Poland. Radiocarbon concentration in atmospheric CO_2 at Schauinsland station (Levin and Kromer, 2004) represents "clean air". All atmospheric data represent mean value for the period between April and September corrected by $\delta^{13}\text{C} = -25\text{‰}$.

period. Since the growing period does not cover the whole year, the amount of CO_2 from domestic use for heating during the winter, are not taken into account in the values derived from tree rings, which results in higher values being observed in Zagreb. Radiocarbon concentration in Niepołomice (Pazdur *et al.*, 2007), about 20 km east from Kraków, are comparable with those observed in "clean air" from Schauinsland, suggest that the Suess effect has strictly local character.

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, giving the correlation coefficient R of 0.98 for tree rings and 0.95 for atmospheric CO_2 data. These analyses provide time decay constants of 16.70 ± 0.22 yr for tree ring data and 14.31 ± 0.20 yr for atmospheric CO_2 data, and differ from 18.70 ± 0.15 yr estimates reported in the literature (Levin and Kromer, 1997). Decreasing ratios calculated from linear data-fitting gave values of $6.75 \pm 0.29\text{‰}$ per year for tree ring data and $7.75 \pm 0.53\text{‰}$ per year for atmospheric CO_2 data. According to the prediction of the linear model, the radiocarbon concentration should have reached the natural level of $\Delta^{14}\text{C} = 0\text{‰}$ in 2007 (atmospheric CO_2) and in year 2010 (tree rings), comparable with the estimates of 2007 for Schauinsland (Levin and Kromer, 1997), 2004 for Groningen (Meijer *et al.*, 1995) and 2000 for Zagreb (Krajcar-Bronić *et al.*, 1998).

Changes of $\delta^{13}\text{C}$ values in annual tree rings from Kraków for the period 1983–2002 are presented in Fig. 3. The values are in the range between -27.5‰ to -25.4‰ , and correspond to the values listed for the C3 cycle

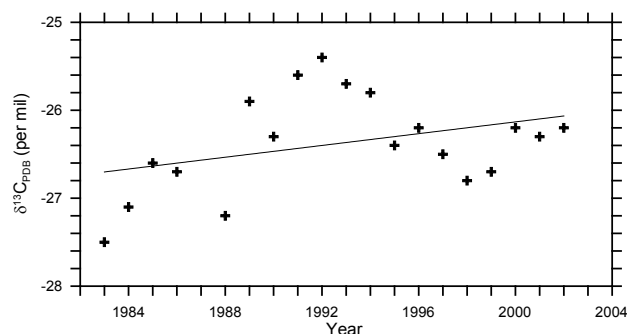


Fig. 3. Stable isotope composition of carbon in tree rings (*Pinus sylvestris*) from Kraków, southern Poland. $\delta^{13}\text{C}_{\text{PDB}}$ measurement error is $\pm 0.1\text{‰}$.

plants. A linear slight increase of 0.03‰ per year was noted for the whole period between years 1983 and 2002. However, the $\delta^{13}\text{C}$ values increase systematically during the period between 1983 and 1992 ($0.198 \pm 0.043\text{‰}$ per year), than decrease between 1993 and 1998 ($-0.221 \pm 0.028\text{‰}$ per year), and finally start to increase for the rest of the analyzed period ($0.160 \pm 0.050\text{‰}$ per year). Kuc and Zimnoch (1998) noted a decrease of $\delta^{13}\text{C}$ values of -0.02‰ per year, for the period 1983–1995, as a result of increase of CO_2 concentration from natural gas use, for which $\delta^{13}\text{C}$ is -54.4‰ .

Valladolid – NH zone 2

^{14}C concentration in tree rings (early wood (EW) and late wood (LW)) from Valladolid is presented in Fig. 4, together with data representing average radiocarbon concentration as reference values. The monthly average temperature in Valladolid for each month of the year being higher than 0°C (Agencia Estatal de Meteorología (AEMet)) permits to make the assumption that the growing period for a pine tree can be extended for the whole year. The average temperature in the coldest months of the year (January and February) for the period between years 1971 and 2000 are 4.0°C and 6.1°C respectively.

In order to compare results obtained for tree rings (EW, LW) data from Schauinsland (Levin and Kromer, 2004) represent summer average (April–September, (EW)) and winter average (October–March, (LW)) for corresponding year were used. $\Delta^{14}\text{C}$ concentrations for 2004–2007 period were estimated by extrapolation on the curves. All data show a gradual decrease of ^{14}C concentration over time. Decrease of $6.2 \pm 1.3\text{‰}$ per year for tree rings was obtained for the period between 1986 and 2007. Atmospheric and tree ring $\Delta^{14}\text{C}$ values measured in Kraków during similar period (1983–2002) decrease at rates $9.2 \pm 3.3\text{‰}$ per year and $7.3 \pm 1.8\text{‰}$ per year, respectively (see above), while data from 2 stations in Croatia show decrease rate 12‰ per year (Zagreb) and 10.6‰ per year (Plitovice) (Krajcar-Bronić *et al.*, 1998).

Radiocarbon concentrations in tree ring samples (EW and LW) from Valladolid, in the whole period between

1986 and 2007, are lower than in “clean air” at the Schauinsland station, which is attributed to a local Suess effect. For example, the $\Delta^{14}\text{C}$ values in tree rings from Valladolid of $167.3 \pm 3.2\%$ EW, $153.4 \pm 3.3\%$ EW and $139.2 \pm 3.2\%$ EW and $166.7 \pm 3.3\%$ LW, $160.3 \pm 3.2\%$ LW, $144.9 \pm 3.2\%$ LW, for 1987, 1988 and 1989, respectively are significantly lower than the mean summer values in maple tree leaves from Quebec (221‰, 211‰ and 194‰, respectively, (McNeely, 1994)), but higher than those observed for tree rings in Krakow (this work) and Nagoya (this work) in whole period.

Differences between radiocarbon concentration ($\Delta^{14}\text{C}$) in EW and LW for each year are presented in Fig. 4b. Average difference between $\Delta^{14}\text{C}$ values in EW and LW of $-1.8 \pm 1.3\%$ for the whole period of 1986–2007 was observed, suggesting values higher during summer (LW) than winter (EW) period. Based on the previously made assumption that growing period for Valladolid spans months from January to December, the EW rings are

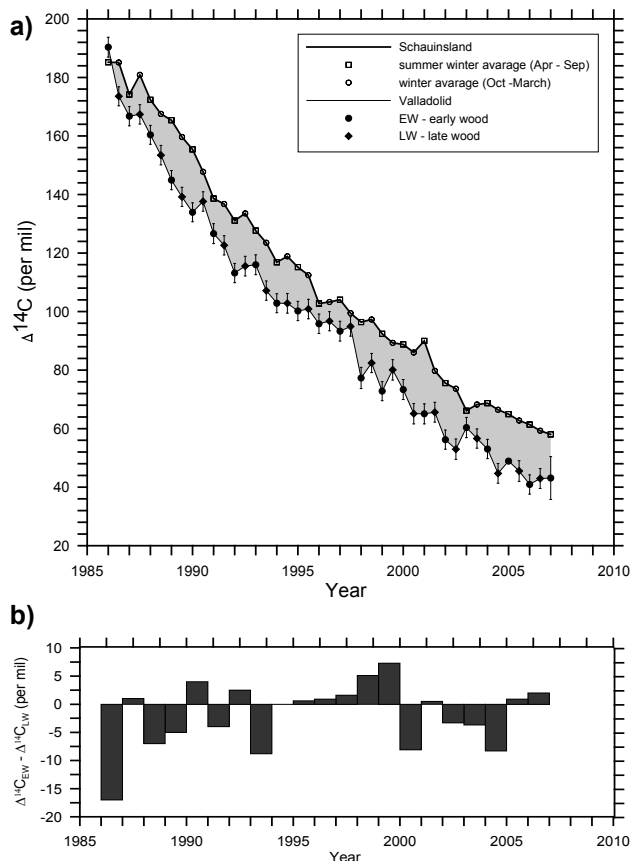


Fig. 4. a) Changes of radiocarbon concentration in tree ring (*Pinus pinea* L.) samples at Valladolid, central Spain. Upper solid line represents radiocarbon concentration ($\Delta^{14}\text{C}$) at Schauinsland station (Levin and Kromer, 2004). Values for the period between 2004 and 2007 were calculated from exponential curve fitted to the observed data for Schauinsland, b) Differences in radiocarbon concentration in early wood (EW, $\Delta^{14}\text{C}_{\text{EW}}$) and late wood (LW, $\Delta^{14}\text{C}_{\text{LW}}$) at each year, during the period between 1986–2006.

forming in the first half of the year including the coldest months of January and February (Agencia Estatal de Meteorología (AEMet)). Assuming that the emission of CO_2 from the local traffic has a constant value in each month, lower $\Delta^{14}\text{C}$ values observed in EW are related to the increase of CO_2 emission from domestic use (i.e. gas heaters, gas stoves). For the period between years 1995 and 1999 radiocarbon concentration in EW rings is higher than in LW rings. The average temperatures in January and February are higher than the average temperatures for those months for the last 30 years (1971–2000, Agencia Estatal de Meteorología (AEMet)). Those values are 5.3°C (1995), 6.7°C (1996), 4.5°C (1997), 5.6°C (1998) for January, and 6.9°C (1995), 9.3°C (1996), 7.9°C (1997), 14.3°C (1998) for February. This can be the reason of lower emission of CO_2 from heating installations during the winter time.

To estimate long-term changes of radiocarbon concentration exponential function was fitted to the results obtained for tree rings from Valladolid, giving the correlation coefficient R of 0.984. These analyses provide time decay constants of 13.02 ± 0.19 yr for tree rings, which is shorter than 18.70 ± 0.15 yr estimates reported in the literature (Levin and Kromer, 1997). In additional, a linear function was fitted to the $\Delta^{14}\text{C}$ data for the whole period 1986–2007 giving the decreasing rate of $6.64 \pm 0.21\%$ per year. Linear data-fitting predicts 2015 as a year that $\Delta^{14}\text{C}$ values will be equal to 0‰, comparable with reported values (see above).

Fig. 5 presents temporal changes of $\delta^{13}\text{C}$ values in annual rings of pine tree (*Pinus pinea* L.) from Valladolid. The values are in the range between -24.2‰ and -33.6‰, and correspond to the values listed for the C3 cycle plants. A linear decrease of $-0.24 \pm 0.04\%$ per year was noted for the whole period between years 1986 and 2007, as a consequence of emission of CO_2 from natural gas (domestic emission) and gasoline (traffic emission) use.

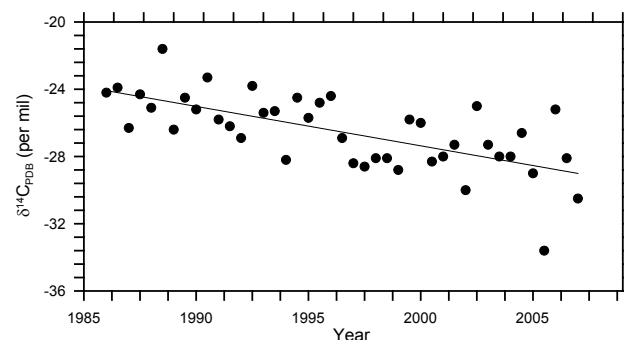


Fig. 5. Stable isotope composition of carbon in tree rings (*Pinus pinea* L.) from Valladolid, central Spain. $\delta^{13}\text{C}_{\text{PDB}}$ measurement error is $\pm 0.1\%$.

Nagoya – NH zone 2

Fig. 6 shows the variation of ^{14}C concentrations in tree rings for the period of 1951 to 2002 (Nagoya A), and for the period 1982 to 2003 (Nagoya B). Data representing average radiocarbon concentration in NH zone 2 (Hua and Barbetti, 2004) are included to represent annual average values of ^{14}C concentration in “clean air”. The annual average values were used instead of seasonal averages, according to mild and maritime climate in Nagoya, which extends the vegetation period for pine trees to almost the whole year. The average temperatures for the coldest months (January and February) are above 0°C (Japan Meteorological Agency (JMA)).

Results show a gradual decrease of radiocarbon activity over time. An average decrease rate of $15.2 \pm 2.1\%$ per year (Nagoya A) for the period between 1968 and 2002, and for the period between 1985 and 2003 the values for Nagoya A and Nagoya B are $6.8 \pm 1.5\%$ per year and $8.2 \pm 1.3\%$ per year, respectively. Atmospheric $\Delta^{14}\text{C}$ 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).

Radiocarbon concentrations in annual rings of the pine tree from Nagoya are lower than those observed in “clean air” of relevant years for NH zone 2 (Hua and Barbetti, 2004). This can be attributed to a local Suess effect. The $\Delta^{14}\text{C}$ values of $55.4 \pm 3.3\%$, $48.7 \pm 3.2\%$ and

$49.5 \pm 3.2\%$ obtained for 1997, 1998 and 1999 (Nagoya A) annual rings of the pine tree, respectively, are slightly lower than those for leaves of a tree (*Quercus variabilis*) collected nearby (N3, $64.1 \pm 3.5\%$, $54.3 \pm 3.2\%$ and $63.2 \pm 3.3\%$, Muraki *et al.* 2001) for respective years. This is possibly due to different values of CO_2 emission from fossil fuel and vegetation period between those two kinds of trees used for the experiments. For Nagoya B, values of $82.6 \pm 5.6\%$ (1997), $80.6 \pm 5.0\%$ (1998) and $78.9 \pm 5.0\%$ (1999) were observed and are higher than data obtained by Muraki *et al.* (2001) for N4, $70.8 \pm 3.3\%$ (1998) $66.7 \pm 3.2\%$ (1999).

To estimate long-term changes in radiocarbon concentration, exponential functions were fitted to the results for tree rings from Nagoya, giving the correlation coefficient R to be 0.99. The functions yield an inverse value of the decay constant to be 11.92 ± 0.16 yr and 14.16 ± 0.20 yr, comparable to the estimates of around 16yr reported in the literatures (Levin and Kromer, 1997, Krajcar-Bronić *et al.*, 1998, McNeely, 1994). In addition, a linear function was fitted to the $\Delta^{14}\text{C}$ data for the periods 1979–1983 and 1984–2002, separately, and the $\Delta^{14}\text{C}$ value was estimated to decrease at a rate of $15.6 \pm 2.5\%$ per year and $7.5 \pm 2.3\%$ per year (Nagoya A), respectively. The value of $7.7 \pm 1.8\%$ per year was obtained for the period 1985–2003 for Nagoya B. Atmospheric $\Delta^{14}\text{C}$ values measured at two stations in Croatia (Zagreb and Plitovice) during a similar period yielded decreasing rates of 12% per year and 10.6% per year, respectively (Krajcar-Bronić *et al.*, 1998). Similarly, for Schauinsland station, decreasing rates were obtained to be 14.1% per year and 9.7% per year for the periods 1983–1985 and 1985–1989, respectively (Levin *et al.*, 1992). The decreasing rates in $\Delta^{14}\text{C}$ 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 regressions predict that $\Delta^{14}\text{C}$ values should be reach natural value in 2006 for Nagoya A and 2010 for Nagoya B, comparable with the estimates of 2007 for Schauinsland (Levin and Kromer, 1997), 2004 for Groningen (Meijer *et al.* 1995) and 2000 for Zagreb (Krajcar-Bronić *et al.*, 1998).

Fig. 7 shows temporal changes of $\delta^{13}\text{C}$ values in annual rings of pine tree (*Pinus densiflora* L.) from Nagoya. The values are in the range between -29.5% and -24.6% , and correspond to the values listed for the C3 cycle plants. A slight linear increase of $0.024 \pm 0.004\%$ per year was noted for the whole period between years 1951 and 2001 for Nagoya A, and decrease of $-0.080 \pm 0.004\%$ per year for Nagoya B was observed for the period 1985–2003. Since there are no data representing isotopic composition of carbon in atmospheric CO_2 from Nagoya, it is difficult to explain the observed discrepancy.

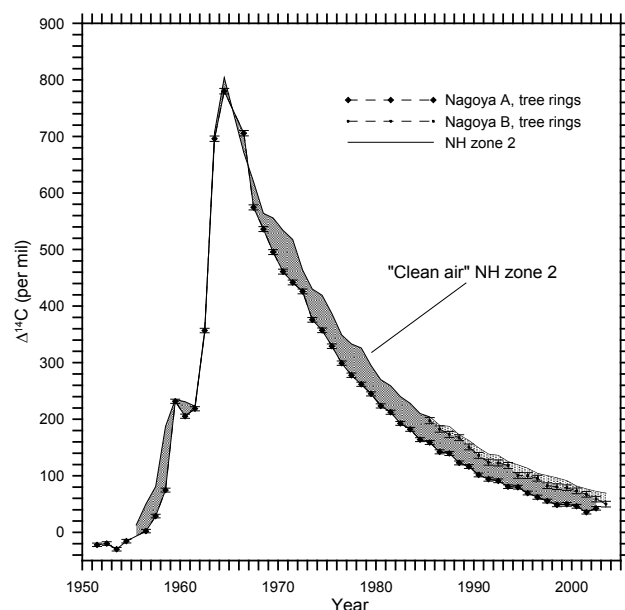


Fig. 6. Changes of radiocarbon concentration in tree rings (*Pinus densiflora*) samples at Nagoya (a. Nagoya A, b. Nagoya B), central Japan. Solid line represents mean radiocarbon concentration ($\Delta^{14}\text{C}$) for Northern Hemisphere (NH) zone 2 (Hua and Barbetti, 2004).

Arequipa – SH zone

Fig. 8 shows radiocarbon concentration between years 1986 and 2001 in tree rings of pine tree (*Pinus radiata*) from Arequipa, Southern Peru. Radiocarbon concentration in “clean air” representing year average values for the Southern Hemisphere (SH) zone was taken from Hua and Barbetti (2004).

Results show a gradual decrease in radiocarbon activity over time. A decrease of $6.9 \pm 1.2\%$ per year for the tree rings data was obtained for the period analyzed. Atmospheric $\Delta^{14}\text{C}$ data measured at Pretoria (South Africa, after Hua and Barbetti, 2004) and average values of radiocarbon concentration in Southern Hemisphere zone (Hua and Barbetti, 2004) during a similar period yielded decreasing values of 10.5% and 8.8% per year, respectively.

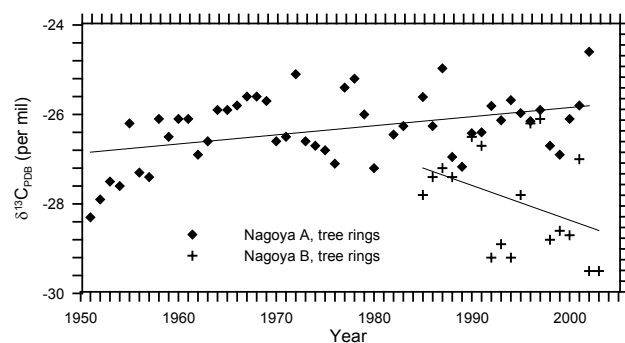


Fig. 7. Stable isotope composition of carbon in tree rings (*Pinus densiflora*) from Nagoya, central Japan. $\delta^{13}\text{C}_{\text{PDB}}$ measurement error is $\pm 0.1\%$.

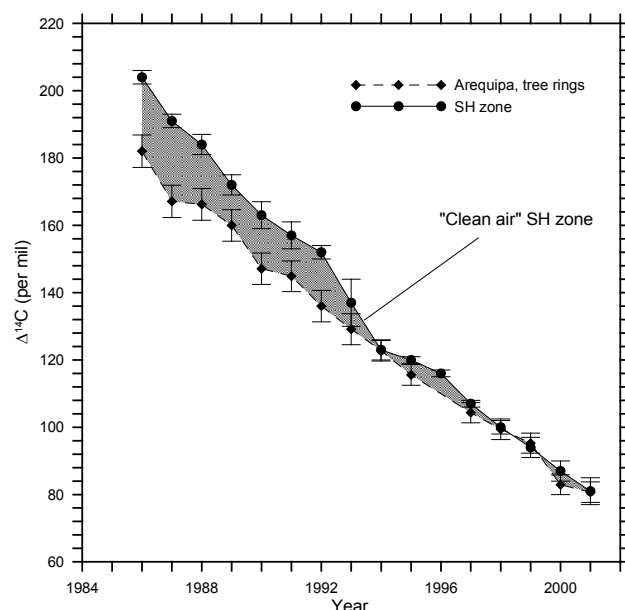


Fig. 8. Changes of radiocarbon concentration in tree rings (*Pinus radiata*) from Arequipa, Southern Peru. Solid line represents trend of the radiocarbon concentration in “clean air” for Southern Hemisphere (SH) zone (Hua and Barbetti, 2004).

Radiocarbon concentration in annual tree rings of pine tree from Arequipa are lower than those observed in Pretoria and Cape Grim but are also lower than average radiocarbon concentration for Southern Hemisphere zone (Hua and Barbetti, 2004). This can be attributed to a local Suess effect.

To estimate long-term changes in radiocarbon concentration, an exponential function was fitted to the observed data, giving the correlation coefficient R of 0.93. The function yields an inverse value of the decay constant to be 18.82 ± 0.18 yr, which corresponds well to the ~ 16 yr reported in literature (Levin and Kromer, 1997, McNeely 1994, Krajcar-Bronić *et al.*, 1998). In addition, a linear function was fitted to the $\Delta^{14}\text{C}$ data for the period 1986–2001 giving the decreasing rate of $6.57 \pm 0.15\%$ per year. Linear data-fitting predicts 2015 as a year that $\Delta^{14}\text{C}$ values will be equal to 0% , comparable with reported data (see above).

Fig. 9 shows temporal changes of $\delta^{13}\text{C}$ values in annual rings of pine tree (*Pinus radiata*) from Arequipa. The values are in the range between -24.6% and -21.7% , and correspond to the values listed for the C3 cycle plants. A slight linear decrease of $-0.05 \pm 0.04\%$ per year was noted for the whole period between years 1985 and 2001. However, for the period between years 1986 and 1992, an increase of $0.35 \pm 0.03\%$ per year can be observed.

4. FOSSIL FUEL COMPONENT c_{foss}

The radiocarbon method is widely known as a method for chronological study but can also be useful for environmental purposes. Radiocarbon concentration in atmosphere changes due to the emission of dead CO_2 from fossil fuel use. Due to this process, the concentration of radiocarbon has decreased over time. This can be observed not only in the atmosphere but also in other reservoirs of carbon (biosphere and ocean). Tree rings, leaves as well as other annual growing plants reflect the changes of radiocarbon concentration in the atmosphere due to processes of photosynthesis and assimilation of carbon

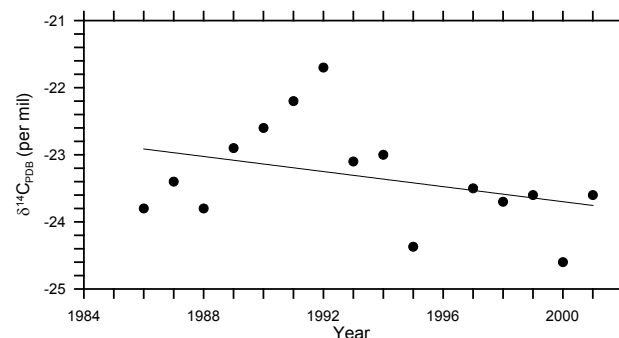


Fig. 9. Stable isotope composition of carbon in tree rings (*Pinus radiata*) from Arequipa, southern Peru. $\delta^{13}\text{C}_{\text{PDB}}$ measurement error is $\pm 0.1\%$.

from the air. By measuring the radiocarbon concentration in biospheric material (tree rings, leaves, grains, etc.) growing in the industrial and/or highly urbanized areas, where high emission of dead carbon is expected, it is possible to estimate the total emission of dead CO_2 . The calculation of this emission is possible by comparison of radiocarbon concentration in industrial areas with those in clean air. To estimate local decrease of radiocarbon concentration due to the Suess effect mathematical equations were used that included a relationship between carbon isotope composition and the concentration of carbon dioxide from fossil fuel combustion and the decreasing trend of radiocarbon content over time (Levin *et al.*, 2003):

$$c_{\text{meas}} = c_{\text{BG}} + c_{\text{bio}} + c_{\text{foss}} \quad (4.1)$$

$$c_{\text{meas}} \delta^{13}\text{C}_{\text{meas}} = c_{\text{BG}} \delta^{13}\text{C}_{\text{BG}} + c_{\text{bio}} \delta^{13}\text{C}_{\text{bio}} + c_{\text{foss}} \delta^{13}\text{C}_{\text{foss}} \quad (4.2)$$

$$c_{\text{meas}} (\Delta^{14}\text{C}_{\text{meas}} + 1000) = c_{\text{BG}} (\Delta^{14}\text{C}_{\text{BG}} + 1000) + c_{\text{bio}} (\Delta^{14}\text{C}_{\text{bio}} + 1000) + c_{\text{foss}} (\Delta^{14}\text{C}_{\text{foss}} + 1000) \quad (4.3)$$

where:

c – concentration of CO_2 (ppmV),

$\Delta^{14}\text{C}$ – radiocarbon concentration (per mil),

BG, bio, foss – atmospheric, biospheric and fossil fuel factors, respectively.

The background concentration of carbon dioxide in the atmosphere is the sum of two components. Global CO_2 concentration in the atmosphere and its variations due the global the Suess effect along with biogenic factors are expressed as c_{BG} , and are referred to as the natural component. CO_2 concentration due to the local effects is expressed as c_{foss} , and is referred to as the emission component. To estimate the concentration of carbon dioxide produced as fossil fuel emission, an assumption that $\Delta^{14}\text{C}$ value in fossil carbon is -1000‰ was used. This reduces fossil factor in the Eq. 4.3, gives the formula:

$$c_{\text{foss}} = c_{\text{BG}} \cdot \frac{\Delta^{14}\text{C}_{\text{BG}} - \Delta^{14}\text{C}}{\Delta^{14}\text{C}_{\text{BG}} + 1000} \quad (4.4)$$

Kraków

Samples of annual rings of pine tree (*Pinus sylvestris*) collected in the city of Kraków (southern Poland), have been used to estimate the value of c_{foss} for the period 1983-2002. Obtained values correspond to the average concentration of CO_2 emitted from combustion of fossil fuels, in the months from April to September (growing period). The highest values of c_{foss} were recorded in years 1986 (10.6 ± 1.3 ppmV), 1983 (9.9 ± 1.7 ppmV), and 1988 (9.1 ± 1.2 ppmV) (Fig. 10). The lowest value throughout the period, 2.8 ± 1.4 ppmV, was recorded in year 2000. The average value of c_{foss} for the whole period between 1983 and 2003, is 6.18 ± 0.51 ppmV. To compare, for the same location, in the work of Kuc and Zimnoch (1998) the seasonal average values of c_{foss} obtained for the period

between 1983 and 1994 are 10 ppmV for summer season (April-September) and 27 ppmV for the winter season (October-March).

Valladolid

The values of the concentration of CO_2 derived from fossil fuel combustion (c_{foss}), have been calculated for the period of 1986-2007 (Fig. 10), based on the records of radiocarbon concentration in annual rings of pine tree (*Pinus pinea*), taken at the center of the city of Valladolid (central Spain). From each annual ring, early and late wood ring was separated and α -cellulose was extracted. The values of the c_{foss} in the early and late wood represent average concentration of CO_2 in the months from January to June – early wood, and the months from July to December – late wood. Average values of c_{foss} for the period of 1986-2007 are respectively 5.08 ± 0.33 ppmV (early wood) and 4.70 ± 0.36 ppmV (late wood). The lowest c_{foss} value of -0.4 ± 1.3 ppmV was obtained for the late wood ring formed in 1986, which is probably the value corresponding to the concentration of CO_2 in the place from

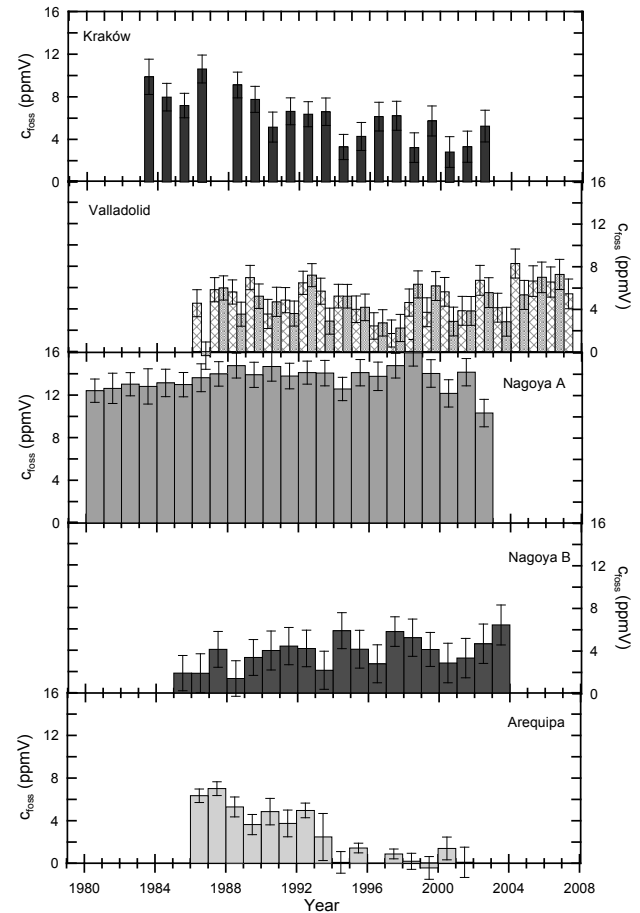


Fig. 10. Changes of fossil fuel component (c_{foss}) of CO_2 concentration calculated from radiocarbon concentration in annual tree rings from Kraków (southern Poland), Valladolid (central Spain), Nagoya (central Japan), Arequipa (Peru).

where the trees were taken (nursery). In the remaining period the lowest values of 2.4 ± 1.2 ppmV (1996 EW), 2.7 ± 1.2 ppmV (1996 LW) and 1.7 ± 1.3 ppmV (1997 EW) and 2.2 ± 1.3 ppmV (1997 LW) were recorded.

Nagoya

Research using annual rings of pine tree (*Pinus densiflora*) from Nagoya city (central Japan) were conducted to determine the influence of CO₂ emission from local sources on radiocarbon concentration in biospheric material. Samples were taken from two different places at the Nagoya University Campus. One was located near the road junction (dense traffic, Nagoya A) and the other close to the sport ground of the university, without sources of CO₂ emission (Nagoya B). The average value of c_{foss} were 13.5 ± 1.5 ppmV for the period of 1967-2002 for Nagoya A and 3.78 ± 0.31 ppmV for the period 1985-2003 for Nagoya B. The significant difference between those values result from different levels of CO₂ emissions from fossil fuel use observed at each location. Since we do not expect any sources of CO₂ emission at Nagoya B (like traffic, households, etc.), we can assume that the observed decrease of radiocarbon concentration in this place is caused by the mixing of air masses originating from various part of the city, including those which contain CO₂ sources.

Arequipa

The set of values of radiocarbon concentration in Arequipa for the period between 1986-2003 has been obtained using a annual rings of pine tree (*Pinus radiata*). Those data were used to determine the c_{foss} component. Analysis based on measurement of carbon isotopic composition indicates that the main source of carbon emissions in this region are volcanoes. The highest values of c_{foss} component recorded for 1986-1992, correspond to the period in which a gradual increase in $\delta^{13}\text{C}$ values can be observed. It is related to the CO₂ of volcanic origin, for which $\delta^{13}\text{C} = -1 \pm 2\%$ (Gupta and Polach, 1985). Since year 1993 a gradual decrease in the c_{foss} value can be observed, which can be related to decreasing CO₂ emissions from the surrounding volcanoes. For the period between 1994 and 2001 the radiocarbon concentration in Arequipa is comparable to the average value of the concentration of this isotope for the entire southern hemisphere zone (SH zone, Hua and Barbetti, 2004). The average value of c_{foss} for the whole periods of the years 1983-2001 is 2.79 ± 0.64 ppmV with the highest values of 6.3 ± 0.6 ppmV and 7.0 ± 0.6 ppmV in year 1986 and 1987 respectively. Different annual average values of c_{foss} component during this period suggest that the amount of CO₂ emitted by the local volcanoes over the years was not constant, with maximum of the emissions in the years 1986-1988.

5. CONCLUSIONS

The aim of this work was to establish an effective method for radiocarbon and carbon dioxide monitoring using annual tree rings. The AMS system gives possibilities to reduce the mass of samples to few milligrams and the material can be obtained using a hollow drill from living trees. By using this method, it is possible to obtain results for places, where concentration of radiocarbon decreases due to the Suess effect. The samples of annual tree rings used in this work were taken from living trees growing in the urban areas of big cities. To confirm the decrease of radiocarbon concentration caused by this effect in investigated sites, measurements of isotopic composition of carbon in annual tree rings were carried out. The results of these investigations lead to the following conclusions:

- 1) Radiocarbon concentrations in tree rings from Nagoya, Arequipa, Valladolid, Kraków and in samples of atmospheric carbon dioxide measured at Kraków during the analyzed period are systematically lower than those in "clean air" in each zone, due to CO₂ emission from fossil fuel use.
- 2) Decrease of the radiocarbon concentrations depends on the value of CO₂ emission from fossil fuel use and differs in time and place according to the total CO₂ emission from fossil fuel use.
- 3) Radiocarbon concentration measured in tree rings from Kraków is similar to an average value obtained for atmospheric CO₂ during the vegetation period. The vegetation period varies from place to place and is necessary to be taken into account to obtain reasonable results.
- 4) Results show that, with isotopic information recorded in tree rings, it is possible to reconstruct radiocarbon concentration in the past, and data like these can also be used for analytical calculation.
- 5) Temporal decrease of radiocarbon concentration can be described by using an exponential function fitted to the observed data for all analyzed periods. The functions yield an inverse value of the decay constant comparable to the estimates reported in the literature.
- 6) Using linear functions fitted to data, it is possible to predict the time that "natural" levels of $\Delta^{14}\text{C}$ will be reached, and the results obtained in this work are comparable with those reported in literature.
- 7) It is possible to calculate fossil fuel component c_{foss} using data of radiocarbon concentration measured in tree rings. For this calculation, data of radiocarbon concentration and concentration of CO₂ in "clean air" reported in literature can be used.
- 8) The differences in average values of c_{foss} between different places can be explained by different amounts of CO₂ emitted into the atmosphere at each location. However, different condition at each location can also cause some difficulties in the process of air mass mixing.

The results show that the assumption of homogeneous carbon content in atmosphere, made for modeling of the carbon cycle, is only approximation. In reality, disturbances may exist at some places due to emission of CO₂ from fossil fuel use, and differences of carbon isotopic composition in the atmosphere can be observed. Because of a local character of those disturbances, it is not necessary to account for them in the modeling of the global carbon cycle. However, to better understand the effects caused by emission of CO₂ from fossil fuel use, it is necessary to create a model of local carbon cycle on the basis of data of carbon isotopic composition, including mechanisms of air mass mixing at investigated locations. As a continuation of this work in future, more samples of tree rings will be analyzed to obtain more input data for modeling local carbon cycle.

ACKNOWLEDGEMENTS

Author would like to express his thanks to all staff of the GADAM Excellence Centre of Silesian University of Technology, Center for Chronological Research of Nagoya University and LIBRA Laboratory of University of Valladolid for their kind support. Special words of thanks are directed to Prof. Anna Pazdur and Prof. Toshio Nakamura for their contribution in my scientific career. To all my friends in Leibniz Labor in Kiel for creative working environment.

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