AIR-POLLUTION EFFECT AND PALEOTEMPERATURE SCALE VERSUS δ^{13}C RECORDS IN TREE RINGS AND IN A PEAT CORE (SOUTHERN POLAND)

MARIUSZ O. JĘDRYSEK[1]*, MAREK KRĄPIEC[2], GRZEGORZ SKRZYPEK[1] and ADAM KAŁUŻNY[1]

[1] *Laboratory of Isotope Geology and Geoecology, Institute of Geological Sciences, University of Wrocław, Wrocław, Poland;* [2] *Department of Stratigraphy and Regional Geology, University of Mining and Metallurgy, Poland*

(* *author for correspondence, e-mail: morion@ing.uni.wroc.pl, Fax: 71 375 9371*)

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Abstract. Carbon isotope analyses of peat profiles from the Karkonosze Mts. (SW Poland) and tree-ring cellulose from Wisła river valley in the Kraków region (S Poland) have been carried out. The samples analysed represent approximately the last 1100 years. The δ^{13}C profile in peat from the Szrenica peat bog ranges from –26.74 to –21.81‰ and the δ^{13}C value of tree rings range from –27.82 to –21.94‰. The observed variations in the δ^{13}C values of the peat samples and tree rings from Poland in general correlated with each other (Figure 1). This suggests that the δ^{13}C value of organic matter in terrestrial conditions is generally controlled by the same environmental factors. On average, over the last millennium (X–XIX century), the δ^{13}C value of peat cellulose has been 1.8‰ isotopically heavier compared to the corresponding tree ring cellulose value. It is not possible to provide a precise calibration of isotope signatures in tree rings, as the assimilation isotope effect depends mostly on local microclimatic conditions and specific species demands. In the region under study, temperature was the dominant factor controlling the δ^{13}C value of tree ring cellulose and peat-bog *Sphagnum* before the XIX century. It is estimated that, in the temperate climate of Poland, the carbon isotope fractionation between living plants and atmospheric carbon dioxide ($\Delta^{13}C_{p-a}$) for C3 plants is about –0.26‰/1 °C. This corresponds to 2.1‰/1000 m of elevation. Since the mid-XIX, in the Wisła valley when the river was regulated and water deficit in the neighbouring areas became common (Trafas, 1975), water availability plays a primary role in isotope fractionation of the vegetation. Since the 1955, just after the 'Lenin' steelworks started operation, pollution became the dominant factor controlling the carbon isotope signature of plants. Contamination of the atmosphere by fossil fuel burning from the 'Lenin' steelworks increased the δ^{13}C value of tree ring cellulose by about 1.3‰. This was probably caused by an increased concentration of atmospheric pollution (SO_x and dust) limiting the ventilation rate of the stomata.

Keywords: atmospheric pollution, carbon isotopes, climate, peat, tree rings cellulose

1. Introduction

Isotope analyses of organic sediments and tree rings constitute a powerful tool for paleoenvironmental reconstructions and may provide answers to key environmental questions. However, early and late wood problems (Hill *et al.*, 1995), the complex biochemical structure of organic matter (wood, peat, etc.) together with

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poorly recognised vital isotope fractionation effects and early diagenetic processes, raise new problems to be solved. One question is which part of the currently observed climatic variations is of natural origin, and how much are they affected by an anthropogenic impact? Anthropogenic activities presently introduce about 6 Gt of the ^{13}C depleted carbon to the atmosphere per annum (Wigley, 1997), of this, fossil fuel burning is the dominant source. Since the middle of the 20th century atmospheric CO_2 concentration has increased from less than 300 to about 360 ppm and, consequently $\delta^{13}C(CO_2)$ has fallen from –6.5 to about –8.5‰(Freidli *et al.*, 1986; Szaran, 1990; Keeling and Whorf, 1996; Levin *et al.*, 1996).

Analyses of stable isotope ratios have been used by many authors dealing with bulk wood (e.g. Yapp and Epstein, 1977; Edwards and Fritz, 1986), and cellulose from inter-annual (Becker *et al.*, 1991; Buhay and Edwards, 1993) or intra-annual sequences (Lipp *et al.*, 1991; Robertson *et al.*, 1997). Likewise, numerous observations and calibrations of the $\delta^{13}C$ response of plants to environmental variations show the dominance of climatic or atmospheric factors on $\Delta^{13}C$ discrimination in plants, including temperature, water availability, atmospheric CO_2, H_2O and SO_2 concentrations (e.g. Freyer, 1979; Stunner and Braziunas, 1987; Feng and Epstein, 1995; Hemming, 1998; Hemming *et al.*, 1998; Leavitt and Long, 1986, 1989; Lipp *et al.*, 1991; Martin *et al.*, 1988; Martin and Sutherland, 1990; Robertson *et al.*, 1997; Saurer *et al.*, 1995; Schleser, 1995; Schleser *et al.*, 1999; Loader and Hemming, 2000). On the other hand, no appreciable anthropogenic change in $\delta^{13}C$ was observed in tree-rings from Finland (Robertson *et al.*, 1997) and peat in Poland and Thailand (Jędrysek *et al.*, 1995, 1996) during the XX century.

Summing up, there are still fundamental questions that need to be answered. Thus, this article aims to address the following three objectives: (i) what does the isotope value in organic matter represent, (ii) how does the isotope signal quantitatively represent climatic parameters? (iii) assess the role of pollutants and natural environmental factors in variations of isotope signature in tree rings cellulose.

2. Materials and Methods

2.1. Peat

Carbon stable isotope analyses have been completed on material from a vertical *Sphagnum* peat profile from the 'Szrenica' raised peat bog (1249 m altitude, an exposed mountain pass above the timberline) Karkonosze Mountains in southwest Poland. The recent mean annual temperature in Szrenica is about 2 °C, mean summer temperature is about 12.8 °C, and the rainfall is about 1300 mm yr^{-1} (*Climatic Atlas*, 1973). The core (total depth of 155 cm) represents approximately the last 1700 years based of ^{14}C dating, and was divided into 3–5 cm thick intervals for sampling.

2.2. Tree rings

Seventeen fragments of subfossil oak wood, most from different tree trunks buried in river sediments, have been collected from a 10 km long stretch of the Wisła river, NE of Krakow (Southern Poland). Huge dimensions of the examined trunks, often with roots and fragments of branches, and the character of the river valley, meandering in this area, indicate that they were either only slightly displaced or buried *in situ* (Kalicki and Krapiec, 1995 – refer to this article for sampling site details). Late wood (approximately early-July to mid-September growth, Hill *et al*., 1995) only was sampled for isotopic analysis. Two sampling strategies were followed; (i) one sample of a single tree ring represented one single year. This was done for the period of 19th and 20th centuries and; (ii) five subsequent tree rings, correspondingly representing five years, were analysed for the period from 10th to 18th centuries. Each wood fragment represented about 80 yr. Thus, in order to cover the millennium record, tuck pairs strategy was applied. Namely, the last (youngest) 10 to 15 tree rings of each wood fragment covered exactly the same years as the oldest 10 to 15 tree rings of the subsequent (younger) wood fragment. On the basis of isotope analysis of all the tree rings representing the tuck pair, an additive correction factor was calculated for each such tuck pair. The additive correction was usually smaller that 0.5‰. Hence, a continuous record has been constructed.

A modified nitration technique (Epstein *et al*., 1976) was applied to determine ^{13}C/^{12}C and D/H ratios. Other details concerning sampling and analytical procedures are described elsewhere (Kalicki and Krapiec, 1995; Jędrysek *et al*., 1995, 1998a, b).

2.3. Paleotemperature

We used paleotemperature data reconstructed for the last millennium in England based on historical and biological data (Lamb, 1977). This was done because we were not aware of any other reliable paleotemperature reconstructions carried out closer to our sampling sites. We attempted to make simple comparisons between the δ^{13}C data from peat (35 data points in the profile), oak early wood tree-ring cellulose (270 data points) and paleotemperature (reconstructed by other authors using non-isotopic techniques – 19 data points; Barber, 1981). This comparison was done for the time period X to XIX century.

2.4. Century precipitation and temperature records

The δ^{13}C values of about 150 yr tree ring cellulose from consecutive years in the Kraków area (S Poland), was compared to temperature (since 1826) and precipitation (since 1881) records from the same area. These meteorological observations represent one of the earliest systematic records in Europe (Trepińska, 1971).

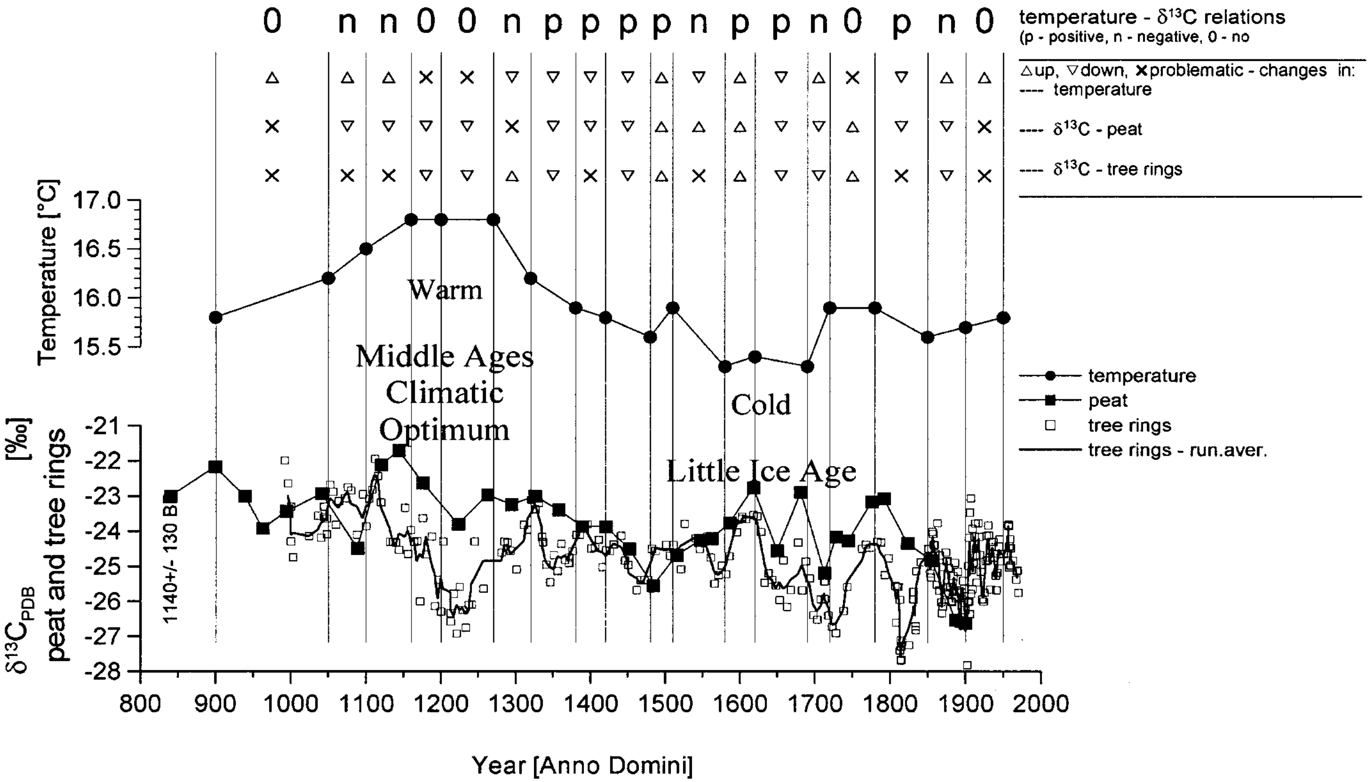

Figure 1. $\delta^{13}C$ in tree-ring cellulose (oak trees near Kraków, S Poland) and in total organic matter of peat core profiles (Szrenica, SW Poland) compared to the temperature variations for lowlands in England (after Lamb, 1977). Data for tree rings are plotted as the running average in 15 yr periods. The upper row symbols shows positively (p), negatively (n) or no correlated (0) drifts in isotope signatures and temperature parameters. The symbols $\triangle$, ∇ and ($\times$) represents: ($\triangle$) increase, (∇) decrease, and $\times$ not synonymous drift in the respective parameter.

3. Results

The δ^{13}C profile of peat from the Szrenica peat bog ranges from –26.74 to –21.81‰. Samples at a depth of 138 and 144 cm below the ground level yield ^{14}C ages of 1140±130 and 1540±120 (BP), respectively. In comparison, the δ^{13}C values of tree rings range from –27.82 to –21.94‰ and the oldest sample analysed was 998 AD. The observed δ^{13}C main peaks in peat and tree rings from Poland correspond well with each other but not really well to the general trends in the temperature variations reconstructed for England (see also Barber (1981) and Figure 1). Some shifts in phase between the tree-ring and peat records may be caused by the ^{14}C dating of the peat, which is not as precise as the dendrochronological dating nevertheless, but accurate enough for the purpose of this study (see the Discussion Section).

The carbon isotope ratios (calculated running average in 5 consecutive tree rings) corresponds well to precipitation of May and July (Figure 2).

The linear best fit for the tree rings grown before 1955 (open symbols) is:

$$\delta^{13}\mathrm{C} = -0.02 * p - 19.85 , \qquad (1)$$

where p is May–June precipitation, n = 49, r^2 = 0.72,

While starting since 1955 (5 yr running average values starts since 1957, Figure 2, solid square symbols) the equation is:

$$\delta^{13}\mathrm{C} = -0.009 * p - 22.05 , \qquad (2)$$

where n = 5, r^2 = 0.63.

Both linear best fits show similar negative correlations. However, in contrast to precipitation, the temperature of the period of the late wood growth does not correlate to δ^{13}C value (Figure 3). This may suggest that, in contrast to many authors, water deficit/abundance but not temperature controls isotope fractionation during photosynthesis. On the other hand, it seems that the industrial atmospheric pollution results in measurable increase in δ^{13}C – by about 1.3‰ in this particular case (see the Discussion Section). Our data do not cover the whole 1955–1970 period – thus this period is represented by 5 points of 5 yr running average. The year 1968, shows outstandingly low δ^{13}C value and corresponds to extensive political perturbations and strikes in Poland resulting especially in temporal stops of the cookery at the 'Lenin' steelwork. Thus, the emission of pollution was very limited and therefore the year 1968 has not been accounted in the 5 yr running average 1955–1970 period (Figures 2 and 3).

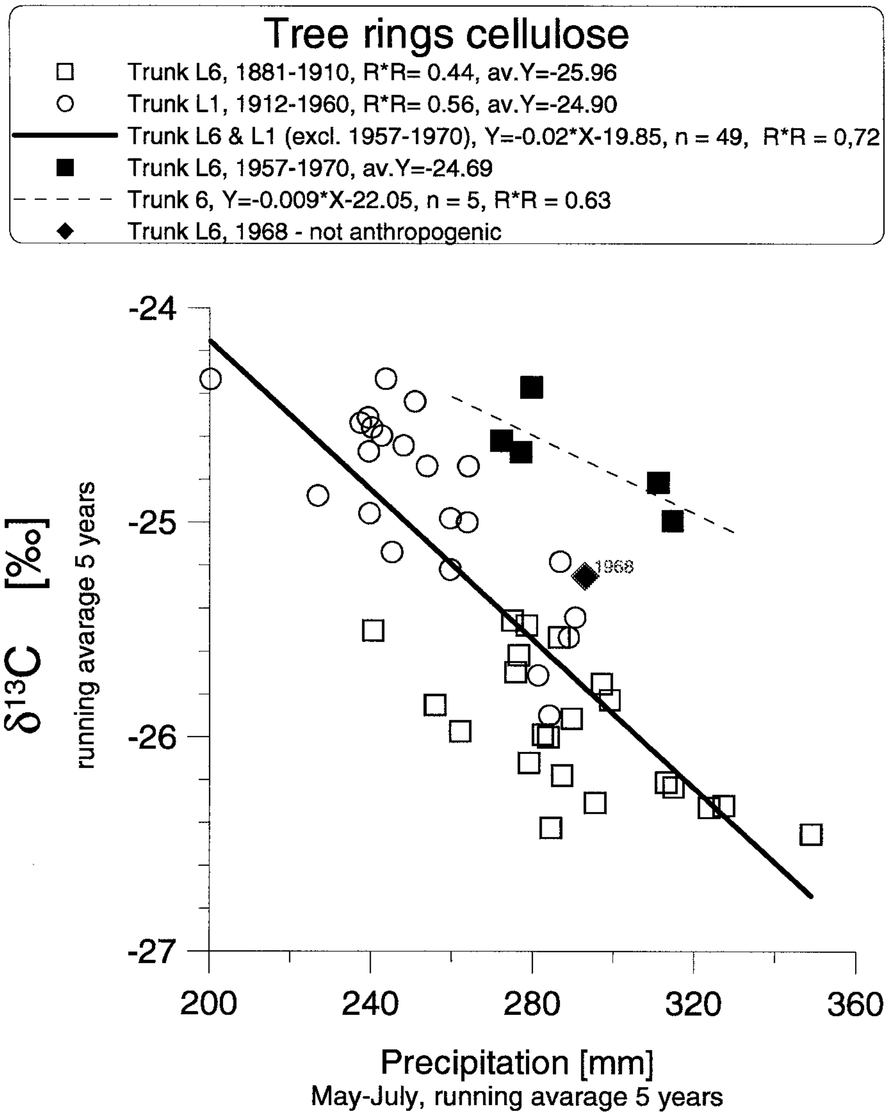

Figure 2. $\delta^{13}C$ from late wood of oak tree rings versus rainfall (May–July). The $\delta^{13}C$ value represents carbon isotope ratios in tree-ring cellulose (oak trees near Kraków, S Poland). Data for tree rings are plotted as the running average in 5 yr periods. Calibration in the period 1850–1970. See to the Results chapter for explanations.

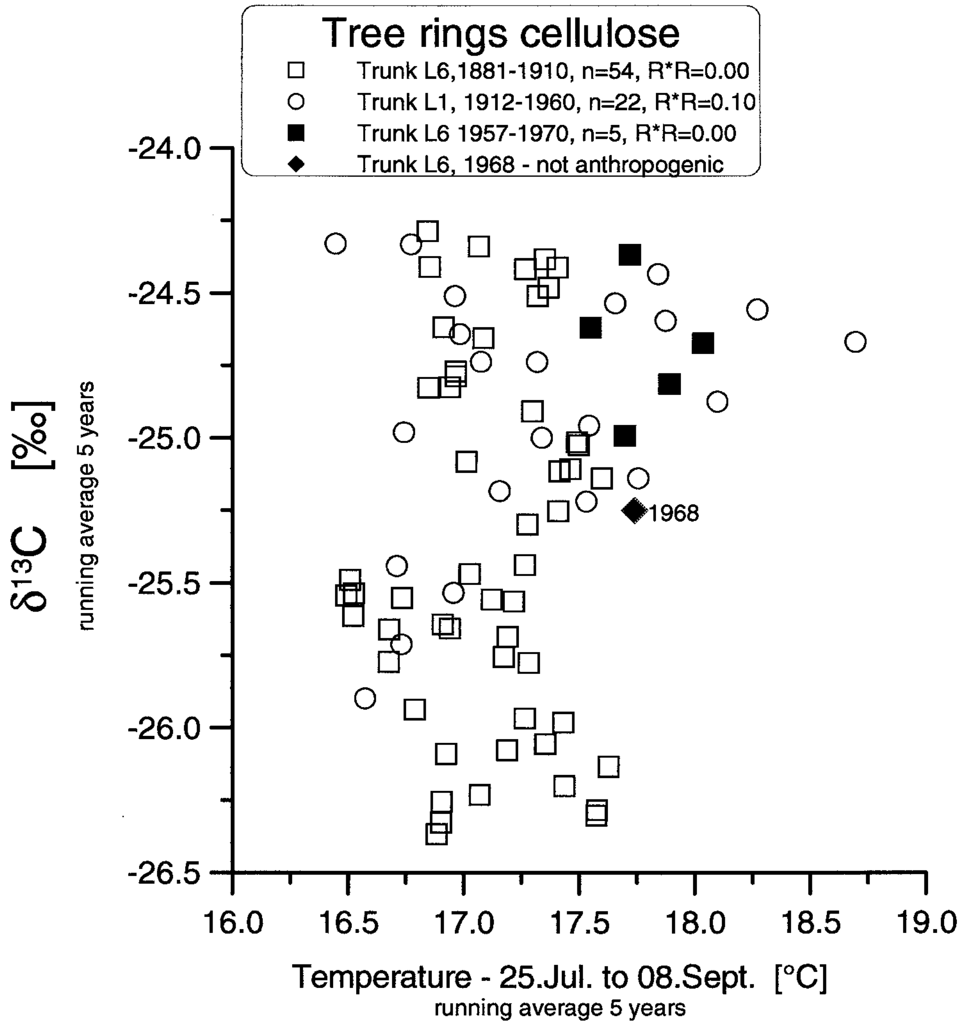

Figure 3. δ^{13}C from late wood of oak tree rings cellulose versus weighted average temperature between 25 July and 8 September (latewood grow period) (oak trees near Kraków, S Poland). Data for tree rings are plotted as the running average in 5 yr periods. Calibration in the period 1826–1970. See to the Results chapter for explanations.

4. Discussion

4.1. Millennium record: Natural conditions

The δ^{13}C variations in peat and tree rings analysed, correspond to the historical (e.g. Matthes, 1939; Stachlewski, 1978) and biological (Barber, 1981) record of climatic variations in Europe, and to the rapid change of environmental conditions, which occurred during the cold period (about 1550 AD) at the beginning of the so-called *Little Ice Age* (Matthes, 1939; Stachlewski, 1978). These $\delta^{13}C$ patterns in tree ring cellulose are similar to those found by Lipp *et al.* (1991), and also such relations are consistent with those of other authors, who found correlations between certain environmental factors and the δD and $\delta^{13}C$ of tree rings (e.g. Leavitt and Long, 1986; Becker *et al.*, 1991; Buhay and Edwards, 1993). Before 1954, when the neighbouring Lenin steelworks went into operation, and afterwards, precipitation largely controlled the $\delta^{13}C$ values in tree rings cellulose. However, one may assume that atmospheric pollutants form the Lenin steelworks resulted in 1.3‰ shift of $^{13}C/^{12}C$ fractionation, i.e. since the end of 1950s the effect of atmospheric industrial pollutants appears to have dominated the $\delta^{13}C$ signal, increasing it by about 1.3‰ (Figure 2).

As atmospheric carbon dioxide is the only source of carbon for plants, $\delta^{13}C$ in plants is controlled by the $\delta^{13}C$ of CO_2 and isotope fractionation during assimilation. Atmospheric $\delta^{13}C(CO_2)$ is rather stable through time, due to buffering by the global ocean (see e.g. Freidli *et al.*, 1986; Szaran, 1990; Keeling and Whorf, 1996; Levin *et al.*, 1996; Hoefs, 1997). Therefore, assimilation fractionation is rather crucial. In general, the carbon isotope fractionation between atmospheric CO_2 and assimilates is the combined result of an enzymatic (RUBISCO) carbon isotope fixation effect, which may be about –27‰, and a diffusion isotope effect that may result in a –4.4‰ isotope fractionation. This interaction in higher plants is complex and discussed by Farquhar *et al.* (1982, 1989).

From Figure 1, it is clear that in general the peat and tree ring cellulose $\delta^{13}C$ records are very similar. Thus, it could be expected that these isotope signals might give similar information. Numerous studies in tree rings yield a wide variety of carbon isotope/temperature calibrations. First, it was suggested that under natural conditions, carbon isotope fractionation between living plants and atmospheric carbon dioxide ($\Delta^{13}C_{p-a}$) depends mainly on temperature, and the $\Delta^{13}C_{p-a}$ value for C3 plants is from about –1‰/1 °C (O'Leary, 1981; Troughton and Card, 1975) to about –0.7‰/1 °C (Grinstead *et al.*, 1979). Similar calibrations based on peat from Poland varied from –0.57 to –1.08‰/1 °C with an average -0.82 (Jędrysek *et al.*, 1988a, 1996; Skrzypek, 1999). However, other authors reported a positive fractionation factor e.g. 0.33‰/1 °C (Lipp *et al.*, 1991) or 0.18‰/1 °C (Freyer and Belacy, 1983). However, one may assume that in our case, for the oak trees analysed, a decrease in carbon isotope ratio with increasing temperature relations is not plausible, because there are both negative and positive correlations between the paleotemperature data (Lamb, 1977) and the value, as shown on Figure 1.

Among the 18 periods shown in Figure 1, 6 of them show negative temperature – $\delta^{13}C$ correlation, 7 of them show positive temperature – $\delta^{13}C$ correlation, and 5 of them show no clear pattern. Thus, in the case considered, temperature seems not to be a single crucial factor which simply controls in C3 plants especially for shorter periods (less than hundred years). However, some authors state that short-term fluctuations (years) seem to contain more climatic information than the long-term trends (Freyer and Belacy, 1983; Leavitt and Long, 1989; Saurer *et al.*, 1995). In this study we cannot find evidence for this.

Humidity has also been noted as a key climatic parameter that can influence leaf gas exchange (ventilation) rate, through its effect on stomatal aperture (see e.g. Farquhar *et al.*, 1982, 1989). In contrast to trees, variations in humidity should not result in remarkable changes in the δ^{13}C of *Sphagnum* mosses as this peat-forming plant has no stomata *sensu stricto*, and ventilation rate should not vary greatly with humidity (Jędrysek *et al.*, 1995, 1996). Consequently, it could be expected that peat profiles more clearly reflect temperature variations than tree rings. However, Figure 1 does not support the previous statement. Likewise, Brenninkmeijer (1983), Brenninkmeijer *et al.* (1982), and Dupont and Brenninkmeijer (1984), studied variation of δ^{13}C, δ^{18}O and δD in peat profiles and suggested that the most important factor determining the isotopic composition of peat is the level of the water table. It has been suggested also that the δ^{13}C and $\delta^{34}S$ peat profiles may represent variations in temperature and water table level in the peat-bog, respectively (Jędrysek *et al.*, 1995, 1996). But, a lower concentration of atmospheric CO_2 could also correspond to higher δ^{13}C values in peat (White *et al.*, 1994), which in turn may be resulted from lower temperature. The secondary role of pCO_2 may be supported by the fact that a comparison of the reconstructed atmospheric pCO_2 from South American mosses and that from Antarctic ice cores in air occluded in the ice (White *et al.*, 1994), showed a poor correlation. Thus, pCO_2 factor should not be considered here.

Few studies have compared $^{13}C/^{12}C$ ratios in peat profiles to those of tree rings. It should be mentioned that the studies of Brenninkmeijer (1983), Brenninkmeijer *et al.* (1982), Dupont and Brenninkmeijer (1984) and White (1994) involved generally longer periods compared to this study and sample resolution was significantly more than one hundred years (500 or more). However, studies of the δ^{13}C in tree rings (Freyer and Belacy, 1983; Leavitt and Long, 1989; Saurer *et al.*, 1995) and peat profiles (Jędrysek *et al.* 1995, 1996) have shown that short-term trends contain more climatic information than long-term, as the frequency of climatic variations are counted in decades and the sampling temporal resolution should not be larger than about 50 yr. Therefore, the earlier peat isotope studies (Brenninkmeijer, 1983; Brenninkmeijer *et al.*, 1982; Dupont and Brenninkmeijer, 1984; White, 1994) may yield different conclusions than the data presented here. In this study, the peat temporal sample resolution is on average about 30 yr, and each tree ring sample up to XIX century represents 5 consecutive years (and 15 yr running average, Figure 1, see also the Materials and Methods Section). Beside sampling resolution, it is also important to mention that the late wood (approximately early-July to mid-September grow), representing full summer of Kraków area with moderate temperature variations (no ground-frosts at this climate), is compared with *Sphagnum* mosses growing approximately at the same summer period. Both might be important reasons why the tree rings and peat record show similar variations (Figure 1).

The best concordance between the peat and tree ring cellulose is for the period of ca. 1500 to 1800, representing the Little Ice Age (Figure 1). One may assume that, at this period in the area under study, the temperature was probably the most limiting factor for vegetation growth and the of δ^{13}C of plants. Moreover, this similarity suggests that neither diagenesis nor the complex structure of the peat analysed significantly influenced the isotope signature in the peat (Jędrysek *et al.*, 1995, 1996). The value of ^{13}C enrichment of peat (Figure 1) as compared to tree ring cellulose is about 0.93‰ and it is rather stable over the record, with three short-term exceptions. These exceptions are coincidental to transitions between dramatic changes in temperature. Namely, at the beginning of the Middle Ages Climatic Optimum (MACO, XI–XII century), then the MACO transition to the Little Ice Age (LIA, XV/XVI century) and the very end of the LIA (second half of XIX century). In these cases the peat became ^{13}C-depleted relative to the tree rings. Nevertheless, two of these peat and tree ring ^{13}C signals show similar trends in δ^{13}C variations. The transition between MACO and LIA (ca. 1330 to 1510) show positive correlation between change in the temperature and isotope signals (Figure 1). This fact may suggest that long-term temperature variations are reflected in δ^{13}C trends. The most reasonable explanation for this is that at the time between MACO and LIA variation in humidity had little influence on the peat and tree ring δ^{13}C. Stomata have to react more frequently to a water deficit at a relatively dry site than at a humid site. Accordingly, Saurer *et al.* (1995) postulated that isotope variations should record humidity variations better on a dry site than on a humid site. The Wisła valley is a relatively humid site and water availability to trees standing along the river is abundant. Thus, the long-term humidity record is probably much less expressed in δ^{13}C of tree rings, than temperature. However, a short-term transition between the climatic optimum and decline could be accompanied with a water deficit. We therefore postulate that in natural conditions, where water deficit is not the case, temperature may be the dominant factor controlling isotope ratios in tree ring cellulose. Even if humidity played a role during transition times, its own changes likely were induced by temperature.

The tree rings show lower δ^{13}C value than peat, despite the fact that water is usually not a deficit factor in peat-bogs. This is probably due to the different metabolism and growing conditions (altitude) of the *Sphagnum* sp. and trees, and the fact that, in contrast to tree-ring late wood cellulose, total peat organic matter has been analysed. Basing on comparative analysis of several peat profiles from Poland, it has been found that in whole peat profiles the δ^{13}C of total peat $\delta^{13}C_p$ was on average 0.86±0.15‰ lower than δ^{13}C in cellulose from peat ($\delta^{13}C_{pc}$), i.e. the $\Delta^{13}C_{p-pc} = \delta^{13}C_p - \delta^{13}C_{pc}$ = –0.86±0.15‰ (Skrzypek, 1999). In this context, the 0.93‰ average depletion of tree rings cellulose as compared with total peat (Figure 1), is not sensible from the isotope fractionation point of view, as these two signals represents different chemical compounds. However, the difference between δ^{13}C values in peat cellulose and tree rings late wood cellulose

($\Delta^{13}C_{pc-trc} = \delta^{13}C_{pc} - \delta^{13}C_{trc}$) is sensible value and, for the whole millennium, it is estimated to about 1.8‰.

The last century is excluded from this simple calculation because fossil fuel burning significantly influenced the CO_2 concentration and δ^{13}C (CO_2) value in the atmosphere. The estimated difference in the δ^{13}C value of peat cellulose and tree ring cellulose (–1.8‰) is in agreement with the fact that the temperature in the peat-bog was several degrees lower than in the region of Kraków. Currently, this difference in temperature of the vegetation period is about 8 °C. Therefore, one may conclude that in natural conditions, carbon isotope fractionation between plants and atmospheric carbon dioxide ($\Delta^{13}C_{p-a}$) for C3 plants is about –0.23‰/1 °C and 1.8‰/1000 m of elevation. Correspondingly, field studies of 100 C3 species from major mountain ranges around the globe reveal generally more positive values of δ^{13}C with increasing altitude. For all species studied, the average change is 1.2‰ per 1000 m of elevation (Korner *et al.*, 1988, 1991). Nonetheless the elevation rate compares with the rate of 1.8‰/1000 m found in our studies. However, the temperature coefficient estimated here of –0.23‰/1 °C is lower than that resulting from calibration of the δ^{13}C value of total organic matter in peat ($\delta^{13}C_{p-tot}$) profiles from several peat-bogs in Poland and Thailand, where the temperature coefficient was from –0.57 to –1.08‰/1 °C (Jędrysek *et al.*, 1996; Skrzypek, 1999).

Similar calculations were made for the LIA period, when the best concordance between the total peat and tree ring cellulose is observed (Figure 1). It suggests that probably temperature was the controlling factor limiting vegetation. The peat average $\delta^{13}C_p$ at this time (between about 1540–1835) is –23.88‰ and the corresponding period (between about 1556–1850) for late wood tree ring cellulose shows average $\delta^{13}C_{trc} = -25.09$‰. The difference between these two values $\Delta^{13}C_{p-trc} = \delta^{13}C_p - \delta^{13}C_{trc} = -1.21$‰ and the $\Delta^{13}C_{p-pc} = -0.86$‰ (Skrzypek, 1999). Thus, the estimated average $\Delta^{13}C_{pc-trc}$ = -2.07‰ (i.e. the depletion of peat cellulose and tree ring late wood cellulose is -2.07‰, and can be accepted roughly as – 2.1‰). Consequently, in natural conditions of LIA, when temperature is the limiting factor, carbon isotope fractionation between plants and atmospheric carbon dioxide ($\Delta^{13}C_{p-a}$) for C3 plants is about –0.26‰/1 °C and 2.1‰/1000 m of elevation. These ratios corresponds well to the Millennium $\Delta^{13}C_{p-a} = -0.23$‰/1 °C and $\Delta^{13}C_{pc-trc}$ = 1.8‰/1000 m ratios. One may believe that the Millennium ratios are more representative and reliable than the LIA ratios because the LIA ratios represent shorter period and extreme climatic conditions. Moreover, the Millennium 1.8‰/1000 m ratio better corresponds to 1.2‰/1000 m ratio found by Korner *et al.* (1988, 1991) for the Recent.

On the other hand, one may assume that during the LIA the temperature was the limiting factor for vegetation. The importance of the limiting factor can be observed when peat and tree rings δ^{13}C records are compared as shown above. We suggest that the best plant material for δ^{13}C paleoenvironmental reconstruction should be selected from areas where one vegetation limiting factor exists. This is most easy to attain, by selecting species from the area representing a limit of natural extension with respect to altitude, longitude, timberline, etc. On the other hand, this is very difficult and more than two species would be required, and evidence for cross-correlation of the limiting factors needs to be very well understood and recorded. In perfect case, when different species are carefully selected, and when temperature is the limiting factor for one and precipitation is the limiting factor for the other, variations in both environmental parameters could be potentially reconstructed.

5. Century Record: Precipitation and Pollution

Continuous measurements of precipitation since 1881, and of temperature since, 1926 in Kraków (e.g. Trepińska, 1971) enabled calibrating these two parameters with isotope ratios of tree ring cellulose from the area (Figures 2 and 3, respectively). It has been observed that the increase in the precipitation corresponds to a decrease in the δ^{13}C value (Figure 2), but the temperature calibration gave no correlations with the isotope ratios (Figure 3). Although, this apparently contradicts our previous estimation based on the millennium record, it is generally in agreement with Lipp *et al*. (1991) and Saurer *et al*. (1995) who suggested that relative humidity is the dominant factor controlling δ^{13}C value in tree rings, especially from dry sites. The reason for this might be based on the difference in habitat of the subfossil and recent trees analysed here. Namely, all the subfossil trees had grown on riverside bogs, directly on the bank of the Wisła river, with no water deficit, at permanent and very high air humidity conditions. However, the recent trees, representing XIX and XIX century, grew several kilometres from the recent Wisła river, as no recent oak trees were available at the Wisła valley. Moreover, in the middle of the last century the river has been regulated and dams have surrounded the river-bed. Thus, in contrast to the subfossil trees, water deficit could be the limiting factor in the case of the XIX and XX trees (annual atmospheric precipitation at this region is limited to ca. 660 mm yr^{-1}, Trepińska, 1971). Therefore, calibrations of the millennium record and the century records are not comparable.

It must be mentioned that Saurer *et al*. (1995) used entire tree-rings, not just the late wood as has been done in this study. They found that when warm and dry conditions prevail during the period from May to July, relatively high δ^{13}C values would be produced in the cellulose of tree rings of beech trees, compared to a period of cold and wet conditions. Thus, according to Saurer *et al*. (1987, 1995) precipitation between May and July most strongly influences the δ^{13}C values. We found such a correlation for the same season for the late wood cellulose (Figure 2), and this effect is about –0.06‰/1 mm of May–July precipitation. There are much worst (spring and summer months) or no correlation (autumn and winter months) of the δ^{13}C value with other month's precipitation. The precipitation coefficient is also in agreement to Stuvier *at al*. (1987) and Lipp *at al*. (1991).

Since about the 1880s the environment in the sampling region was increasingly controlled by anthropogenic industrial impact, with its peak between the mid-50s and early 90s. Numerous observations (Gebauer *et al*., 1991, 1994; Bruckner *et al*., 1993) shows that trees can tolerate low levels of gaseous and aerosol compounds including SO_2. Although, it has been shown, that at higher concentrations of pollutants, stomata may close as photosynthetic metabolic processes have also been suggested to be sensitive to gaseous pollutants (Freyer, 1979; Freyer and Belacy, 1983; Reinert, 1984; Olszyk and Tingey, 1986; Reich *et al*., 1986, 1987), especially SO_x and dust (Jędrysek *et al*. 2002). Stomatas closure may result in an appreciable increase in the δ^{13}C value (e.g. Farquhar *et al*., 1982, 1989) and δ^{34}S (organic an inorganic independently) values (Jędrysek *et al*., 2002) of plants. In fact, fumigation experiments and exposure to exhaust gases (1972–1976, gas plant at Lacq, France) of conifer trees (*Pseudotsuga menziensii* and *Pinus strobus*) resulted in about a 1‰increase in the δ^{13}C of the entire wood (Martin *et al*., 1988). We do not have details to compare pollution loads of the Lacq plant gas and the 'Lenin' steelworks, but the latter, about 30 yr ago, was the biggest steelworks in the Eastern Europe. Moreover, comparing the technology in the 50s to the more advanced technology in France in the 70s there is no doubt that the environmental impact of 'Lenin' was much larger. Thus, the observed 1.3‰increase in the δ^{13}C value of tree ring cellulose (Figure 2) could be explained by a pollution effect.

6. Conclusions

1. Tree ring and peat carbon isotope curves show visual similarities over the last millennium. This suggests that the δ^{13}C value of the organic matter in these two terrestrial environments is generally controlled by the same factors.
2. Although, it is not possible to provide a universally precise calibration as assimilation isotope effects depend mostly on local microclimatic conditions and specific species demands. In the area studied, precipitation has been found to be the limiting factor controlling carbon isotope variations in tree ring cellulose. This calibration is valid for the time from the middle of 19th till the middle of 20th centuries.
3. Carbon isotope fractionation effects between living plants and atmospheric carbon dioxide ($\Delta^{13}C_{p-a}$) for C3 plants is about –0.26‰/1 °C. It corresponds to and 2.1‰/1000 m elevation.
4. A remarkable anthropogenic impact caused by the neighbouring 'Lenin' steelworks in Nowa Huta (constructed in 1954 near Kraków), as shown in Figure 2, suggests that such a calibration should be limited to the pre-industrial time.
5. In the region under study, temperature was the factor controlling δ^{13}C value of tree ring cellulose and peat-bog *Sphagnum* before the 19th century. The primary role of humidity appeared in the Wisła valley when the river was regulated and water deficit in the neighbouring areas became common. Since the 1955, after 'Lenin' steelworks started operation, pollution became the dom-

inant factor controlling assimilation isotope fractionation, hence the $\delta^{13}C$ value of tree ring cellulose was lower.

6. It has been observed that contamination of the atmosphere by the products of fossil fuel burning from the 'Lenin' steelworks (mostly SO_x and dust etc.) increased the $\delta^{13}C$ value of tree ring cellulose by about 1.3‰.

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