

# HYDROGEN, CARBON AND OXYGEN ISOTOPES IN PINE AND OAK TREE RINGS FROM SOUTHERN POLAND AS CLIMATIC INDICATORS IN YEARS 1900 - 2003

MAŁGORZATA SZCZEPANEK<sup>1</sup>, ANNA PAZDUR<sup>1</sup>, SŁAWOMIRA PAWEŁCZYK<sup>1</sup>,  
TATJANA BÖTTGER<sup>2</sup>, MARIKA HAUPT<sup>2</sup>, STANISŁAW HAŁAS<sup>3</sup>,  
ZDZISŁAW BEDNARZ<sup>4</sup>, MAREK KRĄPIEC<sup>5</sup> and ELŻBIETA SZYCHOWSKA-KRĄPIEC<sup>5</sup>

<sup>1</sup>Department of Radioisotopes, Institute of Physics, Silesian University of Technology,  
Krzywoustego 2, 44-100 Gliwice, Poland  
(e-mail: malgorzata.szczepanek@polsl.pl)

<sup>2</sup>UFZ-Umweltforschungszentrum Leipzig-Halle GmbH, Sektion Hydrogeologie, AG Palaeoklimatologie;  
Theodor-Lieser-Strasse 4, 06120 Halle/Saale, Germany

<sup>3</sup>Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University,  
Plac Marii Curie-Skłodowskiej 1, 20-031 Lublin, Poland

<sup>4</sup>Department of Forest Botany and Nature Conservation, Faculty of Forestry, Agricultural University of Cracow,  
Listopada 46, Mickiewicza 21, 31-425 Cracow, Poland

<sup>5</sup>Dendrochronological Laboratory, AGH University of Science and Technology, Mickiewicza 30, 30-059 Cracow, Poland

**Key words:**  
STABLE ISOTOPES <sup>2</sup>H,  
<sup>13</sup>C, <sup>18</sup>O, TREE RINGS,  
CLIMATE

**Abstract:** Carbon, oxygen and hydrogen stable isotopes in tree rings are sensitive indicators of climate changes. We have measured carbon, oxygen and hydrogen isotope ratios in  $\alpha$ -cellulose extracted from annual rings of pine (*Pinus sylvestris* L.) and oak (*Quercus robur* L.) growing in the Niepołomice Forest, Southern Poland. The presented isotope records cover the period 1900-2003. In this paper we compare the values of  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  observed in the wholewood of pine and in the latewood of oak with meteorological data (temperature, precipitation and sunshine). The highest significant values of correlation coefficients calculated between  $\delta^{13}\text{C}$  and the meteorological data are: -0.26 for temperature, 0.25 for precipitation and 0.41 for sunshine. On the basis of our investigations we deduced that pine is a more sensitive indicator of environmental changes than oak. Our investigation proves that the best indicators are: hydrogen for summer temperature and oxygen for summer precipitation. We noticed a rapid decrease of pine  $\delta^{13}\text{C}$  values in 1966 from -22.46‰ to -24.64‰.

## 1. INTRODUCTION

In the region of moderate climate, like Poland, trees usually produce one ring during each year. Information about climate is stored in tree ring widths. As a result, reconstruction of climate changes in the past is obtained with yearly resolution.

Wood is composed of cellulose, hemicellulose and lignin. Cellulose, particularly  $\alpha$ -cellulose, is a good indicator of environmental changes in the past. Other components are removed during chemical preparation.

Pine (*Pinus sylvestris* L.) is a common plant used for palaeoclimate reconstruction (McCarroll and Loader, 2004). Stable isotope composition in  $\alpha$ -cellulose is deter-

mined for oak latewood (*Quercus robur* L.) and pine wholewood (*Pinus sylvestris* L.) In the case of deciduous trees, latewood is used for paleoclimate analysis because  $\delta^{13}\text{C}$  in earlywood records the climate of the previous year – tree rings initially grow at the expense of accumulated organic components.

Oak is a ring-porous wood. The tree produces large vessels at the beginning of spring growth and smaller vessels mixed with thick walled fibres later in the growing season. The cells of the spring wood are formed by the cambium before the leaves have expanded. Cellulose is formed using photosynthates from the previous years, presumably accumulated as starch during the winter (Plicher, 1995).

The value of  $\delta^{13}\text{C}$  in trees is influenced by many factors like concentration of  $\text{CO}_2$  and  $\delta^{13}\text{C}$  in atmospheric  $\text{CO}_2$ , temperature, precipitation, and humidity.

Previous studies proved that there exists a correlation between  $\delta^{13}\text{C}$  and temperature. Results of measurements demonstrate that the correlation between  $\delta^{13}\text{C}$  and temperature can be positive:  $0.18 \text{‰}/^\circ\text{C}$  for *Pinus sylvestris* (Freyer and Belacy, 1983),  $0.27$  to  $0.39 \text{‰}/^\circ\text{C}$  for *Quercus robur* (Tans and Mook, 1980),  $0.51 \text{‰}/^\circ\text{C}$  for *Pinus sylvestris* from Augustów, Poland (Pawelczyk and Pazdur, 2004). It can also be negative, e.g.  $-0.27 \text{‰}/^\circ\text{C}$  for *Juniper monosperma* (Leavitt and Long, 1982).

For each plant, there exists an optimal temperature with respect to net photosynthesis. If the temperature is higher or lower than the net, photosynthesis decreases.

Krapiec (1998) observed a relationship between the amounts of precipitation and  $\delta^{13}\text{C}$  of ring cellulose in oak (*Quercus robur*) for the period May-July. The increase of the amount of precipitation by about 30 mm corresponds to a decrease of  $\delta^{13}\text{C}$  by about  $1 \text{‰}$ .

When investigating the correlation between temperature and  $\delta^2\text{H}$  values, we can observe a wide range of values:  $5.80 \text{‰}/^\circ\text{C}$  for *Pinus sylvestris* (Yapp and Epstein, 1982);  $89.5 \text{‰}/^\circ\text{C}$  for *Quercus petraea* (Libby and Pandolfi, 1974);  $5.30 \text{‰}/^\circ\text{C}$  to  $17 \text{‰}/^\circ\text{C}$  for different species of trees from Northern America (Feng and Epstein, 1995). Correlations between  $\delta^{18}\text{O}$  and temperature, as well as relative humidity were also investigated. In this case, changes of  $\delta^{18}\text{O}$  with changes of temperature are following:  $1.3 \text{‰}/^\circ\text{C}$  for *Picea galuca* (Gray and Thompson, 1976);  $5.29 \text{‰}/^\circ\text{C}$  for *Quercus petraea* (Libby and Pandolfi, 1974); and with changes of relative humidity:  $0.19 \text{‰}/\%$  for *Abies pindow* (Ramesh *et al.*, 1986). In addition, relationships between temperature of February and March and tree ring values were established for *Pinus sylvestris* from northern part of Poland (Zielski, 1997) and for southern regions (Wilczyński, 1999).

Investigations of the influence of industrial contamination on tree ring widths for *Pinus sylvestris* from the Niepołomice Forest confirmed that the first decrease of tree ring widths was observed in 1959. Niepołomice Forest is a region strongly influenced by contamination from

Cracow agglomeration, Ironworks T. Sendzimira in Nowa Huta since 1954 and Nitrate Works in Tarnów. The contamination is carried by north-west wind from Cracow side and from Tarnów. The development of industry in this region was intensified in the 60s and caused maximum tree ring width reduction (Fig. 2) in the Niepołomice Forest for years 1970-1980 (Szychowska-Krapiec and Krapiec, 2002).

Stable isotope compositions of light elements such as oxygen, hydrogen and carbon are reported as  $\delta$ -values in parts per thousand (denoted as ‰) relative to the standard of known composition. For example,  $\delta^{13}\text{C}$  values for carbon are calculated using the following equation:

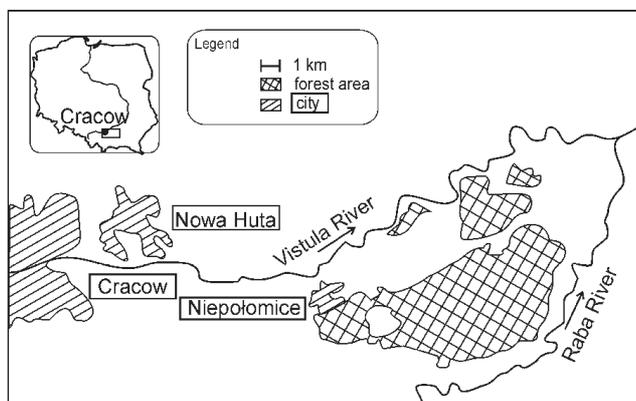
$$\delta^{13}\text{C} = \left[ \frac{\left( \frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{sample}}}{\left( \frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{standard}}} - 1 \right] \cdot 1000 \text{‰} \quad (1.1)$$

$\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values are normally reported with respect to the SMOW standard (Standard Mean Ocean Water; Craig, 1961) or the equivalent VSMOW (Vienna-SMOW) standard.  $\delta^{13}\text{C}$  values are reported with respect to either the PDB (Pee Dee Belemnite) or the equivalent VPDB (Vienna-PDB) standard.

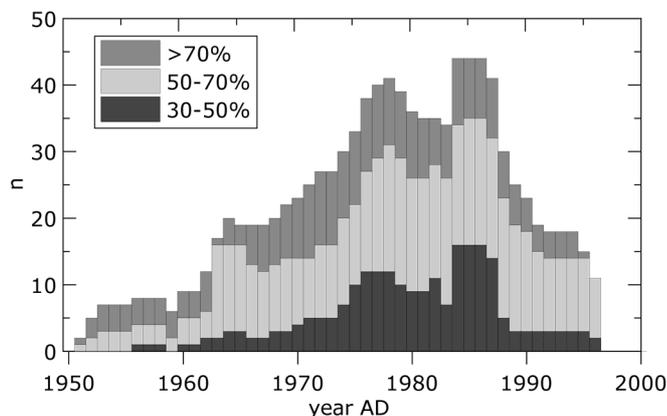
## 2. SITE

Samples for isotopic analyses were collected from long-living pines and oaks growing in the Niepołomice Forest (184-212 m n.p.m.) which is located in Southern Poland ( $49^\circ 59' - 50^\circ 07' \text{N}$   $20^\circ 13' - 20^\circ 28' \text{E}$ ). The Niepołomice Forest is situated in the area between the Vistula and Raba rivers. It consists of four complexes (Fig. 1) which were aggregated in the past. The main complex has an area of about  $89 \text{ km}^2$ , the remaining area: Grobla –  $15.0 \text{ km}^2$ , Grobelczyk –  $2.6 \text{ km}^2$  and Koło  $2.2 \text{ km}^2$ . The total area of the Niepołomice Forest is about  $110 \text{ km}^2$ . It is only a small part of the primeval Niepołomice Forest, which was situated between Cracow and Sandomierz.

The area of the Niepołomice Forest is characterized by a geological and geomorphologic variety and diversity of ecosystems.



**Fig. 1.** The complex including 4 parts of the Niepołomice Forest is situated in the area between the Vistula and Raba rivers. The nearest urban agglomerations are marked in the figure.



**Fig. 2.** Reduction values of tree ring widths in years 1952-1996 for the Niepołomice Forest (Szychowska-Krapiec and Krapiec, 2002).

The mixed forest complex in the Niepołomice Forest is a representative of poorer habitat conditions. The climatic conditions like temperature, precipitation, humidity and human activities in the past caused that pine (*Pinus sylvestris* L.), oak (*Quercus robur* L. and *Quercus petraea* L.) and black alder (*Alnus glutinosa* L.) are the main tree species in the Niepołomice Forest.

### 3. DENDROCHRONOLOGY

Samples for isotopic investigations originated from disks taken from 4 trees of pines and oaks (PSPNF and QRPNF chronologies). These trees were especially selected for dendrochronological dating. Samples from 4 trees with similar tree ring widths were homogenized. Previous investigation connected with isotopic composition of tree rings shown that results obtained for four trees are representative for the sampled region (Leavitt and Long, 1984; Robertson et al., 1997).

### 4. TREES AND CLIMATE (1900 – 2003 AD) FOR CRACOW UPLAND

The climate in Poland is greatly influenced by oceanic air currents from the West, cold polar air from Scandinavia and Russia, as well as warmer, sub-tropical air from the South. In winter, the polar-continental fronts dominate bringing crisp and frosty weather. The late summer and autumn months enjoy plenty of warm days thanks to the influence of the dry, sub-tropical, continental air mass. The greatest amount of sunshine in summer is found on the Baltic coast, whilst in winter it is found in the Carpathian Mountains.

Cracow is located in Southern Poland, in the Vistula River Valley, between Jura Highland in the North and the Carpathians in the South. Meteorological data for Cracow such as temperature, precipitation and sunshine come from the local meteorological station (50°07'N 19°58'E). The vegetative period lasts for about 218 days, the annual mean temperature is ca 8.6°C (for last 100 years), and the annual sum of precipitation is ca 700 mm (Szarek-Lukaszewska et al., 2002).

Fig. 3 shows varying periods of the different climatic components: temperature, amount of precipitation and sunshine hours as annual means compared with tree ring indices for the period 1900-2003. We observed a rapid increase of tree ring indices (pine and oak), temperature and precipitation in the early 40's. In addition, trends in tree ring indices for oak and trends in temperature for the period 1940-2003 are very similar. At the end of 80's, a rapid decrease of tree ring indices and temperature were observed.

Correlation coefficients between climate conditions and tree ring indices for *Pinus sylvestris* (PSPNF) and *Quercus robur* (QRPNF) (Fig. 4) were obtained using correlation functions from DendroClim2002 (Biondi and Waikul, 2004). DendroClim 2002 is a statistical tool for the analysis of climate/tree growth relationships. For the analysis of the tree ring indices and climatic variables (temperature, precipitation or sunshine) appropriate files were prepared.

Correlation coefficients for the time period 1901-2000 for pine are presented in Fig. 4. Black bars denote significant values based on 95% confidence level. The height of the bar corresponds to value of the coefficient. In the case of temperature it positive, ranging from 0.2 to 0.3 in January, February and March of the current year. In the case of precipitation, more significant correlation coefficients are observed, but they are both positive and negative. Significant correlation coefficients between sunshine and tree ring indices were obtained for May of previous year, and January and April of the current year.

All correlation coefficients for years 1901-2000 for oak are presented also in Fig. 4. Significant values were obtained only for temperature and precipitation. In the case of temperature, it has a positive value for February and August of the current year. Significant correlation coefficients for precipitation were obtained for March and July of the current year. In the case of sunshine hours, no correlation coefficient is significant.

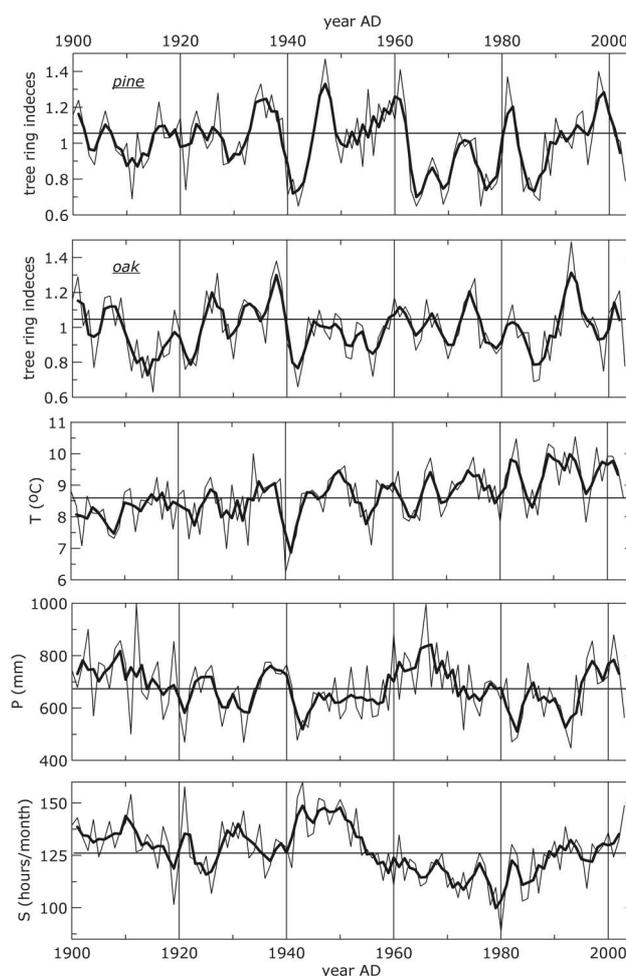
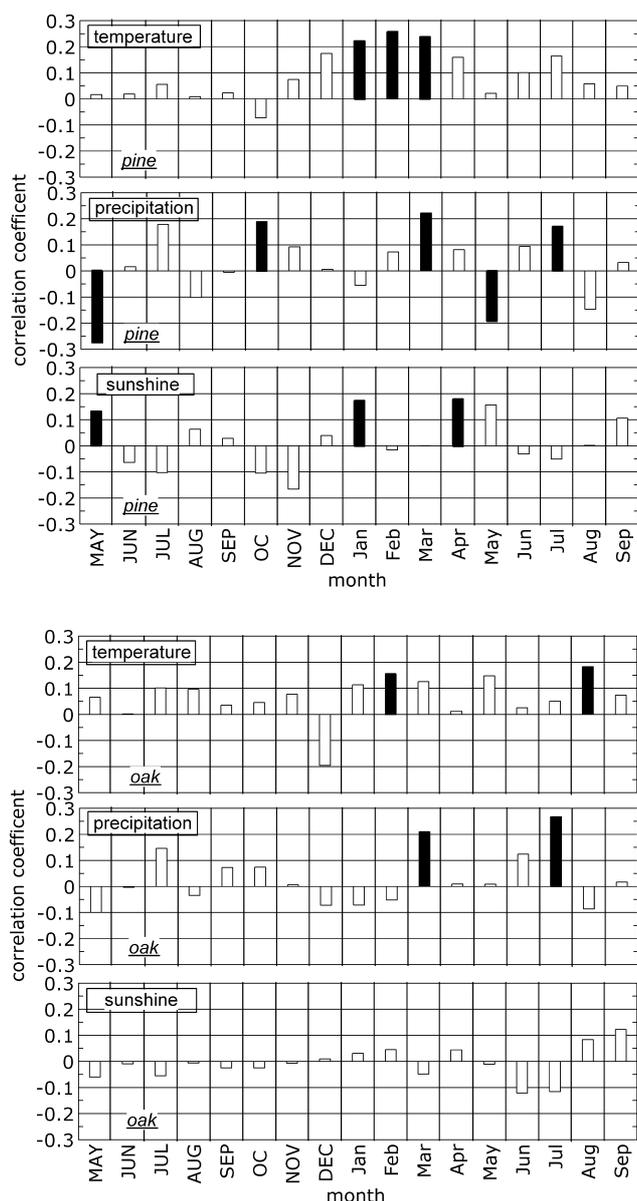


Fig. 3. Tree ring indices from pine and oak (PSPNF and QRPNF chronologies) in comparison to the annual averaged climatic conditions temperature (°C), precipitation amount (mm) and sunshine hours (hours/month) smoothed by 3-point moving average.



**Fig. 4.** Correlation coefficients between climate conditions (monthly means) and tree ring indices of pine and oak (PSPNF and QRPNF chronologies) for the time period 1901-2000. The monthly meteorological data (temperature, precipitation, sunshine) values of the previous year are labeled with capital letters; lower case represents the monthly meteorological data of the current year. Black bars denote significant values according to 95% level.

## 5. ISOTOPIC METHODS

### $\delta^{13}\text{C}$ analysis

$\alpha$ -cellulose is the most reliable part of wood for palaeoclimatic analyses (Epstein *et al.*, 1976; Switsur *et al.*, 1995). Lignin and other components of wood were removed using sodium chlorite and acetic acid solution. The procedure is based on the methods given by Green (1963) and Loader *et al.* (1997). The extraction procedure of  $\alpha$ -cellulose and the procedure of  $\text{CO}_2$  received for isotopic analyses in the Gliwice laboratory was fully described in Pazdur *et al.* (2005) and Pawełczyk *et al.* (2004).  $\delta^{13}\text{C}$  was measured using dual inlet and triple collector mass

spectrometer (significantly modified MI-1305 type) in the Mass Spectrometry Laboratory in Lublin. The standard deviation ( $1\sigma$ ) of  $\delta^{13}\text{C}$  is  $0.07\text{‰}$ . The samples were measured with respect to gas standards and final results were expressed using the V-PDB scale. More information about this technique is available in Pazdur *et al.* (2005).

### $\delta^{18}\text{O}$ analysis

The stable oxygen isotopes ratios of  $\alpha$ -cellulose samples were analyzed in the mass spectrometric laboratory of UFZ (Halle, Germany) with mass spectrometer Delta plus XL (ThermoFinnigan) coupled with a high temperature ( $1450^\circ\text{C}$ ) pyrolysis reactor (HEKAtech, HT-O). The results are given as  $\delta$ -values in  $\text{‰}$  versus the IAEA standard material VSMOW. The error margin of this method is  $\pm 0.3\text{‰}$  (Knöller *et al.*, 2005).

### $\delta^2\text{H}$ analysis

The non-exchangeable hydrogen ratios of  $\alpha$ -cellulose were analyzed also in the mass spectrometric laboratory of UFZ (Halle, Germany) after nitration according to the method developed by Alexander and Mitchell (1949), and Gray and Song (1984). The  $\delta^2\text{H}$  measurement conditions were analogous to that of  $\delta^{18}\text{O}$ . The error margin of this method is  $\pm 3\text{‰}$ .

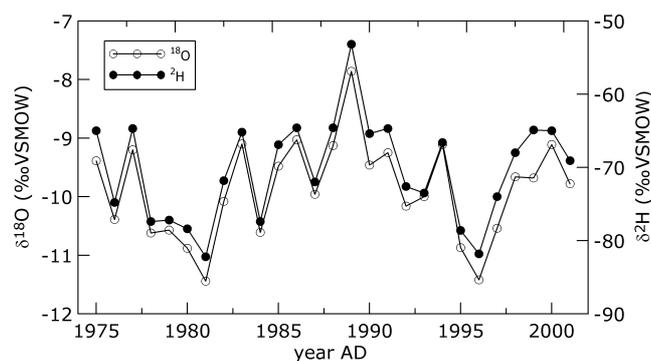
## 6. $^2\text{H}$ AND $^{18}\text{O}$ ISOTOPES IN PRECIPITATION

Hydrogen and oxygen isotopic data in precipitation for Cracow concern the years 1975-2001 (GNIP data). Precipitation was collected in the Wola Justowska station. Variations of stable isotope ratios in this period are shown in **Figs 5** and **7**. Arithmetic averages of these isotope ratios in precipitation (GNIP) are related by the following equation:

$$\delta^2\text{H} = 8.04 \cdot \delta^{18}\text{O} + 9.05, \quad (n=27; r=0.98) \quad (6.1)$$

The slope of the obtained straight line ideally agrees with the slope of the world meteoric line.

The monthly mean values of temperature and the amount of precipitation presented in **Fig. 6** showed a typical trend for moderate climate. Summer months are characterised by a rather high value of mean monthly tem-



**Fig. 5.** Changes of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in precipitation in years 1975-2001 (GNIP data, Wola Justowska station, near Cracow).

perature (ca 16°C) and the monthly amount of precipitation is equal to 80 mm. A longer vegetation period is caused by warm and humid spring (April-May) and summer months, which is connected with better conditions for plants growth. The monthly changes of oxygen and hydrogen ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) in modern precipitation (1975-2001), monthly changes of atmospheric temperature and monthly sum of precipitation give very good compatibility (Fig. 6).

Table 1 shows correlation coefficients between oxygen and hydrogen in precipitation and in  $\alpha$ -cellulose. Significant values ( $p < 0.05$ ) were indicated in boldface. Isotopic fractionation connected with physiological processes in plants is the reason why the values of isotopic composition of plant do not reflect directly isotopic composition of precipitation. Variations in fractionation due to physiological processes were not taken into account.

## 7. ISOTOPIC RECORDS IN TREE RINGS

### Comparison of isotopic records in pine and oak

Trees respond physiologically and physically to environmental conditions and record some of this information in annually growing rings. Over the course of the growing season, this signal is transferred and stored in tree rings in the form of isotopic composition of cellulose and tree ring widths.

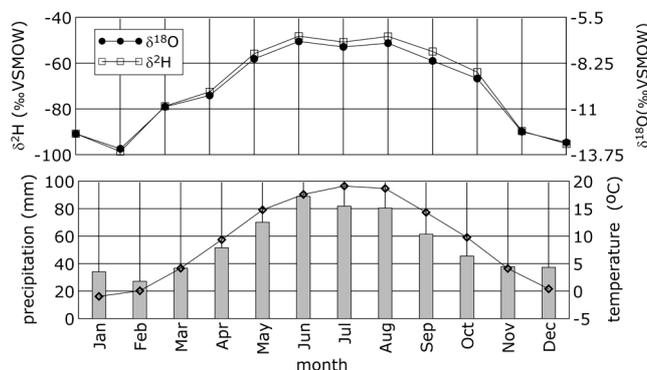


Fig. 6. Monthly changes in amount of precipitation (mm), temperature (°C), arithmetic mean values of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in precipitation.

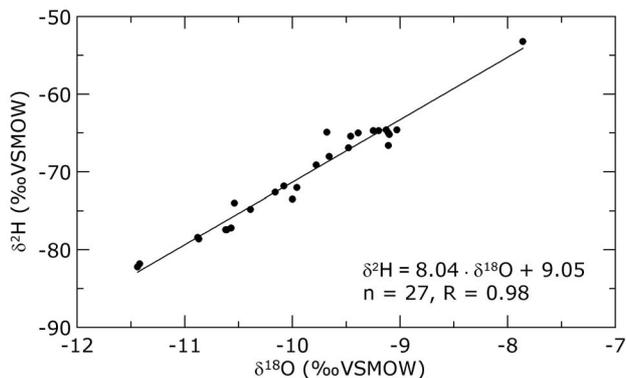


Fig. 7.  $^2\text{H}$  and  $^{18}\text{O}$  correlation in precipitation.

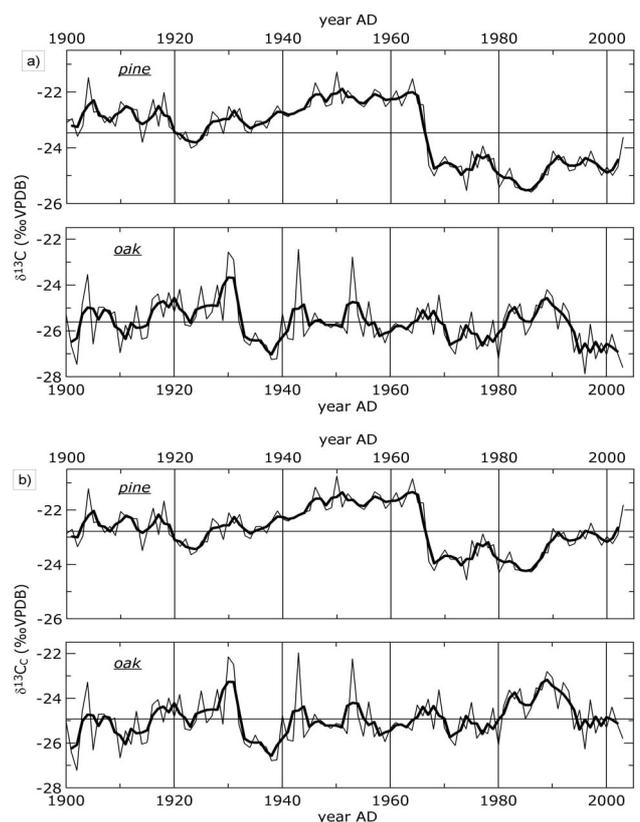


Fig. 8. **a)** Time records (1900 – 2003) of uncorrected  $\delta^{13}\text{C}_c$  in  $\alpha$ -cellulose of pine (PSPNF) and oak (QRPNF) (smoothed by 3- point running average). Average value of  $\delta^{13}\text{C}$  is  $-23.4\text{‰}$  for pine,  $-25.6\text{‰}$  for oak **b)** Time records (1900 – 2003) of corrected  $\delta^{13}\text{C}$  in  $\alpha$ -cellulose of pine and oak (smoothed by 3- point running average). Average values of  $\delta^{13}\text{C}_c$  are  $-22.7\text{‰}$  and  $-24.9\text{‰}$  for pine and oak respectively. Correction of  $\delta^{13}\text{C}$  values results from carbon isotopic composition in atmospheric  $\text{CO}_2$  (Leuenberger, <http://www.isonet-online.de/>) connected with  $\text{CO}_2$  from fossil fuel burning.

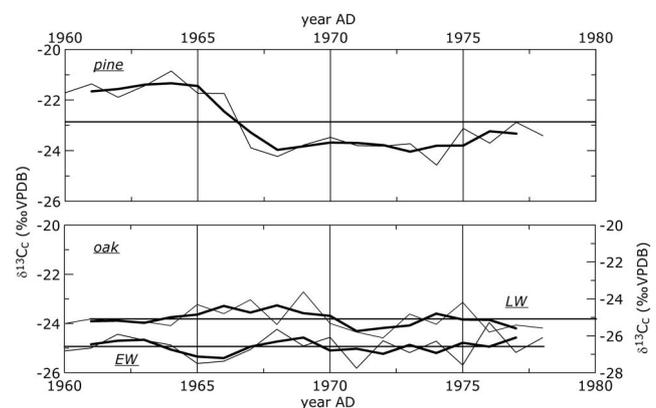


Fig. 9. Time records (1960 – 1978) of corrected  $\delta^{13}\text{C}$  in  $\alpha$ -cellulose of wholewood of pine and earlywood (EW), latewood (LW) of oak (smoothed by 3- point running average). Average values of  $\delta^{13}\text{C}$  are  $-25.1\text{‰}$  for latewood of oak (LW),  $-24.9\text{‰}$  for earlywood of oak (EW) and  $-22.9\text{‰}$  for wholewood of pine. All values were corrected for change of carbon isotopic composition in atmospheric  $\text{CO}_2$  (Leuenberger, <http://www.isonet-online.de/>).

**Table 1.** Correlation coefficients for different delta values in tree rings and precipitation for years 1975 – 2001. Significant values ( $p < 0.05$ ) were indicated using boldface.

		Pine		Oak	
		$\delta^{18}\text{O}$ (‰VSMOW)	$\delta^2\text{H}$ (‰VSMOW)	$\delta^{18}\text{O}$ (‰VSMOW)	$\delta^2\text{H}$ (‰VSMOW)
Precipitation	$\delta^{18}\text{O}$ (‰VSMOW)	<b>0.44</b>	<b>0.43</b>	<b>0.39</b>	0
	$\delta^2\text{H}$ (‰VSMOW)	<b>0.45</b>	<b>0.46</b>	<b>0.37</b>	0.02

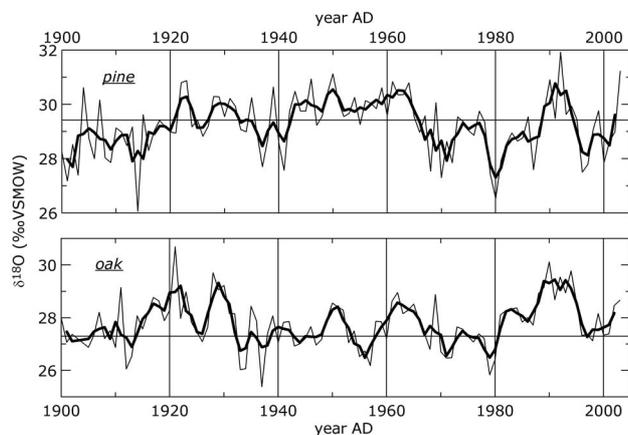
Investigations of trees from Niepołomice Forest were a part of the European project ISONET; in its frame corrections of  $\delta^{13}\text{C}$  values (Fig. 8) were carried out in accord with the data given by Leuenberger (<http://www.isonet-online.de/>). The values of correction given for each year separately were subtracted from the  $\delta^{13}\text{C}$  values obtained by spectrometric measurements. Fractionation of carbon isotopes during  $\text{CO}_2$  concentration increase was not taken into account similarly to the case of oxygen.

A rapid decrease of  $\delta^{13}\text{C}$  value is observed in wholewood  $\alpha$ -cellulose in pine, but it is not recorded in latewood  $\alpha$ -cellulose in oak. Additional investigations for oak earlywood were carried out (Fig. 9) and they showed that the rapid decrease is not observed similarly to the oak latewood.

The difference in the mean  $\delta^{13}\text{C}$  values of the two C3 plants (pine, oak) growing under similar conditions in the upland habitat can be due to three possible reasons:

- different species are known to have different isotopic fractionations (Leavitt and Long 1989);
- different photosynthesizing parts of plants show minimal differences in their isotopic values (Long 1982);
- the physiognomy of the plants could also be an important factor for explaining the isotopic differences in the two C3 species.

Trends of  $\delta^{18}\text{O}$  (Fig. 10) changes in pine and oak are similar for the investigated period 1900-2003. The average  $\delta^{18}\text{O}$  value is 29.3‰ for pine and 27.2‰ for oak. The differences in the average value can result from species differences as well as from the fact that measurements of  $\delta^{18}\text{O}$  were made for cellulose obtained in the case of pine



**Fig. 10.**  $\delta^{18}\text{O}$  records (1900 – 2003) in pine (PSPNF) and oak (QRPNF) in  $\alpha$ -cellulose (smoothed by 3-point running average).

from the entire annual growth, whereas in the case of oak only from the summer part of the wood.

Trends of  $\delta^2\text{H}$  (Fig. 11) changes in pine and oak for the investigated period are not similar. The variability of  $\delta^2\text{H}$  ranges from -40 to -115‰ for pine (average value is -73‰), and -60 to -95‰ for oak (the average value is 75‰). Differences in the average value can result from similar facts as in the case of  $\delta^{18}\text{O}$ .

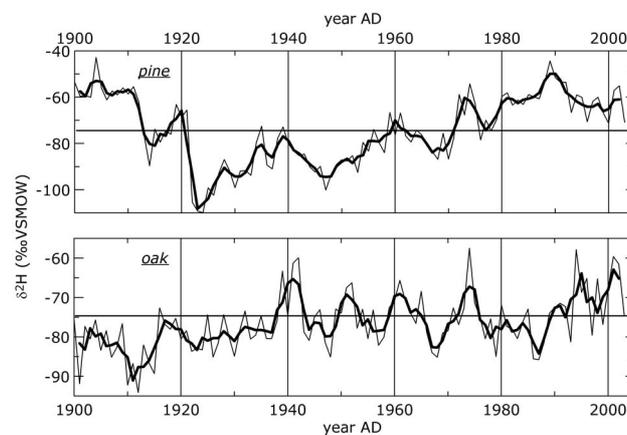
#### Climatic evidence in isotopic records

Fig. 12 shows deviations from the average value for  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in cellulose of pine and the deviation from the average value of weather conditions (temperature -  $\Delta\text{T}$ , precipitation -  $\Delta\text{P}$  and sunshine hours -  $\Delta\text{S}$ ) for the period 1900-2003. The observations may be summarised as follows:

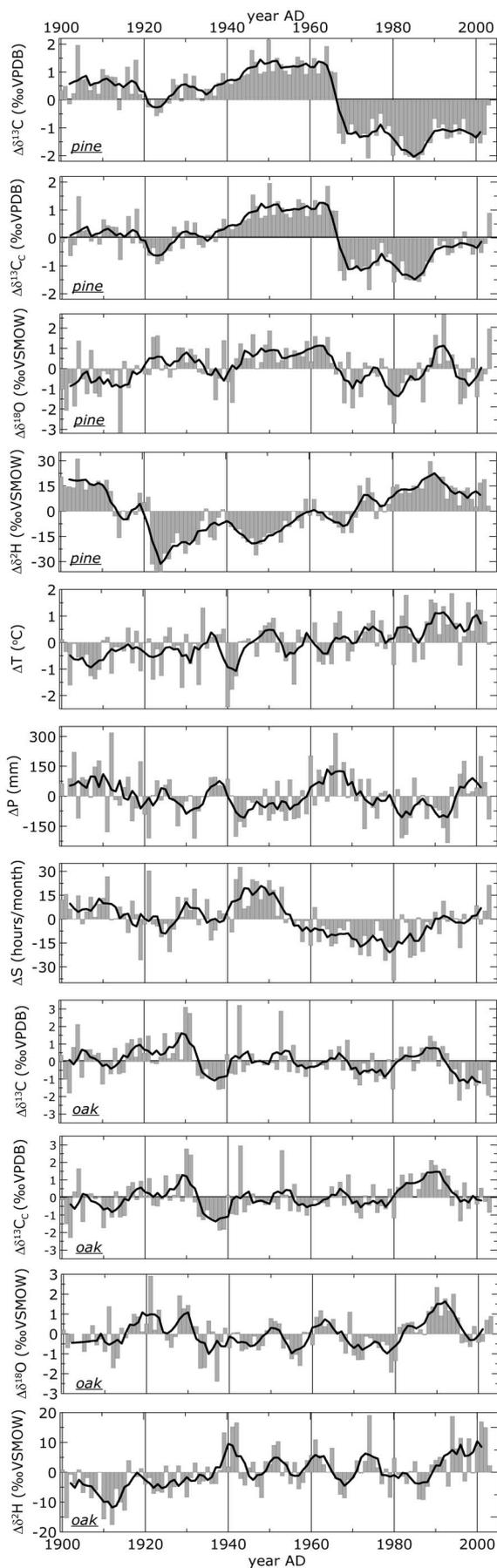
- a strong relationship exists between  $\delta^{13}\text{C}$  (both corrected and uncorrected) and  $\Delta\text{S}$ ;
- there is no distinct relationship between  $\delta^2\text{H}$  and values of  $\Delta\text{P}$ ;
- also no relationship between deviations of the temperature  $\Delta\text{T}$  and deviations of sunshine hours was observed.

Fig. 12 shows also deviations from the average value for  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in cellulose of oak for the period 1900-2003. Observations are the following:

- a strong relationship exists between  $\delta^{13}\text{C}$  (both corrected and uncorrected) and  $\Delta\text{T}$ ;
- anti-correlation exists between  $\delta^{18}\text{O}$  and precipitation  $\Delta\text{P}$ ;
- relation exists between  $\delta^2\text{H}$  and temperature  $\Delta\text{T}$ .



**Fig. 11.**  $\delta^2\text{H}$  records (1900 – 2003) in pine (PSPNF) and oak (QRPNF) in cellulose nitrate (smoothed by 3-point running average).

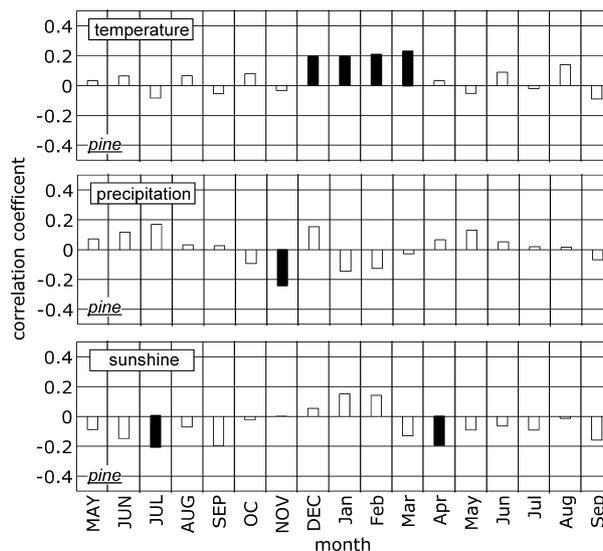


**Fig. 12.** Deviations from the mean values of  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  (uncorrected and corrected), temperature ( $^{\circ}\text{C}$ ), precipitation amount (mm) and sunshine hours (hours/month) for pine (PSPNF) and oak (QRPNF) (smoothed by 3-point running average).

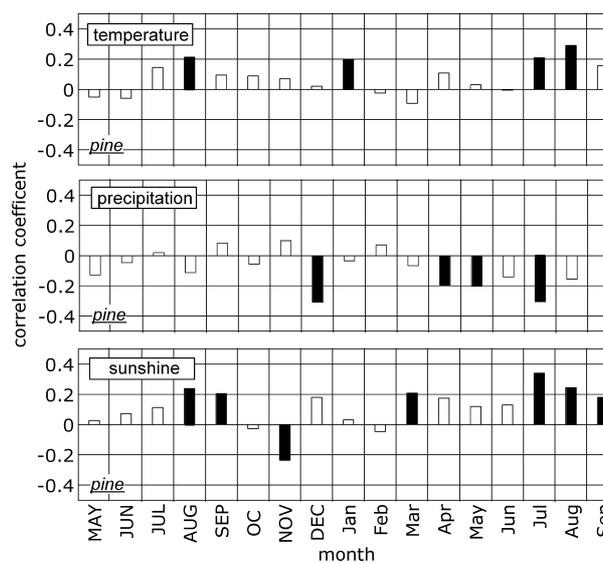
Correlation coefficients between stable isotope ratios in wood (wholewood of pine and latewood of oak) and mean monthly meteorological data (temperature, precipitation and sunshine hours) for years 1901 – 2000 are presented in the **Figs 13-20**. For calculations, the detrended and raw values of  $\delta^{13}\text{C}$  were used. The highest correlation coefficients were indicated using boldface.

The monthly meteorological data (temperature, precipitation, sunshine) values for the previous year are labeled with capital letters; lower case represents the monthly meteorological data of the current year.

The highest significant correlation coefficients are summarized in the **Table 2**.



**Fig. 13.** Correlation coefficients between  $\delta^2\text{H}$  and meteorological data for pine (PSPNF) for years 1901-2000. Black bars denote the significant values. The highest values are for temperature 0.23 (March of current year), precipitation -0.24 (November of previous year) and sunshine -0.20 (July of previous year).



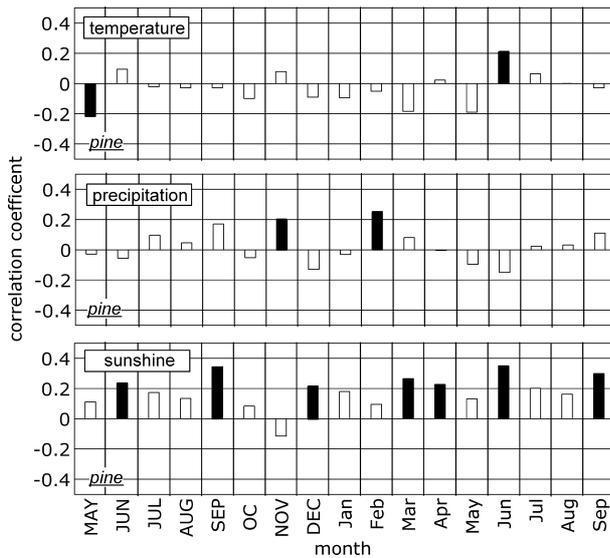
**Fig. 14.** Correlation coefficients between  $\delta^{18}\text{O}$  and meteorological data for pine (PSPNF) for years 1901-2000. Black bars denote significant values. The highest values are for temperature 0.29 (August of current year), precipitation -0.31 (July of current year) and sunshine 0.34 (July of current year).

8. SUMMARY

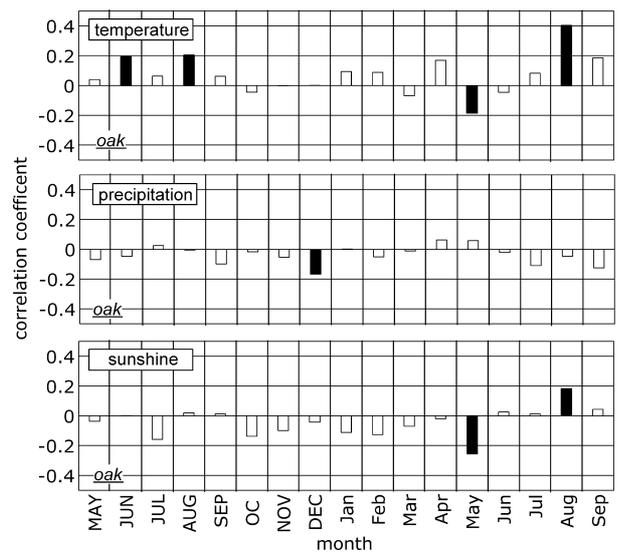
The  $\delta^{13}\text{C}$  ratio in the cellulose of the whole wood of pine from the Niepołomice Forest, Southern Poland, reflects the global trend of decreasing of  $\delta^{13}\text{C}$  in the atmospheric  $\text{CO}_2$  due to fossil fuel burning. The observed rapid decrease of  $\delta^{13}\text{C}$  values for 1966 from the level -22.46‰ to -24.64‰ is an unexpected result. This decrease is observed even after correcting the measured values for changes of  $\delta^{13}\text{C}$  in the atmospheric  $\text{CO}_2$ . This is not a seasonal effect because the low values of  $\delta^{13}\text{C}$  are observed

during next several years from 1967 to 1973. The rapid change is not visible in the early and late wood of oak from the same region. A reduction of the tree ring widths was observed in the same time span.

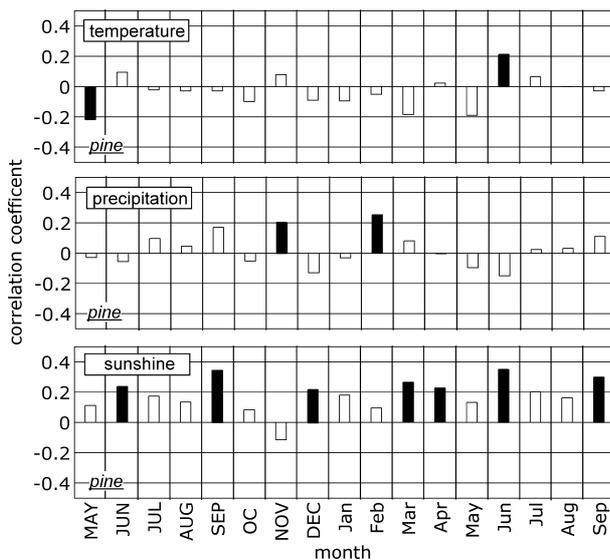
The highest significant values of correlation coefficients calculated between  $\delta^{13}\text{C}$  and the meteorological data are -0.26 for temperature (May of the previous year), 0.25 for precipitation (February of the current year) and 0.41 for sunshine (September of the previous year). On the basis of our investigations we deduced that pine is a more sensitive indicator of environmental changes than oak.



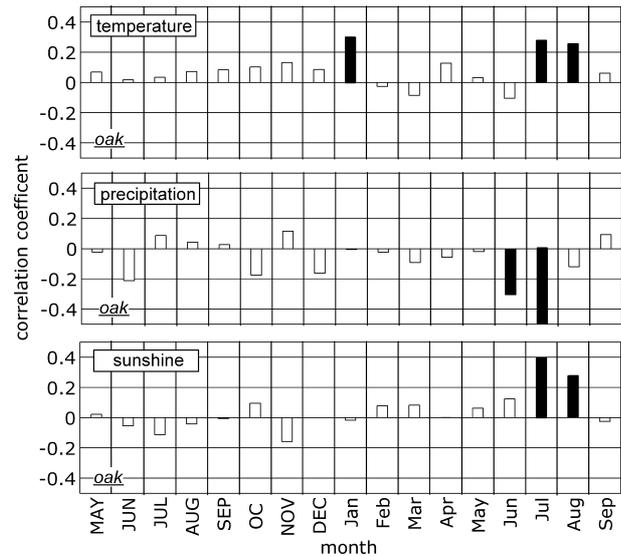
**Fig. 15.** Correlation coefficients between  $\delta^{13}\text{C}$  (before correction) and meteorological data for pine (PSPNF) for years 1901-2000. Black bars denote significant values. The highest values are for temperature -0.26 (May of previous year), precipitation 0.21 (February of current year) and sunshine 0.41 (September of previous year).



**Fig. 17.** Correlation coefficients between  $\delta^2\text{H}$  and meteorological data for oak (QRPNF) for years 1901-2000. Black bars denote significant values. The highest values are for temperature 0.40 (August of current year), precipitation -0.17 (December of previous year) and sunshine -0.25 (May of current year).



**Fig. 16.** Correlation coefficients between  $\delta^{13}\text{C}_c$  (detrended) and meteorological data for pine (PSPNF) for years 1901-2000. Black bars denote significant values. The highest values are for temperature -0.22 (May of previous year), precipitation 0.25 (February of current year) and sunshine 0.35 (June of current year).



**Fig. 18.** Correlation coefficients between  $\delta^{18}\text{O}$  and meteorological data for oak (QRPNF) for years 1901-2000. Black bars denote significant values. The highest values are for temperature 0.30 (January of current year), precipitation -0.49 (July of current year) and sunshine 0.40 (July of current year).

The water in trees originates from soil water and precipitation, and the variations in  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are correlated with corresponding values in tree rings. The correlation coefficient is significant for both pine and oak trees (see **Table 1**).

The highest values of the correlation coefficient between  $\delta^{18}\text{O}$  and temperature were observed for summer months (July and August) in the case of pine and oak from Niepołomice Forest. These values are comparable to results obtained by Switsur *et al.* (1994) for *Quercus robur* L. from United Kingdom in years 1890-1990.

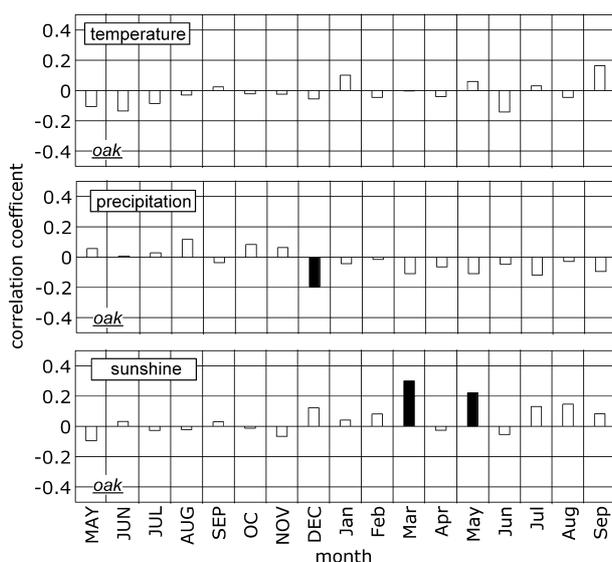
The highest value of the correlation coefficient between  $\delta^2\text{H}$  and temperature in the case of oak is observed for August. Correlation  $\delta^2\text{H}$  with summer temperature was observed by Scheigl (1974) for *Picea* from Germany (1785-1970). In the case of pine,  $\delta^2\text{H}$  values of tree ring cellulose nitrate have the strongest association with tem-

perature of winter months (XII-III). The same relationship was observed by Epstein and Yapp (1976) for various species from Scotland and North America in time span 1841-1970.

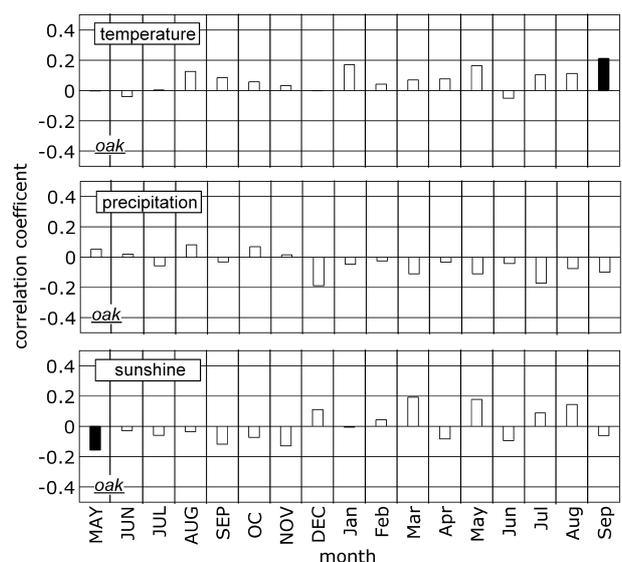
Our investigation prove that hydrogen is the best indicator of summer temperature for oak ( $r = 0.40$ ,  $n=100$ ,  $p<0.05$ ). The same refers to oxygen in the case of pine ( $r = 0.29$ ,  $n=100$ ,  $p<0.05$ ). For both, pine and oak, oxygen is the best indicator of summer precipitation ( $r = -0.49$ ,  $n=100$ ,  $p<0.05$  for oak,  $r = 0.29$ ,  $n=100$ ,  $p<0.05$  for pine). Similarly, oxygen is the best indicator of summer sunshine for pine and oak ( $r = 0.40$ ,  $n=100$ ,  $p<0.05$  for oak,  $r = 0.34$ ,  $n=100$ ,  $p<0.05$  for pine). The correlation between autumn sunshine of previous year and carbon does exist also for pine ( $r = 0.40$ ,  $n=100$ ,  $p<0.05$  for uncorrected  $\delta^{13}\text{C}$ ;  $r = 0.35$ ,  $n=100$ ,  $p<0.05$  for corrected  $\delta^{13}\text{C}$ ).

**Table 2.** The highest significant correlation coefficients between meteorological and isotopic data for pine and oak. The months relate to the current year unless otherwise indicated.

		T (°C)	P (mm)	SH (hours/month)
Pine	$\delta^{13}\text{C}$	-0.26	0.21	0.41
	(‰VPDB)	May of previous year	February	September of previous year
	$\delta^{13}\text{C}_c$	-0.22	0.25	0.35
	(‰VPDB)	May of previous year	February	June
	$\delta^{18}\text{O}$	0.29	-0.31	0.34
(‰VSMOW)	August	July	July	
	$\delta^2\text{H}$	0.23	-0.24	-0.20
	(‰VSMOW)	March	November of previous year	July of previous year
Oak	$\delta^{13}\text{C}$	no significant value	-0.19	0.30
	(‰VPDB)		December of previous year	March
	$\delta^{13}\text{C}_c$	0.21	no significant value	0.16
	(‰VPDB)	September		May of previous year
	$\delta^{18}\text{O}$	0.30	-0.49	0.40
	(‰VSMOW)	January	July	July
	$\delta^2\text{H}$	0.40	-0.17	-0.25
	(‰VSMOW)	August	December of previous year	May



**Fig. 19.** Correlation coefficients between  $\delta^{13}\text{C}$  (before correction) and meteorological data for oak (QRPNF) in years 1901-2000. Black bars denote significant values. The highest values are for precipitation -0.19 (December of previous year) and sunshine 0.30 (March of current year).



**Fig. 20.** Correlation coefficients between  $\delta^{13}\text{C}_c$  (detrended) and meteorological data for oak (QRPNF) in years 1901-2000. Black bars means significant values. The highest values are for temperature 0.21 (September of current year), and sunshine -0.16 (May of previous year).

## ACKNOWLEDGMENTS

This work is a part of EU ISONET project No. EVK2-CT-2002-0014 (400 years of Annual Reconstructions of European Climate Variability using a High Resolution Isotopic Network) and supported by State Committee for Scientific Research special grant for ISONET project SPB-12/RMF-1/2003.

## REFERENCES

- Alexander W.J. and Mitchell R.L., 1949: Rapid measurement of cellulose viscosity by the nitration method. *Analytical Chemistry* 21(12): 1497-1500.
- Biondi F. and Waikul K., 2004: DENDROCLIM2002: A C++ program for statistical calibration of climate signals in tree-ring chronologies. *Computers & Geosciences* 30: 303-311.
- Craig H., 1961: Mass-spectrometer analysis of radiocarbon standards. *American Journal of Science Radiocarbon Supplement* 3: 1-3.
- Epstein S., Yapp C.J. and Hall J.H., 1976: The determination of the D/H ratios of non-exchangeable hydrogen in cellulose extracted from aquatic and land plants. *Earth and Planetary Sciences Letters* 30: 241-251.
- Epstein S. and Yapp C.J., 1976: Climatic implications of the D/H ratio of hydrogen in C-H groups in tree cellulose. *Earth and Planetary Science Letters* 30: 252-261.
- Feng X. and Epstein S., 1995: Carbon isotopes of trees from arid environments and implications for reconstructing atmospheric CO<sub>2</sub> concentrations. *Geochimica et Cosmochimica Acta* 59: 2599-2608.
- Freyer H.D. and Belacy N., 1983: <sup>13</sup>C/<sup>12</sup>C records in Northern Hemispheric trees during the past 500 years- anthropogenic impact and climate superpositions. *Journal of Geophysical Research* 88: 6844-6852.
- Gray J. and Song S.J., 1984: Climatic implications of the natural variations of D/H ratios in tree ring cellulose. *Earth and Planetary Science Letters* 70: 129-138.
- Gray J. and Thompson P., 1976: Climatic information from <sup>18</sup>O/<sup>16</sup>O ratios of cellulose in tree rings. *Nature* 262: 481-482.
- Green J.W., 1963: Wood cellulose. In: Whistler R.L., ed., *Methods in Carbohydrate Chemistry* 3, Academic Press, New York: 9-21.
- Knöller K., Böttger T., Weise S.M. and Gehre M., 2005: Carbon isotope analyses of cellulose using two different on-line techniques (elemental analysis and high-temperature pyrolysis) - a comparison. *Rapid Communications in Mass Spectrometry* 19: 343-348.
- Krapiec M., 1998: Oak dendrochronology of the neoholocene in Poland, *Folia Quaternaria* 69: 5-133.
- Leavitt S.W. and Long A., 1982: Evidence for <sup>13</sup>C/<sup>12</sup>C fractionation between tree leaves and wood. *Nature* 298: 742-743.
- Leavitt S.W. and Long A., 1984: Sampling strategy for stable carbon isotope analysis of tree rings in pine. *Nature* 311: 145-147.
- Leavitt S.W. and Long A., 1989: Intertree variability of δ<sup>13</sup>C in tree rings. In: Rundel P.W., Ehleringer J.R. and Nagy K.A., eds, *Stable isotopes in ecological research*. Springer Verlag, New York: 95-104.
- Leuenberger M., WEB site <<http://www.isonet-online.de/>>
- Libby L.M. and Pandolfi L.J., 1974: Temperature dependence of isotope ratios in tree-rings. *Proceedings of the National Academy of Sciences of the United States of America* 71: 2482-2486.
- Loader N. J., Robertson I., Barker A.C., Switsur V.R. and Waterhouse J.S., 1997: An improved technique for the batch processing of small whole wood samples to α-cellulose. *Chemical Geology* 136: 313-317.
- Long A., 1982: Stable isotopes in tree rings. In: Hughes M.K., Kelly P.M., Pilcher J.R. and LaMarche Jr.V.C., eds, *Climate from Tree Rings*. Cambridge University Press, Cambridge: 13-18.
- McCarroll D. and Loader N.J., 2004: Stable isotopes in tree rings. *Quaternary Science Reviews* 23: 771-801.
- Pazdur A., Korput S., Fogtman M., Szczepanek M., Hałas S., Krapiec M. and Szychowska-Krapiec E., 2005: Carbon-13 in α-cellulose of oak late wood (Jędrzejów, Southern Po land) during the Maunder Minimum. *Geological Quarterly* 49(2): 165-172.
- Pawelczyk S. and Pazdur A., 2004: Carbon isotopic composition of tree rings as tool for biomonitoring CO<sub>2</sub> level. *Radiocarbon* 46(2): 701-719.
- Pawelczyk S., Pazdur A. and Hałas S., 2004: Stable carbon isotopic composition of tree rings from a pine tree from Augustów Wilderness, Poland, as a temperature and local environment conditions indicator. *Isotopes Environmental and Health Studies* 40(2): 145-154.
- Plicher J.R., 1995: Biological considerations in the interpretation of stable isotope ratios in oak tree-rings. In: Frenzel B., ed., *Problems of stable isotopes in tree-rings, lake sediments and peat-bogs as climatic evidence for the Holocene*. Palaoklimaforschung/ Palaeoclimate Research ESF 15: 157-161.
- Ramesh R., Bhattacharya S.K. and Gopalan K., 1986: Climatic correlations in the stable isotope records of silver fir (*Abies pindrow*) trees from Kashmir, India. *Earth and Planetary Science Letters* 79:66-74.
- Robertson I., Rolfe J., Switsur V.R., Carter A.H.C., Hall M.A., Barker A.C., and Waterhouse J.S., 1997: Signal strength and climate relationships in <sup>13</sup>C/<sup>12</sup>C ratios of tree ring cellulose from oak in southwest Finland. *Geophysical Research Letters* 24: 1487-1490.
- Switsur V.R., Waterhouse J.S., Field E.M.F., Carter A.H.C., Hall M., Pollard M., Robertson I., Pilcher J.R. and Heaton T.H.E., 1994: Stable isotope studies of oak from the English Fenland and Northern Ireland. In: Funnell B.M., Kay R.L.F., eds, *Palaeoclimate of the Last Glacial/Interglacial Cycle*. Special publication No. 94/2 of the Earth Sciences Directorate, Natural Environment Research Council, Swindon: 67-73.
- Switsur V.R., Waterhouse J.S., Field E.M., Carter A.H.C. and Loader N.J., 1995: Stable isotope studies in tree rings from oak - techniques and some preliminary results. *Palaoklimaforschung* 15: 129-140.
- Szarek-Lukaszewska G., Grodzińska K. and Braniewski S., 2002: Heavy metal concentration in the moss *Pleurozium schreberi* in the Niepolomice Forest, Poland: changes during 20 years. *Environmental Monitoring and Assessment* 79(3): 231-237.
- Szychowska-Krapiec E. and Krapiec M., 2002: Kondycja drzewostanów sosnowych w Ojcowskim Parku Narodowym w świetle analizy dendroekologicznej (Health of pine forests from the Ojców National Park in the light of dendrochronological studies) *Chrońmy Przyrodę Ojczystą* 58(5): 5-22 (in Polish).
- Tans P.P. and Mook W.G., 1980: Past atmospheric CO<sub>2</sub> levels and <sup>13</sup>C/<sup>12</sup>C ratios in tree rings. *Tellus* 32: 268-283.
- Wilczyński S., 1999: *Dendroklimatologia sosny zwyczajnej (Pine) z wybranych stanowisk w Polsce. Rozprawa doktorska (Dendroclimatology of Scots pine (Pine) from selected sites in Poland. PhD Thesis)*. AR Kraków. WEB site: <<http://nauka-polska.pl/raporty/opisy/synaba/76000/sn76369.htm>>. 85 pp. (in Polish).
- Yapp C.J. and Epstein S., 1982: Climatic significance of the hydrogen isotope ratios in tree cellulose. *Nature* 297: 636-639.
- Zielski A., 1997: *Uwarunkowania środowiskowe przyrostów radialnych sosny zwyczajnej (Pinus sylvestris L.) w Polsce północnej na podstawie wielowiekowej chronologii Rozprawa habilitacyjna. (Environmental conditions of radial growth of Pinus sylvestris from North Poland on the basis of long time chronology. Dissertation)*. UMK Toruń. WEB site: <<http://bazy.opi.org.pl/raporty/opisy/synaba/73000/sn73431.htm>> 127 pp. (in Polish).