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Climatic sensitivity of $\delta^{13}\text{C}$ in tree rings of *Quercus robur* L., *Populus tremula* L. and *Pinus sylvestris* L. in Vilnius region (eastern Lithuania)

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Abstract: The aim of this work was to evaluate the possibilities of using carbon isotope measurements to determine a strong climate signal of trees influenced by the pollutant stress as well as to examine the difference in reaction of several investigated species to the climate change. Eurasian aspen (*Populus tremula*), pedunculate oak (*Quercus robur*) and Scots pine (*Pinus sylvestris*) trees from Vilnius region were selected for the stable carbon isotope analysis. Our results showed that over the last 70 years (1940–2009) the climate during summer months was the most important factor for the variation of stable carbon isotope values in tree rings, but its influence on different tree species slightly differed. $\delta^{13}\text{C}$ measurements in Eurasian aspen best corresponded to the air temperature and the precipitation signal in July–August. Oak was more sensitive to the temperature and relative humidity in June–July. A positive correlation coefficient with temperature in the period of transition from the previous vegetation to dormancy season (previous September–October) was specific to oak as well. Scots pine grown at a polluted site was sensitive only to precipitation in summer months of the growing season. The correlation between $\delta^{13}\text{C}$ measurements and climate data was determined to be from low to moderate in all the investigated trees and did not exceed the value of $|r| \geq 0.71$ suggested by McCarroll et al. (2003) as a necessary value for the reliable climate reconstruction. However, the highest correlation coefficient values of 0.65 and 0.61, obtained between the maximal air temperature throughout the hydrological year (previous September–current August) and $\delta^{13}\text{C}$ in oak rings or between mean monthly sunshine hours throughout July–August and $\delta^{13}\text{C}$ values in aspen rings, respectively, are comparable with those used in many palaeoclimatic reconstructions that were based even on weaker correlations.

Keywords: $\delta^{13}\text{C}$, climate, tree-rings, dendroclimatology

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Introduction

Measurements of the stable carbon, oxygen and hydrogen isotope ratio exhibit a statistically significant relationship with environmental variables such as temperature, precipitation, drought, sunshine, cloud cover (Gori et al., 2013; Hiltunen & Berninger, 2010; Loader et al., 2008; McCarroll et al., 2003; Treydte et al., 2007; Young et al., 2012). The mechanisms responsible for the isotope fractionation in tree rings are fairly well-known (Farquhar et al., 1982; Gessler et al., 2014; McCarroll & Loader, 2004; Waterhouse et al., 2004). The main part of isotopic data was obtained from the trees growing in remote, climatically extreme and sparsely populated areas, e.g. boreal forests mostly of Northern Scandinavia (bulk of them were published by scientists of Swansea University: N.J. Loader, D. McCarroll, M. Gagen, G.H.F. Young), high latitude locations in European Alps (Gori et al., 2013), western South and North America and Southern Europe (Ferrio & Voltas, 2005; Johnstone et al., 2013). There are no so many publications on stable isotope ratio measurements in tree-rings from the East European and former Soviet Union countries. Only in the last ten years publications dealing with correlations between climatic data and tree-ring measurements in Siberia appeared (Knorre et al., 2010; Loader et al., 2010; Saurer et al., 2004; Sidorova et al., 2012).

There is considerably less information about the tree-ring response to climatic changes in temperate and densely populated areas, even from Western Europe areas where instrumental climatic records extend to the 18th century. Although strong correlations between isotopic and instrumental data from temperate areas such as Britain (Loader et al., 2003; Loader et al., 2008; Robertson et al., 1997b), Northern France (Etien et al., 2009), Southern Finland (Hiltunen & Berninger, 2010) and Swiss Central Plateau (Saurer et al., 2008) were evaluated, and only one publication concerning the climate reconstruction of the site neither strongly limited by temperature nor precipitation (temperature in Central England) (Young et al., 2012) was found.

In this work trees belonging to three different species groups, i.e., coniferous Scots pine (*Pinus sylvestris* L.), temperate broadleaved pedunculate oak (*Quercus robur* L.) and hardy broadleaved Eurasian aspen (*Populus tremula* L.), from Vilnius region were selected for the carbon stable isotope analysis. As the

influence of anthropogenic pollution on the tree ring isotope ratio was observed in earlier works (Rinne et al., 2010; Savard, 2010; Wagner & Wagner, 2006), the rural-urban fringe sites for tree samples were selected to check the possibility of using trees growing under these conditions to observe significant correlations with climate parameters.

Pine and oak were selected as widespread and long-living trees. They are the most common species used in dendroclimatology. Aspen was chosen as it is a very hardy species with its distribution ranging north of the Arctic Circle, prefers the moist sites and could reveal the influence of precipitation and relative humidity on the isotope ratio in tree-rings that are rarely stressed by lack of moisture.

Pine was sampled in the forested territory situated about 10 kilometers from the city center near the pollution source because conifers are less influenced by temperature or relative humidity than broadleaf trees as differences in morphology of needles and leaves determine different evaporating cooling systems (Warren et al., 2001), but they are very sensitive to SO₂ pollution (Ozolincius et al., 2005).

The aim of this study was a) to examine the difference in response of all investigated species to changes in precipitation (humidity) and temperature; b) to evaluate the potential of using $\delta^{13}\text{C}$ measurements for climate reconstructions in rings of trees influenced by pollutant stress; c) to complement the current research gap in high-resolution palaeoclimatology using stable isotopes in tree rings in the temperate region.

Materials and Methods

All climate data for correlation analysis were provided by the Lithuanian Hydrometeorological Service under the Ministry of Environment.

Study area

Trees for the stable carbon isotope analysis were sampled in three different places in Vilnius surroundings, eastern Lithuania. All three sampling sites are located at the distance of no more than 40 km from each other. Meteorological data of the years 1940–2009, habitat description according to the EU-NIS Habitat Classification (Davies et al., 2004) and location coordinates are presented in Table 1. The tree samples were taken at 0.4–0.7 m height.

Table 1. Geography, meteorological data (mean for 1945–2009) and habitat types

| | Habitat code | Latitude (N) | Longitude (S) | Altitude (m) | Annual mean T (°C) | Mean T (°C) of vegetation period | Annual rainfall (mm) | Rainfall of vegetation period (mm) |
|-------|--------------|--------------|---------------|--------------|--------------------|----------------------------------|----------------------|------------------------------------|
| Aspen | G4.4 | 54°42'21.06" | 25°34'26.99" | 159 | | | | |
| Oak | G1.A | 54°58'43.33" | 25°10'54.35" | 141 | 6.4 | 15.7 | 665 | 292 |
| Pine | G3.4 | 54°38'39.43" | 25°11'3.37" | 169 | | | | |

Tree ring series

The samples of felled trees were collected in 2010 and 2013 but the exact dating of tree death was known only for aspen. In order to obtain calendrically dated tree rings for $\delta^{13}\text{C}$ measurements the ring series of the collected tree samples were analyzed using dendrochronological techniques. The tree ring width series were built by measuring every ring on the cross-sections of the stem discs along two radii from the pith to the bark. For the determination of tree ring boundaries the surface of the cross-sections was cut with the razor blade. The measurement was carried out by using the semi-automatic tree-ring measurement stage made in the Sheffield University (accuracy ≤ 0.01 mm). Measured ring width series were processed with the *Dendro* software package. Radial ring series were verified for double and missing rings; an average ring with series was built for every tree and dated against dated chronologies of the same species. Cross-dating between the series and calendrical dating was based on statistical tests and visual cross-matching. The *t*-test according to Baillie and Pilcher (1973) was used as a statistical test for cross matching of tree ring series.

Only the aspen tree had the last ring formed in the year of sampling. The obtained aspen tree ring series consisted of 68 annual rings and covered the period of 1943–2010.

The dating of tree ring series of the oak was established by synchronizing it against several living oak chronologies from different regions of Lithuania (Kairaitis, 1978). The obtained tree ring series consisted of 72 annual rings and covered the period of 1923–2005.

The pine also showed a suppressed growth at the end of its life. The last rings were very narrow or missing. The tree ring series were dated against living pine tree chronologies from Lithuania. The latest distinguishable ring was formed in 1985. The tree ring series of pine consisted of 97 annual rings and covered the period of 1889–1985.

$\delta^{13}\text{C}$ measurements

The $^{13}\text{C}/^{12}\text{C}$ isotope ratios were analyzed separately for each single tree. Since earlywood $\delta^{13}\text{C}$ values are influenced by the climate of the previous year (McCarroll & Loader, 2004), only wood from latewood samples was used for isotope ratio measurements. The latewood rings were cut with a scalpel for each tree disc and then were ground in a centrifugal mill.

As the *Populus tremula* presented very narrow rings with indistinguishable latewood bands, the whole annual ring was used in isotopic measurements.

The first 30 years were excluded because of the influence of the juvenile effect (Gagen et al., 2008; McCarroll & Loader, 2004).

The analysis of cellulose as the dominant and most easily isolated component of wood has been performed in most studies since 1977 when Wilson and Grinsted (1977) showed that different component of wood has different isotope values. The main problem of using either the whole wood or its components such as cellulose or lignin is the differential degradation of wood components. Lignin and cellulose have different $\delta^{13}\text{C}$ values. The isotopic difference of cellulose and lignin relative to the whole wood is approximately 1‰ and –2‰, respectively (Loader et al., 2003). If there are variations in the cellulose to lignin ratio that are related to degradation, this may influence the $\delta^{13}\text{C}$ value of the whole wood. Thus, for using samples of sub-fossil trees, cellulose extraction is necessary. We chose analysis of the whole wood as several authors have obtained better results using the whole wood. Loader et al. (2003) found that $\delta^{13}\text{C}$ values of cellulose in tree-ring of oaks grown in East England was more strongly correlated with climate variables than that of lignin, but the strongest correlations were obtained using the whole wood. Gori et al. (2013) stated that extraction of cellulose and lignin for *Picea abies* grown in the southern Alpine region was not necessary. The same conclusion was made by Ferrio and Voltas (2005) for *Pinus halepensis* grown in the East Iberian Peninsula.

The dry latewood sample of 0.5–0.8 mg from each annual ring was weighed into the tin foil cups and combusted over chromium (III) oxide at 1020°C. Combustion and isotope ratio measurements were performed using a Thermo Scientific Delta V Advantage mass spectrometer coupled to a Flash EA 1112 elemental analyzer. The ratio of $^{13}\text{C}/^{12}\text{C}$ is expressed in delta (δ) notation with reference to a standard material for which the isotope ratio is known. The carbon isotope ratio is expressed, in parts per thousand (‰), as

$$\delta^{13}\text{C} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3 \quad (1)$$

where R_{sample} and R_{standard} are $^{13}\text{C}/^{12}\text{C}$ ratios in a sample and standard, respectively. The IAEA-600 and IAEA-CH-3 standards from the International Atomic Energy Agency (Vienna) with known $^{13}\text{C}/^{12}\text{C}$ ratios were used. Repeated analyses of homogeneous standard material yielded standard deviations of less than 0.08‰.

Data treatment

$\delta^{13}\text{C}$ values in tree rings depend on diffusion and biochemical processes during photosynthetic CO_2 assimilation. Trees take CO_2 via leaf stomata, through

which water is lost during transpiration. $\delta^{13}\text{C}$ values of newly assimilated C_3 plant organic matter can be described as (Farquhar et al., 1982):

$$\delta^{13}\text{C}_{\text{plant}} = \delta^{13}\text{C}_{\text{atm}} - a - (b-a)ci/ca \quad (2)$$

where $\delta^{13}\text{C}_{\text{atm}} = -8.1\text{‰}$ is the isotopic ratio of atmospheric CO_2 , a (4.4‰) and b (28‰) are constants representing fractionation due to diffusion and carboxylation, ci and ca are intercellular and atmospheric CO_2 concentrations, respectively. As can be seen from Eq. (2), the only non-constant factors that control $\delta^{13}\text{C}$ of tree rings are intercellular and ambient concentrations of CO_2 . The concentration of CO_2 within the leaf is balanced by the rate at which CO_2 enters, that is controlled by the stomatal conductance, and the rate at which carbon is incorporated into carbohydrate, that is controlled by the photosynthetic rate. If ca is stable, an increase in the ring $\delta^{13}\text{C}$ value shows a reduction in the stomatal conductance, an increase in the photosynthetic rate or some combination of these two.

The meteorological parameters that could be reconstructed from tree-ring $\delta^{13}\text{C}$ measurements are those which influence the stomatal conductance and the photosynthetic rate. In dry environments or for shallow rooted trees growing in well drained soils, the stomatal conductance will be dominating, and a strong correlation of $\delta^{13}\text{C}$ with the air relative humidity and antecedent precipitation will be observed. In moist environments, or where the trees are rarely moisture stressed, the photosynthetic rate will dominate and a high correlation with sunlight and temperature will be observed.

The isotopic composition of atmospheric CO_2 ($\delta^{13}\text{C}_{\text{atm}}$) has changed as a consequence of industrialization. The value of the isotopic ratio of carboxylation products, including tree rings, has declined. Thus, for all our measured tree samples $\delta^{13}\text{C}$ values were corrected to the pre-industrial $\delta^{13}\text{C}_{\text{atm}}$ value of -6.4‰ using:

$$\delta^{13}\text{C}_{\text{cor}} = \delta^{13}\text{C}_{\text{plant}} - (\delta^{13}\text{C}_{\text{atm}} + 6.4). \quad (3)$$

McCarroll et al. (2009) proposed the so called preindustrial 'pin' correction procedure to calculate $\delta^{13}\text{C}$ value changes related with the physiological response of trees to the increased atmospheric CO_2 concentration. This procedure improves the value of the correlation coefficient r between $\delta^{13}\text{C}$ measurements and climate parameter data by > 0.1 .

The intercellular CO_2 level is related to the intrinsic water-use efficiency (iWUE), the ratio of the assimilation rate (A) to leaf conductance to water vapour (g_w) is related to the stomatal conductance to CO_2 (g_s), as $g_w = 1.6 g_s$. According to the Fick's law, the assimilation rate could be calculated as $A = g_s(ca-ci)$. The increased

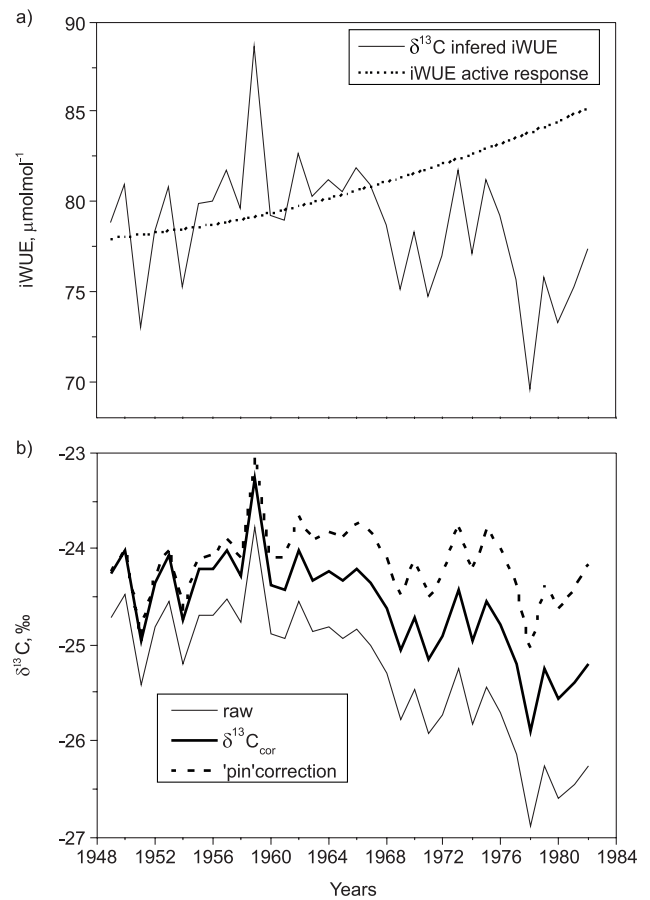


Fig. 1. a) Active response and measured response from iWUE; b) The $\delta^{13}\text{C}$ values in tree rings of *Quercus robur* L.

atmospheric CO_2 concentration (ca) affects the value of $\delta^{13}\text{C}_{\text{plant}}$. Trees use a strong stomatal control to limit the changes in ci because of the rise in ca . In case of the active response, iWUE increases with raising ca to keep the ci/ca ratio nearly constant. Trees are adapted to react to the increased ca level. The response of g_s to the increased CO_2 level might depend on the tree species and conditions of water stress at the leaf level.

Preindustrial 'pin' correction was applied to $\delta^{13}\text{C}$ measurements in tree-rings of *Quercus robur* tree. As

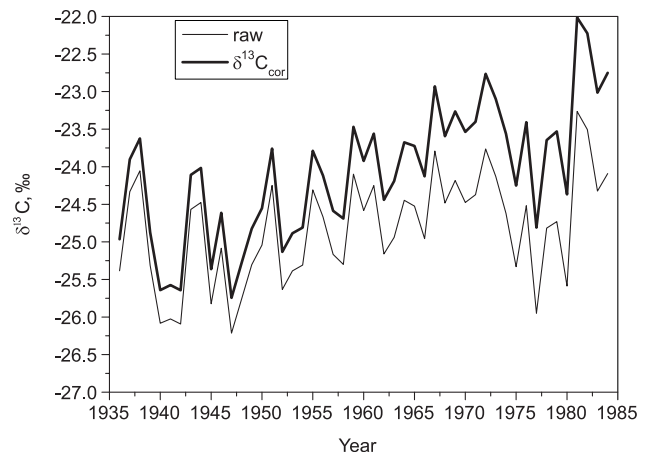


Fig. 2. The $\delta^{13}\text{C}$ values in tree rings of *Pinus sylvestris* L.

seen in Fig. 1, the switch to the passive response for oak occurred in the late 1960s. For aspen, a decline in $\delta^{13}\text{C}$, which is typical of the passive response, was not observed probably because of a too short measurement period of only 40 years from 1973 to 2009. Thus, 'pin' correction was not done, even taking into account that the atmospheric CO_2 concentration after the 1980s could exceed the critical CO_2 value for the switch to the passive response (Masson-Delmotte et al., 2005; McCarroll & Loader, 2004).

Preindustrial 'pin' correction was not performed for pine tree as the observed increase in $\delta^{13}\text{C}$ values was not typical of the switch to the passive response (Fig. 2).

Results

The $\delta^{13}\text{C}$ measurement data in tree-rings of oak (from 1948 to 1984), pine (from 1935 to 1984) and aspen (from 1973 to 2009) were correlated to monthly values of temperature, precipitation and

relative humidity at annual resolution. Correlation coefficients are presented in Table 2. The analysis was conducted for individual months of the current and previous years and their combinations. The correlation with sunshine hours was made only for aspen. Unfortunately, it was impossible to provide correlations of this parameter (or cloud cover, which highly correlates with sunshine hours) and $\delta^{13}\text{C}$ measurements for the other investigated tree species because of lack of the instrumental data before 1977.

As aspen is a shade-intolerant species, thus $\delta^{13}\text{C}$ measurements in its rings exhibited the highest sensitivity to mean monthly sunshine hours ($r = 0.61$, $p < 0.001$ for July–August). Aspen exhibited the highest sensitivity to moisture stress in summer months among all the investigated species ($r = -0.54$, $p < 0.001$ for precipitation and $r = -0.58$, $p < 0.001$ for relative humidity in July–August). A significant positive correlation of $\delta^{13}\text{C}$ with the relative humidity in May ($r = +0.43$, $p < 0.01$) was also observed (Table 2).

Table 2. Pearson's correlation coefficients describing the statistical relationship between the maximal monthly average temperature (Max temperature), precipitation, relative humidity, sunshine duration and $\delta^{13}\text{C}$ measurements in *Populus tremula* L.; *Pinus sylvestris* L.; *Quercus robur* L. Hydrological year (HDyear) includes October of the previous year – September of the growing year. Significant values are indicated with asterisks

| Months | Max temperature | | | Precipitation | | | Relative humidity | | | Sunshine duration |
|-------------|-----------------|--------|-------|---------------|-------|---------|-------------------|---------|--------|-------------------|
| | Aspen | Oak | Pine | Aspen | Oak | Pine | Aspen | Oak | Pine | Aspen |
| pr_9 | 0.07 | 0.43** | -0.23 | 0.09 | -0.16 | -0.18 | 0.22 | -0.08 | 0.06 | -0.17 |
| pr_10 | -0.09 | 0.50* | 0.16 | 0.07 | -0.09 | 0.27 | 0.14 | -0.07 | 0.46** | -0.12 |
| pr_11 | -0.09 | 0.11 | 0.00 | 0.31* | -0.03 | 0.29 | 0.01 | -0.18 | 0.15 | 0.14 |
| pr_12 | 0.00 | 0.19 | 0.00 | 0.06 | -0.01 | 0.31* | 0.09 | -0.20 | 0.27 | -0.01 |
| 1 | 0.20 | 0.32* | 0.11 | 0.07 | 0.15 | 0.08 | 0.10 | -0.04 | 0.05 | 0.19 |
| 2 | 0.28 | 0.26 | 0.18 | 0.29 | 0.34* | -0.27 | 0.27 | 0.18 | 0.04 | -0.22 |
| 3 | 0.31 | 0.14 | 0.27 | 0.20 | -0.02 | 0.10 | 0.27 | -0.12 | -0.06 | -0.29 |
| 4 | -0.19 | 0.34* | -0.07 | 0.12 | 0.14 | -0.11 | 0.14 | 0.07 | -0.09 | -0.18 |
| 5 | -0.07 | 0.19 | 0.03 | -0.09 | 0.33* | 0.06 | 0.43 | 0.26 | 0.18 | 0.06 |
| 6 | 0.27 | 0.27 | -0.26 | 0.11 | 0.06 | -0.08 | -0.01 | -0.23 | 0.25 | 0.20 |
| 7 | 0.32* | 0.46** | -0.23 | -0.49** | -0.19 | -0.31* | -0.49** | -0.49** | -0.02 | 0.55** |
| 8 | 0.33* | 0.26 | -0.07 | -0.33* | 0.15 | -0.36* | -0.52** | -0.06 | -0.33* | 0.39* |
| 9 | 0.18 | 0.24 | -0.11 | -0.01 | -0.03 | -0.10 | -0.07 | -0.19 | 0.06 | 0.04 |
| 10 | -0.31* | 0.41** | 0.09 | -0.10 | -0.17 | -0.02 | 0.04 | -0.23 | 0.18 | -0.17 |
| Annual | 0.21 | 0.51** | -0.04 | -0.34* | 0.10 | -0.26 | -0.02 | -0.25 | 0.19 | 0.21 |
| Mean2/3 | 0.33* | 0.23 | 0.26 | 0.33* | 0.20 | -0.10 | 0.36* | 0.04 | -0.02 | -0.35* |
| Mean3/4 | 0.10 | 0.31* | 0.14 | 0.21 | 0.10 | -0.02 | 0.23 | -0.02 | -0.09 | -0.30 |
| Mean4/5 | -0.16 | 0.38* | -0.02 | 0.01 | 0.34* | 0.00 | 0.35* | 0.21 | 0.04 | -0.08 |
| Mean5/6 | 0.09 | 0.27 | -0.13 | 0.04 | 0.29 | -0.01 | 0.25 | 0.03 | 0.29 | 0.16 |
| Mean6/7 | 0.39* | 0.48** | -0.30 | -0.34* | -0.13 | -0.30 | -0.36* | -0.49** | 0.15 | 0.50** |
| Mean7/8 | 0.37* | 0.42** | -0.18 | -0.54** | -0.04 | -0.41** | -0.58** | -0.32* | -0.21 | 0.61** |
| Mean8/9 | 0.30 | 0.30 | -0.09 | -0.28 | 0.09 | -0.33* | -0.35* | -0.13 | -0.19 | 0.26 |
| Mean9/10 | -0.07 | 0.37* | -0.02 | -0.08 | -0.14 | -0.09 | -0.02 | -0.26 | 0.15 | -0.08 |
| Mean5/6/7 | 0.25 | 0.42** | -0.20 | -0.36* | 0.06 | -0.22 | -0.16 | -0.28 | 0.21 | 0.42** |
| Mean6/7/8 | 0.42** | 0.47** | -0.26 | -0.45** | -0.01 | -0.39* | -0.49** | -0.36* | -0.05 | 0.57** |
| Mean7/8/9 | 0.35* | 0.43** | -0.16 | -0.54** | -0.04 | -0.41** | -0.49** | -0.32* | -0.15 | 0.49** |
| Mean6/7/8/9 | 0.40* | 0.48** | -0.23 | -0.47* | -0.02 | -0.41** | -0.43** | -0.37** | -0.02 | 0.49** |
| HDyear | 0.24 | 0.65** | -0.09 | -0.14 | 0.11 | -0.20 | 0.07 | -0.19 | 0.16 | 0.15 |

* $p < 0.05$; ** $p < 0.01$.

Scots pine did not exhibit sensitivity to the growing year summer temperature showing sensitivity only to the precipitation amount in July–August ($r = -0.41$, $p < 0.01$).

$\delta^{13}\text{C}$ measurement in *Q. robur* showed the highest correlation values with the growing season maximal temperature ($r = 0.46$, $p < 0.005$). Significant correlations of $\delta^{13}\text{C}$ measurements in oak rings with temperature in September–October of the previous year ($r = 0.5$, $p < 0.05$) and with the hydrological year temperature ($r = 0.65$, $p < 0.001$) were also observed. Contrary to the isotopic measurements in pine and aspen rings, $\delta^{13}\text{C}$ data of oak at this site did not significantly correlate with the summer precipitation amount but were sensitive to the relative humidity in summer months, especially in July ($r = -0.49$, $p < 0.005$). Besides, oak like aspen exhibited sensitivity to the moisture stress in May, as a weak positive correlation of $r = 0.33$ ($p < 0.05$) was observed with the precipitation amount in May (Table 2).

Discussion

As it was expected from the other studies concerning data from the temporal region, the most significant correlations between $\delta^{13}\text{C}$ measurements in tree rings and climatic data were determined in summer of the growing season for all three species. Positive correlation coefficients with temperature and negative coefficients with precipitation and relative humidity (Table 2) were observed.

The exception was Scots pine as it did not exhibit sensitivity to the growing year summer temperature in our study (Table 2), only showing sensitivity to the precipitation amount in July–August of the growing year. This is not in agreement with Treydte et al. (2007), where results from 23 European sites were presented. In this publication it was shown that the correlation coefficients between $\delta^{13}\text{C}$ measurements in Lithuanian pines from a rural site (Panemune pinewood) and climate parameters, especially July–August temperature ($r = 0.48$, $p < 0.01$), were among the highest. A more significant correlation coefficient of $\delta^{13}\text{C}$ measurements and temperature ($r > 0.6$) among all the investigated European sites was observed only in Northern Finland, where temperature was the main limiting factor of the tree growth. However, correlation coefficient values of $\delta^{13}\text{C}$ in tree-rings with July–August precipitation in Vilnius ($r = -0.42$, $p < 0.01$) (our study) and in Panemune pinewood ($r = -0.43$, $p < 0.01$) were very similar.

We observed the increasing trend of $\delta^{13}\text{C}$ values in Scots pine. The increase of $\delta^{13}\text{C}$, meaning a reduction in *ci/ca*, can be caused by either a reduction in the stomatal conductance (at a constant photosynthetic

rate) or the increased photosynthetic rate at unchanged or even increased stomatal conductance (Guerrieri et al., 2009; Savard, 2010). As the pine was sampled at the polluted urban site, we consider that this trend could be a consequence of reduction in the stomatal conductance caused by pollution stress (Fig. 2). Such trends in trees from polluted sites were observed by the other authors (Rinne et al., 2010; Savard, 2010; Wagner & Wagner, 2006). Typical short-term variations of $\delta^{13}\text{C}$ in trees from unpolluted sites are $\sim 0.5\text{‰}$, whereas at polluted sites, where the SO_2 concentration reaches the critical concentration limit of $20\text{--}25 \mu\text{g}/\text{m}^3$ or near highways with increased NO_x and NH_3 concentrations (Guerrieri et al., 2009), positive shifts in $\delta^{13}\text{C}$ values can exceed $+3\text{‰}$ in comparison to mean stable isotope values of rings grown during the clean periods (Savard, 2010).

In September 1951 at a distance of 4.5 kilometres from the pine growing place Vilnius Heat Plant began operating. The power plant was heated by heavy fuel oil and partially by peat. Furthermore, in 1977, a local boiler-house using heavy fuel oil at a distance of about 300 meters from the pine began operating. Unfortunately, there are no data of SO_2 or NO_x concentrations in Vilnius during the period of 1935–1990, but with reference to Perkauskas and Mikeliniskiene (1998), SO_2 concentration levels in Vilnius had exceeded $23 \mu\text{g}/\text{m}^3$ during the 1995/96 winter season. The SO_2 concentration value of $20\text{--}25 \mu\text{g}/\text{m}^3$ was determined as the critical concentration limit, below which a significant harmful effect on forest ecosystems does not occur (Rinne et al., 2010). During 1950–1990, before the reduction in the sulphur content in fuels was set, the SO_2 concentration value of $20\text{--}25 \mu\text{g}/\text{m}^3$ had to be achieved near the pine growing site, in the close vicinity of these two local pollutant sources.

To confirm that pollution was the cause of the increasing $\delta^{13}\text{C}$ trend, the $\delta^{18}\text{O}$ measurements in tree rings are necessary because the stomatal closure has a lower effect on $\delta^{18}\text{O}$ than on $\delta^{13}\text{C}$ values (Guerrieri et al., 2009; Rinne et al., 2010; Savard, 2010; Wagner & Wagner, 2006). This can be explained by the isotopic equilibration between the leaf sucrose and xylem water during cellulose and/or lignin synthesis (McCarroll & Loader, 2004; Rinne et al., 2010). During this process about a half of produced sucrose oxygen is exchanged with oxygen of xylem water (Rinne et al., 2010). Thus, changes in $\delta^{18}\text{O}$ trends caused by the reduction in stomatal closure are less pronounced.

As it was mentioned above, preindustrial ‘pin’ correction was not performed for pine as the industrial pollution causes stomatal aperture changes and leaf injury, thus affecting changes in photosynthesis. The switch to the passive response could be hidden by the growing $\delta^{13}\text{C}$ trend. As it was mentioned above, trees

are able to keep the ci/ca ratio nearly constant at a limiting ca value. It was established that this limiting ca value for *Pinus sylvestris* was $355 \mu\text{mol mol}^{-1}$ (Waterhouse et al., 2004). In remote Fennoscandia boreal forests a tendency of the stopped rise of $iWUE$ in conifers from the mid-1970s was observed (Gagen et al., 2011; McCarroll et al., 2009). Whereas in Idaho, USA, the value of $ca-ci$ remained constant from the 20s of the past century for various pine and fir species (Marshall & Monserud, 1996). The limiting ca value of $340 \mu\text{mol mol}^{-1}$ for *Quercus robur* is very similar as for the pine (Beerling et al., 1996). The switch to the passive response for oak occurred in the late 1960s (Fig. 1.), during the same period as in the remote area in West Wales, UK (Young et al., 2012).

Robertson et al. (1997b) showed high correlation values of $\delta^{13}\text{C}$ measurements in *Q. robur* tree rings from dry and moist sites of East England with July–August temperature ($r = 0.72$, and $r = 0.57$, $p < 0.01$, respectively); in this case high-frequency filtering was used. Loader et al. (2008) demonstrated high temperature data correlation values ($r = 0.64$) with combined stable carbon and oxygen isotope measurements in *Q. robur* from Southern Scotland. In eastern Lithuania the temperature signal of summer months (June–July) in oak rings is weaker, similar to that in Southern Finland ($r = 0.45$ and $r = 0.42$, $p < 0.01$, Robertson et al. (1997a) and Hiltavuori et al. (2010), respectively). Our *Q. robur* samples were taken from a rather wet site. That could be the reason why $\delta^{13}\text{C}$ measurements in tree rings did not significantly correlate with precipitation data (Table 2) but significantly correlated with relative humidity. However, Robertson et al. (1997a, 1997b) showed that both relative humidity and precipitation had the similar impact on the growth of *Q. robur*, no matter whether the trees were sampled at dry or wet sites. Correlation coefficient values at both wet and dry sites were very similar. Measurements were performed in trees from East England and Southern Finland.

$\delta^{13}\text{C}$ measurement data indicated that the moisture regime was more important than temperature for the growth of oak in Southern Finland (Robertson et al., 1997a; Hiltavuori et al., 2010). Southern Finland is the northern distribution limit for *Q. robur*, but a similar tendency was observed in Eastern (Robertson et al., 1997b) and Central England, North-western France (Treydte et al., 2007). No significant correlations were observed between climate parameters and $\delta^{13}\text{C}$ measurements in trees from Southern Scotland and Southern Poland (Treydte et al., 2007).

Our measurements revealed that moisture was important in July of the growing season, but temperature influenced different physiological growing stages of oaks (Table 2), as a significant correlation of $\delta^{13}\text{C}$ in oak tree rings with hydrological year temperature ($r = 0.65$, $p < 0.001$) was determined.

Aspen was sampled at a wet, poorly drained site, but it exhibited the highest sensitivity to the moisture stress in summer months among all the investigated species. These results were not unexpected as they coincided with those in Mackay et al. (2003), where it was established that, among a number of forest tree species, aspens showed the maximum stomatal sensitivity to the moisture stress.

Nevertheless, the obtained correlation coefficients between $\delta^{13}\text{C}$ measurements in the chosen tree species and climate data did not exceed the value of $|r| \geq 0.71$ suggested by McCarroll (McCarroll et al., 2003; McCarroll & Loader, 2004) for the reliable climate reconstruction.

Conclusions

Three investigated tree species, i.e., hardy coniferous *P. sylvestris*, hardy broadleaved *P. tremula* and temperate broadleaved *Q. robur* showed the highest correlation coefficient values of stable isotope measurements with climate data in summer months: positive with the maximal temperature and negative with the relative humidity and precipitation.

The determined $\delta^{13}\text{C}$ data of both deep rooted and broadleaved trees *P. tremula* and *Q. robur* additionally exhibited a significant positive correlation with moisture in May of the growing season, which is the time of foliage formation. $\delta^{13}\text{C}$ measurements in *Q. robur* revealed that temperature not only of the growing season but also of the previous season was more important than moisture for the growth of oak, contradicting data from the various European regions, where it was observed stronger moisture not temperature impact to the tree growth. Isotopic data of *P. tremula* also exhibited the highest stomatal sensitivity among all the investigated species to low vapor pressure deficit conditions. $\delta^{13}\text{C}$ measurements in *P. sylvestris* did not significantly correlate with temperature, showing sensitivity only to the precipitation amount in summer months. As the tree was growing at a polluted site, the pollution impact on decreased transpiration could be the reason for the observed increase of $\delta^{13}\text{C}$ values in tree ring measurements.

Correlation between $\delta^{13}\text{C}$ measurements in all trees and climate data was from low to moderate in all the investigated trees, thus we suggest testing the other isotopes such as oxygen, and hydrogen or their combination with carbon as this could provide a better sensitivity to climate changes.

Stable carbon and oxygen isotope ratio measurements in tree rings are very useful for identification of the periods when trees were exposed to potentially phytotoxic pollutants, whereas the increases in $\delta^{13}\text{C}$ values are systematically observed, although $\delta^{13}\text{O}$ values do not shift distinctly or even remain unchanged.

Usually, these period $\delta^{13}\text{C}$ data remains unanalyzed. For the future climate change studies we recommend to check the possibility to use $\delta^{13}\text{C}$ values of those periods to study climate induced signals in tree rings after the mathematical corrections of the $\delta^{13}\text{C}$ trend according to $\delta^{18}\text{O}$ trend were done.

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