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ANTHROPOGENIC CO_2 EMISSION RECORDS IN SCOTS PINE GROWING IN THE MOST INDUSTRIALIZED REGION OF POLAND FROM 1975 TO 2014

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ABSTRACT. Stable carbon isotope ratios and radiocarbon (^{14}C) concentrations in samples of pine wood (AD 1975–2012) from 3 sites, as well as needles (AD 2012–2014) collected from 15 sites, in a heavily urbanized area in proximity to heavy industrial factories in Poland were analyzed as bio-indicators of CO_2 emissions. The sampling sites were located at different distances from point sources. The stable isotopic composition was determined using an isotope ratio mass spectrometer, and the ^{14}C concentration was determined using a liquid scintillation counter and an accelerator mass spectrometer. Spatial and temporal variability of $\delta^{13}C$ and $\Delta^{14}C$ in tree ring cellulose and needles was noted in all regions. A negative correlation between $\delta^{13}C$ tree ring cellulose and anthropogenic CO_2 emissions has been observed. The ratio of $\delta^{13}C$ in tree ring cellulose to $\delta^{13}C$ in needles created in the same year is equal to 1.2 at the investigated sites.

KEYWORDS: CO_2 emission, forests, industrial region, radiocarbon, stable isotopes.

INTRODUCTION

During the last centuries, the carbon isotopic composition of the atmosphere and biosphere has been modified due to fossil fuel (e.g., coal, petroleum, natural gas) combustion in industrial areas (Martin et al. 1988; Farquhar and Lloyd 1993; Vitousek et al. 1997; Choi et al. 2005; McCarroll et al. 2009; Levin et al. 2010; Pazdur et al. 2013; Sensuła and Pazdur 2013a; Boden et al. 2016). CO_2 from fossil fuels is devoid of any ^{14}C (Suess 1955). Also a progressive lowering of ^{13}C in the air and thus in the biosphere is associated with the emission of ^{13}C-depleted CO_2 into the atmosphere from fossil fuel (Craig 1954; Farquhar and Lloyd 1993; McCarroll and Loader 2004; Pazdur et al. 2007, 2013; Keeling et al. 2010; Sensuła and Pazdur 2013a, 2013b; Leonelli et al. 2012).

In Poland, according to the Statistical Review of World Energy (2016), the carbon dioxide emission in 1975 was approximately 380 million tons, whereas the carbon dioxide emission in 2014 was approximately 291 million tons. In central and east European countries, there has been a strong and durable reduction in emissions from the beginning of the 1990s and parallel to this, there has been an improvement in the health status of forests in this part of Europe (Juknys et al. 2003; Wilczyński 2006; Elling et al. 2009).

The aims of this study were to determine the spatial and temporal carbon isotope fractionation associated with industrial activity, pollution from vehicles, household heating and low stack emissions in southern Poland. The purpose of this study was to extend current knowledge on interactions between trees and CO_2 emissions from different sources in three forests in the Silesia Region (Poland). In the factories in Silesia many different units and production facilities have been constructed and expanded over the last century. Although numerous projects dedicated to environmental protection have been implemented in these factories over many years aimed at a reduction of the negative impact of production processes on the environment, most factories were on the list of the most environmentally noxious factories until the 1990s. The studies answer following questions: (1) how trees adapted to environmental contamination: how trees reacted to high industrial emission of carbon dioxide; (2) if the negative impact of

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industrial pollution on trees was stronger than the positive influence of an increase in CO_2 in the atmosphere; (3) if there is any similar response in carbon stable isotopic composition of annual tree rings in sampling sites located nearby different factories; (4) if there is any spatial (taking into account a distance of sampling sites from factories) similarity in variation of carbon isotopic composition of the foliage; (5) what differences can be noted between the values of $\Delta^{14}C_o$ in atmospheric CO_2 and $\Delta^{14}C$ in tree ring cellulose and needles; (6) if there is any correlation between carbon isotopic composition of tree ring cellulose and anthropogenic CO_2 emissions; and (7) how global decrease in radiocarbon (^{14}C) concentrations in the air is recorded in pine tree rings in Silesia region over last decades.

The annual ring growth variability of Scots pine (*Pinus Silvestris* L.) has been used as a bioindicator of environment change (Schweingruber 1996; Wilczynski 2006; Wagner and Wagner 2006; Malik et al. 2012; Sensuła and Pazdur 2013a, 2013b; Pazdur et al. 2013; Sensuła et al. 2015a, 2015b). The width of annual tree rings is considered an appropriate monitor of forest conditions (Eckstein 1989; Schweingruber 1996; McLaughlin et al. 2002; Dobbertin 2005). Tree foliage may act as a filter, concentrating the contamination. Observations show that, due to air pollution in the 20th century, different trees species populations have demonstrated a different sensitivity to weather conditions (for example Leonelli et al. 2012; Battipaglia et al. 2014; Sensuła and Pazdur 2013a, 2013b; Sensuła 2016a). Carbon dioxide molecules are absorbed from the atmosphere by plants, and during photosynthesis, plants convert CO_2 and H_2O to cellulose which is the basic structural component of plant cell walls.

The observed anthropogenic impact on the carbon cycle, related to regional and global diffusion of industrial CO_2 emissions and some other local human activities (such as, industrial factories, vehicles, housing energy, low stack emission of CO_2) has led to changes in the isotopic composition of carbon in the atmosphere and biosphere (Craig 1954; Suess 1955; Leavitt and Long 1982; Martin et al. 1988; Ehrelinger 1990; Ehrelinger and Vogel 1993; McCarroll and Loader 2004; Sensuła et al. 2006; Pazdur et al. 2007; McCarroll et al. 2009; Keeling et al. 2010; Rinne et al. 2010; Savard 2010; Sensuła et al. 2011; Pazdur et al. 2013; Sensuła 2015; Boden et al. 2016; Sensuła 2016a, 2016b, 2016c; Sensuła and Wilczyński 2017). The carbon isotopic composition of trees may be affected by changes in carbon isotopic composition of atmospheric CO_2 and during enzymatic reactions and due to changes in temperature, sunshine, water stress, or contamination (Farquhar and Sharkey 1982; Ehleringer 1990; Ehrelinger and Vogel 1993; Sensuła 2016b). The studies indicated that tree ring $\delta^{13}C$ residuals sensitively respond to CO_2 emission and changing climate. Spatial difference in the long-term declining trend in the raw $\delta^{13}C$ may be driven by changes in stomatal conductance (i.e., supply of CO_2), or in photosynthetic rate (i.e., demand for CO_2), or both. Pines might show a decreasing $\delta^{13}C$ pattern in tree rings due to increases in atmospheric CO_2 concentration, to ^{13}C and ^{14}C-depleted CO_2 emission from soil organic carbon decomposition and fossil fuel combustion or to other effects. At the same time increased atmospheric CO_2 concentration can induce stomatal closure due to high intercellular CO_2 concentration that leads to less C isotope discrimination and thus may mask ^{13}C depleted CO_2 effect on $\delta^{13}C$ plant to some degree (McCarroll et al. 2009). The effect of different sensitivity to weather conditions and masking climatic signal due to air pollution in last decades has been noted also in other parts of Europe (for example Leonelli et al. 2012; Battipaglia et al. 2013; Sensuła et al. 2013a, 2013b).

The impact of air pollution and carbon dioxide emission on tree ring width, $\delta^{13}C$ and ^{14}C concentration in trees is evident (for instance, Craig 1954; McCarroll and Loader 2004; Pazdur et al. 2007, 2013; Keeling et al. 2010; Rinne et al. 2010; Savard 2010; Sensuła et al. 2011; Sensuła and Pazdur 2013a, 2013b; Sensuła 2015). Elevated concentration of CO_2 from industrial sources

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can be also associated with emission of other industrial pollutants, such as for example NO_x, SO_2 and O_3 (Freyer 1979; Choi and Lee 2012), which can also influence on carbon stable isotope composition in plant tissue. In our studies, the influence of NO_x, SO_2, and O_3 on carbon stable isotope fractionation cannot be excluded. There is a lack of anthropogenic gaseous emission data for the Silesia region, due to the lack of access to data from factories and due to the changes in the administrative division of Poland.

MATERIALS AND METHODS

The analysis reported in this paper included 15 pine sites within three regions of significant urban areas: Dabrowa Gornicza near a steelworks Huta Katowice (HK), Kedzierzyn-Kozle near chemical factories (KK) and Laziska near a combined heat and power plant (LA) (Figure S1, Table 1).

The sampling sites (Table 1, Figure S1) were located at different distances: between approximately 5 and 20 km from industrial factories. Needles were collected from 15 sampling sites.

Table 1 Characteristics of the sampling sites in three regions: Dabrowa Gornicza near Huta Katowice (HK; 50°20'31"N 19°16'1"E), Kedzierzyn-Kozle near chemical factories (KK; 50°18'20"N 18°15'27"E) and Laziska near a combined heat and power plant (LA; 50°07'58"N 18°50'47.1"E).

Stand (region)	Lab code	Geographical coordinates	m a.s.l.	Distance from factories, km	Samples
Kedzierzyn-Kozle (KK)	KK_1	50°19'15,2"N,18°15'25,6"E	189	1	Tree rings, needles
	KK_2	50°17'17,6"N,18°19'29"E	197	4	Needles
	KK_3	50°20'15,7"N,18°19'52,5"E	203	6	Tree rings, needles
	KK_4	50°21'0,08"N,18°18'57,7"E	140	6	Tree rings, needles
	KK_5	50°20'3,6"N,18°20'29,9"E	214	6.5	Needles
	KK_6	50°22'14,9"N,18°23'39,9"E	218	11.5	Tree rings, needles
	KK_7	50°21'26,4"N,18°28'14,5"E	208	16	Needles
	KK_8	50°19'55,6"N,18°30'11,8"E	243	17	Needles
Laziska (LA)	LA_9	50°8'55,4"N,18°53'4,9"E	265	3	Tree rings, needles
	LA_10	50°9'38,8"N,18°56'4,4"E	304	7	Tree rings, needles
	LA_11	50°10'35,1"N,18°58'52,8"E	270	11	Tree rings, needles
Dabrowa Gornicza (HK)	HK_12	50°21'48,5"N,19°19'24"E	378	3	Tree rings, needles
	HK_13	50°24'58,4"N,19°22'56,8"E	327	10	Tree rings, needles
	HK_14	50°24'13,16"N,19° 28'56,9"E	335	14.5	Tree rings, needles
	HK_15	50°26'27"N,19°29'30,6"E	330	17	Tree rings, needles

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Samples of needles collected in January 2013 (11 samples) had been created in the previous year, i.e. 2012. The needles collected in September 2013 (15 samples), grew during 2013, and the needles collected in July 2014 (15 samples) had also been created during 2014. The difference in number of samples collected in winter 2013 and in summer 2013 and in summer 2014 was due to banning entry into the part of the forests (Sensuła 2015).

Tree rings were collected from 11 sampling sites (Table 1, Figure S1). In each of 11 selected sites, 20 pines, aged between 80 to 100 years, were sampled by taking one increment per tree at a height of 1.3 m above ground. All 220 sampled trees were dominant and codominant individuals without damage. Dendrochronological analysis has been described in detail already (Sensuła et al. 2015a, 2015b, 2017). The average ring width was computed for 3 time intervals: low level of emissions of industrial pollution (1940–1960), culmination of emissions (1961–1990) and reduction of industrial emissions (since 1991). Dendrochronological analyses (Sensuła et al. 2015a, 2015b, 2017) enable the selection of sites for analysis of the stable isotopes and ^{14}C concentration in trees. From each region, one sampling site per stand, where the strongest and the longest tree ring width reductions were observed due to an increase in industrial pollution emission, was chosen for isotopic investigation (LA_11 in Laziska region, KK_3 in Kedzierzyn-Kozle region, and HK_14 in Dabrowa Górnicza region, respectively).

The dendrochronologically dated annual tree rings were manually separated, pooled, homogenized, and cut into small pieces. α-cellulose samples were extracted (from 10 trees per site) by applying procedures based on Green's method (1963) used in the mass spectrometry laboratory of the Silesian University of Technology (Pazdur et al. 2007, 2013; Sensuła et al. 2011; Sensuła and Pazdur 2013a, 2013b; Sensuła et al. 2016a, 2016b).The stable isotopic compositions of annual tree rings were analyzed with annual resolution for the period 1975–2012.

The ^{14}C isotopic compositions of annual tree rings α-cellulose were analyzed with annual resolution for the period 1990–2012 and for each 5th year resolution for the period 1975–1990. Additionally, ^{14}C isotopic composition was measured also in tree rings created in 1986 to evaluate the effect of the accident at the Chernobyl nuclear power plant in Ukraine.

STABLE ISOTOPES

$\delta^{13}C$ were determined at the mass spectrometry laboratory of the Silesian University of Technology using an Isoprime continuous flow isotope ratio mass spectrometer (GV Instruments, Manchester, UK).

The isotope values were reported in the delta notation (Equation 1, in ‰)

$$\delta^{13}C = \left(R_{sample} / R_{standard} - 1\right) \cdot 1000 \quad (1)$$

relative to the international V-PDB (Vienna Pee Dee Belemnite) standard. $R_{standard}$ and R_{sample} are the molar fractions of $^{13}C/^{12}C$ for the sample and the standard, respectively.

The standard deviation for the repeated analysis of an internal standard (C-3 and C-5, IAEA) was better than 0.2‰.

To describe the variation of the carbon isotope composition of tree ring cellulose caused by climate changes and anthropogenic emission of CO_2, we used a model (Sensuła et al. 2011) based on multiple regressions (Equation 2) using Statistica 12 (Statsoft Inc. 2014):

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$$\delta = R + \sum_{M=Oct}^{Sep} b_{MT} T_M + \sum_{M=Oct}^{Sep} b_{MT} P + \sum_{M=Oct}^{Sep} b_{MT} S_M + b_E E_{\frac{1}{CO_2}} \quad (2)$$

where R corresponds to the interdependences between the monthly climate factors and other environmental changes (for instance: pollutant emission, "potential for growth," carbon flux from biosphere to atmosphere or error connected to the assumptions (Pazdur et al. 2013, Sensuła et al. 2013a), M is the month (from October of the previous year to September of the given year), b is the regression coefficient for the following variables: T (average of the monthly temperatures), P (total monthly precipitation), S (monthly hours of sunshine), E_{1/CO_2} = emission of $CO_2$was used in statistical analyses.

Additionally, raw $\delta^{13}C$ data can be mathematically corrected to a preindustrial atmospheric $\delta^{13}C_{cor}$ using the data from McCarroll and Loader (2004).The correction reduces the decline of the last decades (Rinne et al. 2010).

Radiocarbon

Samples of α-cellulose were converted to graphite for AMS ^{14}C measurements. The process was performed in an AGE automated graphitization system (Wacker et al. 2010). Subsamples of ca. 3 mg of cellulose were weighed to tin capsules, combusted in a VarioMicroCube elemental analyzer and the CO_2 was reduced with hydrogen over the Fe catalyst. Coal was used as a blank material and was prepared with the standard ABA treatment (Piotrowska 2013). Oxalic Acid II (NIST SRM4990C) was used as a reference material, without any chemical pretreatment. The blank and OxII samples were combusted and graphitized as described above. ^{14}C concentration was determined at the DirectAMS laboratory, Bothell, WA, USA (Zoppi et al. 2010). Three to four graphites of blank and OxII were measured in the same run as unknown α-cellulose samples. The average blank for these series was 0.3 pMC, which corresponds to 46.6 ka BP, and was subtracted from measured concentrations.

The needles were prepared using a standard acid-alkali-acid treatment and converted to benzene for LSC measurements. Measurement of ^{14}C concentrations in pine needles was performed with a ultra-low liquid scintillation spectrometer of the type Quantulus 1220 (Pawlyta et al. 1998).

The measured ^{14}C concentration or activity was corrected for $\delta^{13}C$ and normalized to the standard of modern biosphere, resulting in the value of $F^{14}C$. The ^{14}C content in a tree ring in a year of its origin was calculated according to the formula (Equation 3; van der Plicht and Hogg 2006):

$$\Delta^{14}C = \left(F^{14}C \cdot e^{-\lambda(Ti-1950)} - 1\right) \cdot 1000 \quad (3)$$

where: $F^{14}C$-normalized ^{14}C concentration, λ-decay constant for ^{14}C isotope, equal to 8267 yr^{-1}; T_i – calendar year of the tree ring or formation of the needles.

Pollution and Meteorological Data

The emission data were obtained from the Carbon Dioxide Information Analysis Center (Boden et al. 2016). The $\delta^{13}C$ changes in the isotopic ratio of atmospheric CO_2 due to global fossil fuel emissions ranged from 0.37‰ (in 1975) to 1.97‰ (in 2012) (McCaroll and Loader 2004; McCaroll et al. 2009). The experimental data were extrapolated to the present.

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Mean $\Delta^{14}C_o$ concentrations ($\Delta^{14}C_o$) in the atmospheric CO_2 from April to September (Table S1) of the given year (reference values, commonly called "background") were calculated on the basis of the data presented by Hammer et al. (2017) and Hua et al. (2013). The former $\Delta^{14}C_o$ values (from Jungfraujoch and Schauinsland) cover the period from 1986 until the present, whereas the latter $\Delta^{14}C_o$ values (for Northern Hemisphere Zone 1) cover the period from 1975 to 1986, due to the lack of $\Delta^{14}C_o$ data for Jungfraujoch for the period prior to 1986.

The data for temperature, humidity and precipitation come from the meteorological station in Katowice and Opole. The meteorological data were obtained thanks to the Polish Institute of Meteorology and Water Management (IMGW-PIB).

RESULTS AND DISCUSSION

Dendrochronology

Previous studies showed that the pollutant emissions weakened the vitality of the pines, especially those exposed to their direct impact (Eckstein 1989; Juknys et al. 2003; Wilczyński 2006; Elling et al. 2009; Sensuła et al. 2015a, 2015b). The strongest and longest-drawn reductions of radial growth were recorded in the stands located in the paths of the dominant winds. A rapid decrease in the annual increment of pines in all pine stands can be observed after 1960, when the industrial pollution strongly increased (Figure S2).

The decrease in the annual radial increment was not dependent on the location of the pollution sources. All sites were located in the path of winds carrying pollutants (Figure S1). The duration of the radial growth depression period in individual stands was similar. It lasted 30 years (Figure S2). The recovery started in the 1990s along with the reduction of pollutant emissions (Figure S2). At the beginning of the 1990s the weakened pines, which greatly reduced their growth, began to rapidly increase their radial increment. This revitalization was very dynamic (Figure S2). This is also confirmed by the results shown in Figure S3.

The results of the correlation shown a very strong and significant ($p < 0.01$) dependence between the radial increment values in the pre-depression, depression and recovery periods (Figure S3). A positive relationship has been found between the radial increment reduction and the degree of recovery. The greater the radial increment of pines in the pre-depression period, the greater the growth reduction during periods of increased pollution, and the more dynamic the incremental recovery (Figure S3).

Stable Isotopes in Tree Ring Cellulose

Spatial difference in long-term trend in the $\delta^{13}C$ chronology has been observed in all investigated sites (Figure S4).

Despite the differences in $\delta^{13}C$ chronology trends in each sampling site, the average value of pine $\delta^{13}C$ in each sampling site was about −24‰.

In the Kedzierzyn-Kozle (KK) pine $\delta^{13}C$ series data range from −24.6‰ to −23.2‰ (uncorrected) and from −23.1‰ to −21.9‰ (corrected), in the Laziska (LA) pine $\delta^{13}C$ series data range from −24.4‰ to −23.1‰ (uncorrected) and from −23.4‰ to −21.6‰ (corrected), in the Dabrowa Gornicza (HK) pine $\delta^{13}C$ series data range from −25.3‰ to −22.9‰ (uncorrected) and from −23.6‰ to −21.5‰ (corrected). The $\delta^{13}C$ values in α-cellulose samples extracted from pine growing in these 3 forests show a significant correlation between them ($r_{LA\ vs\ HK} = 0.71$; $r_{KK\ vs\ LA,} = 0.78$, $r_{HK\ vs\ KK} = 0.78$ $n = 39$, $p < 0.001$), which confirms the similarity in tree

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response to changes in the ecosystem. The admixture of large amounts of fossil-fuel derived CO_2, which is depleted in $^{13}CO_2$ resulted in a dilution of the atmospheric $^{13}CO_2$ (Suess effect) (Figure S4). An inverse trend between CO_2 emission and $\delta^{13}C$ was observed: the increase in CO_2 emission decreased $\delta^{13}C$ and decreased CO_2 emission increased $\delta^{13}C$ (Figure S4).

The relationships between climate and isotopic composition exhibit spatiotemporal diversity. The variation of the carbon isotope composition of tree ring cellulose caused by climate changes and anthropogenic emission of CO_2, based on multiple regressions is illustrated in Figure S5.

The value of the correlation coefficient between the measured and modeled $\delta^{13}C$ in α-cellulose are above 0.9 ($n = 39$).

Different b-values (Table S1) for climatic parameters may confirm that not only individual climatic parameters but also other interrelated components of the climate system may affect the correlation coefficient for the isotopic series from these trees. Therefore, this model suggests that the Silesia region may not be a uniform region for isotopic composition in Scots pine due to these other sources of variability.

Our model (Sensuła and Pazdur 2011) attempts to assess the CO_2 emission component based on multiple regression analyses of the $\delta^{13}C$ records. The total fossil fuel emission of CO_2 estimated from the multiple regression model followed a nationally reported pattern with the anthropogenic industrial emission and showed a similar trend as that evaluated for Poland earlier by Boden et al. (2016) (Figure S5).

Radiocarbon in Tree Ring Cellulose

The comparison of the ^{14}C concentrations in tree ring cellulose of the examined populations and $\Delta^{14}C_o$ concentration reference values ("background") is presented in Figure S6, and in Tables 1 and S2.

During the period investigated, the values of $\Delta^{14}C_o$ show a significant decrease: from approximately 400 to 40‰ in an exponential form. The high initial value of $\Delta^{14}C_o$ was due to the anthropogenic production of the ^{14}C isotope during nuclear tests in the atmosphere, mainly in the 1960s. The $\Delta^{14}C_o$ decrease following this period is primarily due to a mixing of $^{14}CO_2$ containing artificially generated ^{14}C atoms with the global surface ocean in the Earth's carbon cycle (Hua et al. 2013).

A similar trend is evident in the results obtained for tree ring cellulose samples from Laziska, Kedzierzyn-Kozle and Dabrowa Gornicza (Table 2, Figure S6).

During the investigated period, not all $\Delta^{14}C$ values in tree ring cellulose are characterized by lower values than $\Delta^{14}C_o$. Differences between the values of $\Delta^{14}C_o$ in atmospheric CO_2 and $\Delta^{14}C$ in tree ring cellulose are observed. These differences (Tables 2 and S2) are not constant over time, but on average for the whole study period, the difference between $\Delta^{14}C_o$ and $\Delta^{14}C$ in tree ring cellulose range from –16.6‰ to 6.1‰ in Dabrowa Gornicza, range from –3.5‰ to 20.6‰ in Laziska, range from –21.6‰ to 7.5‰ in Kedzierzyn-Kozle, respectively.

$\delta^{13}C$ and ^{14}C in Needle Samples

The patterns of the spatial and short-temporal variability of $\delta^{13}C$, $\Delta^{14}C$ in pine needles of the three forests in the most industrialized part of Poland – in proximity to the heat and power plant

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Table 2 Mean value of $\Delta^{14}C_o$ in the atmosphere (from April to September of the given year) and $\Delta^{14}C$ in tree ring cellulose and its uncertainty (u) in the given year. $\Delta^{14}C_o$ in the atmosphere for the period 1975–1986 was taken from the work of Hua et al. (2013), whereas for the period 1986–2014 from the work of Hammer et al. (2017).

	$\Delta^{14}C$ (‰)							
	Atmosphere		Tree ring cellulose					
Year	$\Delta^{14}C_o$,‰	SD ($\Delta^{14}C_o$),‰	HK	u	LA	u	KK	u
2014	19.2	2.1						
2013	22.5	3.3						
2012	30.6	1.4	32.5	2.7	34.2	3.2	32.1	2.8
2011	37.4	2.1	34.9	2.6	25.7	3.2	33.7	2.6
2010	41.3	3.5	50.6	3.0	40.5	3.5	42.1	2.7
2009	45.8	3.6	46.2	2.8	42.1	3.1	38.3	2.6
2008	46.5	2.3	49.9	2.9	28.7	3.1	51.1	2.7
2007	51.2	2.3	57.9	3.0	45.8	3.5	58.3	3.0
2006	57.0	2.4	58.5	2.8	54.2	3.4	56.9	2.7
2005	58.6	2.8	57.3	2.9	38.8	2.8	59.9	2.8
2004	62.3	2.6	72.2	2.7	63.5	3.5	68.5	2.7
2003	69.5	2.2	73.1	3.0	52.9	2.8	74.3	2.6
2002	75.8	3.4	71.0	3.2	55.2	2.6	78.7	2.9
2001	80.6	2.5	79.6	3.1	65.6	3.1	79.3	2.6
2000	87.4	2.5	83.3	3.2	69.4	2.6	89.5	3.0
1999	92.5	4.0						
1998	99.2	3.4						
1997	100.7	2.9						
1996	105.8	4.0						
1995	114.2	4.4	130.1	3.8	110.3	3.3	110.4	3.0
1994	120.3	2.4						
1993	126.4	2.0						
1992	134.5	3.6						
1991	139.5	4.3						
1990	149.9	3.7	159.1	3.4	142.3	3.6	143.4	3.6
1989	162.0	3.9						
1988	168.6	2.5						
1987	182.2	4.4						
1986	189.2	2.8	197.8	3.6	187.2	3.3	192.9	3.3
1985	204.9	2.8	198.8	3.8	197.3	3.2	207.0	3.8
1984	211.8	2.0						
1983	229.3	3.0						
1982	239.2	2.0						
1981	255.3	4.7						
1980	268.7	4.1	285.2	3.6	258.5	3.3	282.8	3.9
1979	292.1	4.0						
1978	323.8	4.8						
1977	333.8	3.0						
1976	348.3	5.1						
1975	387.7	9.6	399.6	3.6	375.9	3.5	409.3	3.7

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in Laziska (LA), the nitrogen plant in Kedzierzyn-Kozle (KK) and the steelworks in Dabrowa Gornicza (HK) are summarized in Tables S3–S5.

A detailed analysis of the carbon isotope composition of needles in each investigated site confirms that environmental records are not homogeneous within a single research region. There are significant differences in the stable isotopic and ^{14}C composition of the needles between pine populations and between needles from year to year.

An analysis of the isotopic composition of pine growing in Laziska region (Tables S3–S5, Figure S1 and Figure 1) shows the lowest $\delta^{13}C$ value in the LA_10 population (located near a road, near detached houses, about 7 km from a factory), while LA_11 and LA_9 show similar values.

For pine growing in Dabrowa Gornicza region (Tables S3–S5, Figure 1) the lowest $\delta^{13}C$ values were noted in HK_15 (20 km from factories, very near a road).

In one population (HK_14), there were no differences in carbon isotopic composition between samples collected at different times, or between the winter or in the summer. Also, there was no significant difference between $\delta^{13}C$ values in samples collected in 2013 and 2014. For pines growing in Kedzierzyn-Kozle region the lowest $\delta^{13}C$ values were noted in KK_1 and KK_4 (near factories and roads). Populations growing at a distance of 6 km from factories and far from the road (KK_3 and KK_5) show no differences in carbon isotopic composition either in the winter or in the summer, also there was no significant difference between $\delta^{13}C$ values in samples collected in 2013 and 2014.

Comparing $\delta^{13}C$ values in the pine needles grown in 2012 (collected in winter 2013) with $\delta^{13}C$ values in the pine needles grown in 2013 (collected in summer 2013), the values varied from −2.3‰ to 1.5‰. Depletion in $\delta^{13}C$ was observed in half of the investigated sites. Usually, but not always, an increase in $\delta^{13}C$ corresponds to an increase in $\Delta^{14}C$ was observed. Comparing $\delta^{13}C$ values in the pine needles created in 2013 (collected in summer 2013) with $\delta^{13}C$ values in

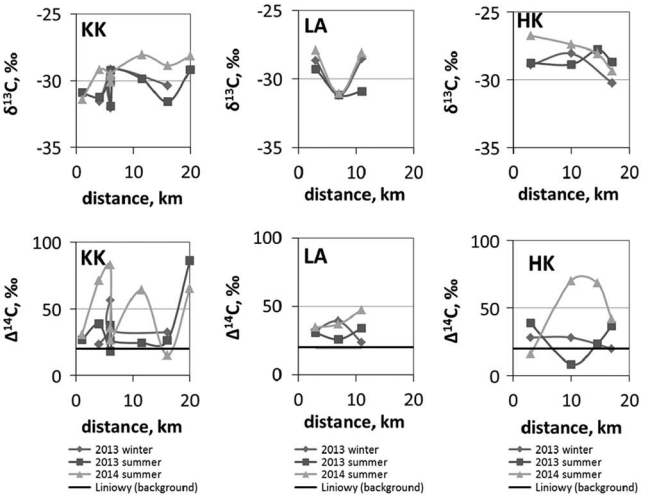

Figure 1 Spatial and short-time variation of the stable carbon isotope and ^{14}C composition of needles from 15 sampling sites in 3 regions (see Table 1).

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the pine needles created in 2014 (collected in summer 2014), $\delta^{13}C$ in summer 2014 was mostly higher than in summer 2013 (in 11 of the 15 sampling sites).

In 2012, $\delta^{13}C$ in tree ring cellulose in KK_3 was equal to –24.1‰, whereas $\delta^{13}C$ in tree ring cellulose in LA_11 was equal to –23.5‰. The difference between $\delta^{13}C$ in the needles (Table S3) and tree ring cellulose was about 5‰ in KK_3 and LA_11, and the $\delta^{13}C$ difference between needles and tree ring cellulose (the ratio of $\delta^{13}C$ in cellulose to $\delta^{13}C$ in needles created in 2012) was a factor of 1.2 in both investigated sites (KK_3 and LA_11). However, the ratio of ^{14}C concentrations in tree rings and foliage varied, in one case >1, while in another sampling site it was <1 as shown in Table 1.

Transect studies $\delta^{13}C$ and ^{14}C gradients have shown inhomogeneous changes in carbon isotopes composition in the needles (Figure 1).

There is no linear response between $\delta^{13}C$, $\Delta^{14}C$ and space localization of the distance of sampling sites from factories. The analysis of ^{14}C in trees shows regional variability and differences between each of the sites investigated. On the one hand, the variability in carbon isotope composition of the biosphere may be related to CO_2 emissions from fossil fuel combustion, which increases the atmospheric CO_2 concentration and alters its isotopic composition (e.g., Craig 1954). In terms of ^{14}C, the global CO_2 becomes depleted in ^{14}C, because the CO_2 from fossil fuels is devoid of any ^{14}C (Suess 1955). Local depletion of the radioactivity concentration (local Suess effect) can be observed in areas with higher CO_2 emissions from fossil fuel combustion (Rakowski et al. 2000; Molnar et al. 2007; Pazdur et al. 2007; Svetlik et al. 2010; Baydoun et al. 2015).

The sites selected for investigation were in the proximity of recognized CO_2 emitters; therefore, the lack of a pronounced Suess effect in two of the sites may seem surprising. This phenomenon might be explained by the factors associated with the local carbon cycle and pine physiology because carbon compounds synthesized in the fall and stored during the winter are utilized when trees start radial growth in the spring. The pines used a material from previous year to create new tissues and the first layer of early-wood (Białobok et al. 1993). Evergreen leaves may contain carbon fixed from the previous season or even previous years. The significant scatter of ^{14}C concentration (up to 70‰) in the plants growing polluted area comparing to the ^{14}C concentration in the plants growing in the clean area has been observed also by Baydoun et al. (2015). Also the results of the systematic $\Delta^{14}C$ measurements of soil CO_2 flux performed in the forest environment for 1998–2001, Gorczyca et al. (2013) from closed-system gas collection at the soil surface suggested that $\Delta^{14}C$ values of the CO_2 emitted from the forest soil were ~40‰ higher than current atmospheric background values. Moreover the influence of bio-components combusted together with fossil fuels cannot be excluded at the moment, as additional research is required. This effect has also been observed in Niepolomice Forest (Pazdur et al. 2013). Relatively high ^{14}C concentration may be also connected with the other effect connected with the emission of $^{14}CH_4$ by factories, that may raise the ^{14}C concentration in the atmosphere (Molnar et al. 2007).

The "masking effect" caused by the carbon cycle is undoubtedly present in all investigated sites, although it may have a different extent, depending of the local soil characteristics. In general, it may even cause the $\Delta^{14}C$ in tree rings to reach values above $\Delta^{14}C_o$, which was observed in a few cases. The values of $\Delta^{14}C$ in tree rings and needles lower than $\Delta^{14}C_o$, i.e. indicating a local Suess effect, were observed in some samples, especially in the Laziska site (LA). The emission of ^{14}C-free CO_2 from the nearby heat and power plant may be assumed to be higher than that from

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other industrial sites (chemical factory for KK or steel factory for HK), and this is consistent with the presented data.

The effect of the nearby Katowice agglomeration, possibly causing an enhanced Suess effect, was not observed in HK. In fact, a local Suess effect in cities has been previously observed for sites close to city centers (Rakowski et al. 2000; Pazdur et al. 2013). However, in our investigation, some sampling sites, $\Delta^{14}C$ in trees (cellulose and needles) is higher than current atmospheric background values. A higher $\Delta^{14}C$ concentration in tree-rings than in the "clean" air has also been observed in specific years (between 1970s and 1990s) in urban areas by Rakowski et al. (2000). The variation in $\delta^{13}C$ and $\Delta^{14}C$ has been noted in all investigated sites. Differences have been noted between the values of $\Delta^{14}C_o$ in atmospheric CO_2 and $\Delta^{14}C$ in tree ring cellulose; some samples of tree rings and needles have a more positive value than $\Delta^{14}C_o$ in atmospheric CO_2. This phenomenon might be explained by the factors associated with the local carbon cycle and additional research is required. The influence of different sources of carbon isotopes connected with the effects of roads, housing energy, household heating sources, low and high stack emission including methane emission by factories, bio-components combustion cannot be excluded at the moment.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2018.59

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