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TREE RINGS AS ARCHIVES OF ATMOSPHERIC POLLUTION BY FOSSIL CARBON DIOXIDE IN BRATISLAVA

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ABSTRACT. Results of radiocarbon (^{14}C) analysis of a tree-ring series from Bratislava, Slovakia, covering the period from 1970 to 2004 are presented. For a part of this time period, monthly ^{14}C measurements of atmospheric carbon dioxide from Bratislava sampling station are compared with the tree-ring results. The effects of fossil CO_2 emissions on ^{14}C levels in the environment are emphasized by comparison with atmospheric clean air reference values (Schauinsland, Germany). The presented results from Bratislava are also set against the previously measured tree-ring series from Low Tatras mountain region in Slovakia, representing regional clean air radiocarbon levels in the biosphere. The observed ^{14}C levels of Bratislava tree rings and atmospheric CO_2 in 1970s and 1980s are significantly lower than clean air data, indicating severe fossil CO_2 pollution in Bratislava during this time period.

KEYWORDS: carbon dioxide, radiocarbon, tree rings.

INTRODUCTION

In environmental research, past radiocarbon (^{14}C) levels are of great interest because they allow us to gain information about carbon cycle dynamics and carbon sources in the past. These data sets are very valuable, especially in studies of human impact on carbon in the environment. There are two anthropogenic effects influencing ^{14}C levels in the atmosphere—input of excess radiocarbon produced by nuclear technology (increasing radiocarbon activity) and input of ^{14}C-free fossil carbon dioxide into the atmosphere (decreasing radiocarbon activity).

Atmospheric nuclear weapons tests that took place in 1950s and at the beginning of 1960s caused up to 100% increase of radiocarbon activity in the atmosphere and biosphere of the northern hemisphere (Hua et al. 2013). Since the Partial Nuclear Test Ban Treaty in 1963, the ^{14}C activity in the atmosphere and biosphere has been decreasing and in recent years the nuclear industry (mainly nuclear power plants and reprocessing facilities) became the main source of anthropogenic radiocarbon released into the environment. Measurements of radiocarbon content of tree rings have been used to study the effects of nuclear power plants and radioactive waste disposal facilities on surrounding environment (Stenström et al. 1997; Ješkovský et al. 2015; Janovics et al. 2016; Ežerinskis et al. 2018).

Since the industrial revolution human activities using fossil fuels have become a significant source of fossil carbon dioxide released into the Earth's atmosphere. As fossil CO_2 does not contain any radiocarbon, it dilutes ^{14}C already present in the atmosphere and therefore decreases its specific activity. This process is called Suess effect (Suess 1955). In areas with heavy industrial activity and in heavily urbanized regions with intense traffic, the burning of fossil fuels has had a significant effect on local radiocarbon levels in the environment. Radiocarbon analysis of annual growth rings has been successfully used to determine the intensity of Suess effect, as well as to estimate CO_2 emissions (Rakowski et al. 2004; Capano et al. 2010).

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There are only a few radiocarbon laboratories with atmospheric $^{14}CO_2$ data sets several decades long (e.g., Levin and Kromer 2004; Kuc et al. 2007; Povinec et al. 2012) and their use for past ^{14}C studies is limited by the length of the record and the sampling location. If past ^{14}C levels outside of the scope of these data sets are required, proxies in other carbon cycle compartments must be used. The biosphere offers an ideal proxy in the form of annual tree rings.

Since the advent of accelerator mass spectrometry in 1977, this analytical technique has become the method of choice for radiocarbon analysis, especially in the case of archaeological samples, where the small sample size presents considerable advantage over the decay counting methods used previously for ^{14}C measurement. However, in the case of environmental samples such as atmospheric $^{14}CO_2$ samples, the sample size is usually not a limiting factor and radiometric methods are still being used (Krajcar Bronić et al. 2009; Levin et al. 2013; Kontuľ et al. 2018).

The radiocarbon laboratory at Comenius University in Bratislava, Slovakia has a long tradition of atmospheric ^{14}C monitoring—first measurements took place in 1967 (Povinec et al. 1968) and continuous monthly measurements of atmospheric $^{14}CO_2$ in Bratislava have started in 1984 and continue to the present day. Two data sets are presented in this paper—monthly atmospheric $^{14}CO_2$ data from the campus of Comenius University in Bratislava, Slovakia, and radiocarbon activity in annual tree ring samples from a tree at the same sampling site. The aim of this study was to determine the past radiocarbon levels in the biosphere of Bratislava, and to compare them with the atmospheric CO_2 measurements. This comparison could show to what extent the observed atmospheric $^{14}CO_2$ variations in an area heavily influenced by fossil CO_2 emissions are recorded in a local tree-ring record.

MATERIALS AND METHODS

The studied tree-ring series comes from a black poplar (*Populus nigra*) tree in the close proximity to the building of the Faculty of Mathematics, Physics and Biophysics of Comenius University in Bratislava, Slovakia (where the monthly atmospheric sampling takes place). Sampling site location on a map of Slovakia can be seen in Figure 1. A whole section from the tree was available, therefore there was enough material for radiometric method of measurement. The tree section was divided into individual growth rings and the samples were further processed and measured at two radiocarbon laboratories—at Faculty of Mathematics, Physics and Informatics at Comenius University in Bratislava, Slovakia, and at Nuclear Physics Institute of Czech Academy of Sciences in Prague, Czech Republic.

At the Prague radiocarbon laboratory, the samples were chemically pretreated in a Soxhlet extraction apparatus with a 2:1 benzene-ethanol mixture. After the pretreatment, the sample was combusted in atmosphere of pure oxygen in a quartz apparatus. The prepared CO_2 was further purified using a wet process with the $AgNO_3$ solution and dried. Consecutively, benzene was synthesized from the CO_2. The procedure involved synthesis of lithium carbide, its hydrolysis to acetylene, purification and catalytic trimerization of the acetylene to benzene form. After one-month storage for radioactive decay of ^{222}Rn, gravimetric dosing of benzene into low background 3 mL Teflon vials was performed with addition of 1.5% (weight) butyl PBD scintillator. The benzene retrieved from the synthesis was measured using a low-background liquid scintillation spectrometer Quantulus 1220

Figure 1 Map of Slovakia showing the location of Bratislava, Bohunice Nuclear Power Plant and Jasná.

(more details can be found in Svetlik et al. 2012). Oxalic acid NIST SRM 4990C was used as a standard for the evaluation of the measurement results.

At the Bratislava radiocarbon laboratory, the chemical pretreatment of tree-ring samples consisted of acid-base-acid treatment with HCl and NaOH followed by $NaClO_2$ bleaching. The bleached wood samples were then dried and subsequently combusted in a stream of pure oxygen. The resulting CO_2 was then purified in a glass vacuum line and then used to prepare methane in a reactor with heated ruthenium catalyst with the addition of hydrogen. The samples were stored in glass containers for one month prior to their measurement in a large-volume gas proportional counter (more details can be found in Povinec 1972, 1978). Oxalic acid NIST SRM 4990B was used as a standard for the evaluation of the measurement results.

At both laboratories a small portion of the sample CO_2 gas was used for determination of $\delta^{13}C$ by isotope-ratio mass spectrometry. The activity of ^{14}C acquired by the measurement is reported in terms of $\Delta^{14}C$ following the Stuiver-Polach convention (Stuiver and Polach 1977).

The atmospheric $^{14}CO_2$ data set from Bratislava used for comparison with tree-ring data is a result of radiocarbon analysis of continuous monthly atmospheric CO_2 samples absorbed in NaOH solution (Povinec et al. 2012).

RESULTS AND DISCUSSION

The results of radiocarbon analysis of tree-ring samples from Bratislava are shown in Figure 2 (a table with the results is included in the supplementary materials). This figure also shows the monthly atmospheric data measured in Bratislava (Povinec et al. 2012) and monthly clean air background values represented by Schauinsland $^{14}CO_2$ data (Hammer and Levin 2017). In general, the comparison with clean air background from Schauinsland shows that both the effect of anthropogenic ^{14}C releases and fossil CO_2 emissions can be seen in this data. Monthly values above the clean air background indicate residual bomb radiocarbon from the stratosphere and ^{14}C releases from Bohunice nuclear power plant about 50 km northeast from Bratislava (Povinec et al. 2009). Atmospheric data in Figure 2 confirm that the influence of fossil CO_2 is the dominant anthropogenic effect influencing atmosphere in

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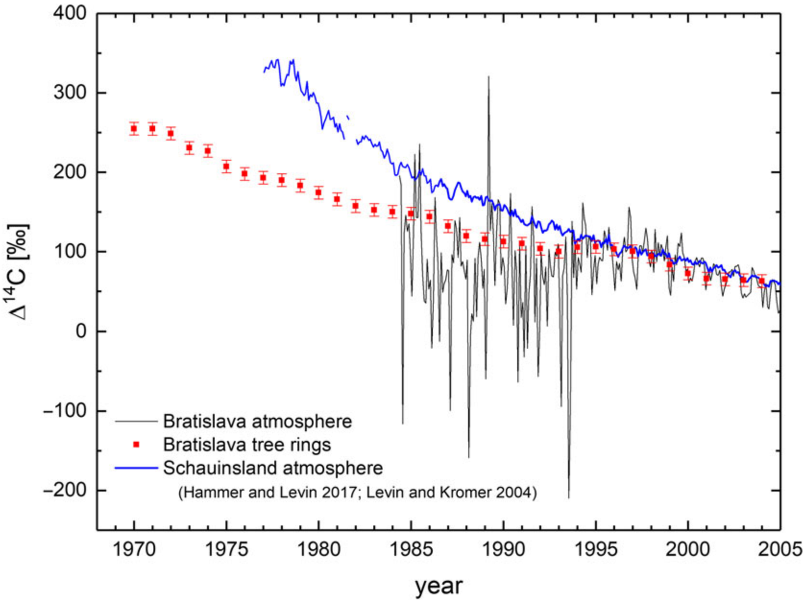

Figure 2 ^{14}C activity in tree rings from Bratislava compared with monthly atmospheric $^{14}CO_2$ data from Bratislava (Povinec et al. 2012) and Schauinsland sampling stations (Hammer and Levin 2017).

Bratislava. This is apparent especially in the 1980s and 1990s, when several extremely low Δ^{14}C values (as low as –210‰) have been observed. They were probably caused by certain meteorological conditions changing the prevailing air mass transport modes and preventing efficient ventilation of air masses from the Bratislava area, thus concentrating fossil CO_2 and depleting radiocarbon activity in the local atmosphere to this extent (Povinec et al. 2012). In these conditions, local fossil CO_2 sources such as oil refinery on the outskirts of Bratislava (only 8 km southeast from sampling location) and other industrial sources in northwest could have significant impact on radiocarbon levels in the affected area. In the period after 1994 the industrial emissions and pollution in Bratislava decreased due to lower activity of heavy industries as some of them ceased their operation.

Tree-ring radiocarbon levels are also considerably lower than clean air background in 1980s and 1990s, however, they do not reach the extremely low atmospheric values, nor do they attain the increased values caused by excess ^{14}C observed in the atmosphere. The majority of the observed deep atmospheric minima occurred outside of spring and summer months, therefore outside of the growing season, and these minima should not be recorded in the tree-ring samples. However, several of the extremely low atmospheric values (–120‰ in July 1984 and –210‰ in July 1993) fall into the expected growing season (April–September) and it appears that in this particular case these low ^{14}C activities were not efficiently recorded in the studied tree rings. The changes of radiocarbon activity in tree-rings from Bratislava are relatively smooth, there are no sudden changes present in the data.

For a better comparison (taking into account the expected vegetation period), we can compare the tree-ring results with mean atmospheric values. From the monthly atmospheric data, we calculated average values for the period from April to September, which represent the mean ^{14}C activity during the probable growing period of this tree. The standard deviation of

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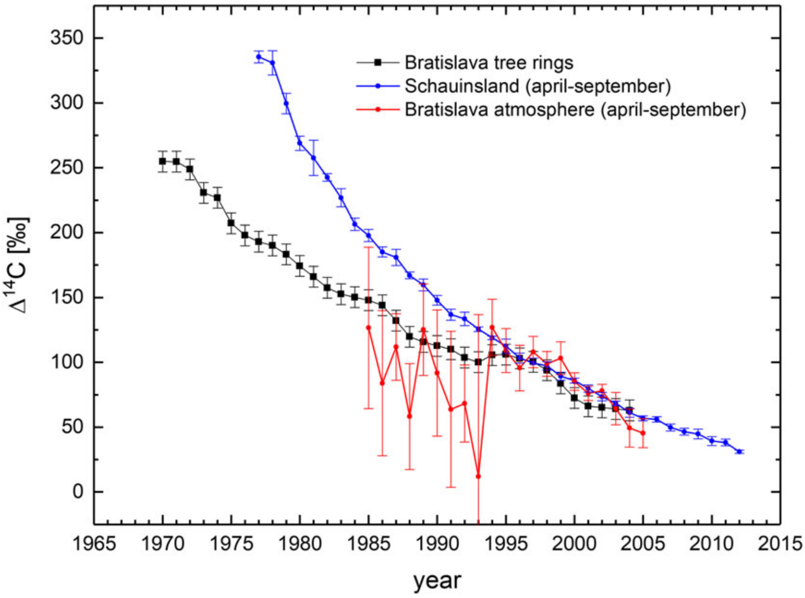

Figure 3 Comparison of Bratislava tree-ring data with mean atmospheric values from Bratislava (Povinec et al. 2012) and Schauinsland (Hammer and Levin 2017).

atmospheric mean values is large because of significant variation of monthly $\Delta^{14}C$ values in the months for which the average was calculated (Figure 2). This comparison is shown in Figure 3 and it demonstrates that in time period prior to 1994, the atmospheric levels are in general lower than tree ring levels. They are not systematically shifted, there is a large scatter of these atmospheric mean values. This suggests that the studied tree probably did not efficiently incorporate and record the erratic and presumably rapid changes of radiocarbon activity in the atmosphere. Changes of local climatological parameters could have affected photosynthetic assimilation and growth of this tree (Weiwei et al. 2018), but we do not have any information suggesting extreme environmental stress for this tree in the past. After 1994, both the atmospheric and tree-ring values get much closer to clean air levels, and there is much better agreement between these two data sets from Bratislava.

$\delta^{13}C$ values measured in tree-ring samples ranged from –26.9 to –24.3‰ (Figure 4). There are no statistically significant trends or discontinuities in the observed $\delta^{13}C$ variation and $\delta^{13}C$ levels in Bratislava tree rings are in agreement with tree rings from a comparable urban area (Krakow; Rakowski et al. 2013).

We have also compared the obtained Bratislava tree-ring data with our regional background tree-ring data set from Jasná sampling location (Figure 5). This site is located in the Low Tatras mountain region in central Slovakia, and it is not influenced by any significant local fossil CO_2 emission sources (Kontuľ et al. 2020). This data set is in very good agreement with clean air reference data from Schauinsland. The tree-ring radiocarbon levels in Bratislava are about 250‰ lower than Jasná clean-air tree rings in 1970. This difference slowly decreases over time to virtually zero difference in 1995–1998, indicating a significantly higher input of fossil CO_2 into the atmosphere of Bratislava in 1970s and 1980s compared to 1990s and 2000s. Bratislava tree-ring data and background data (Jasná and Schauinsland) can be used

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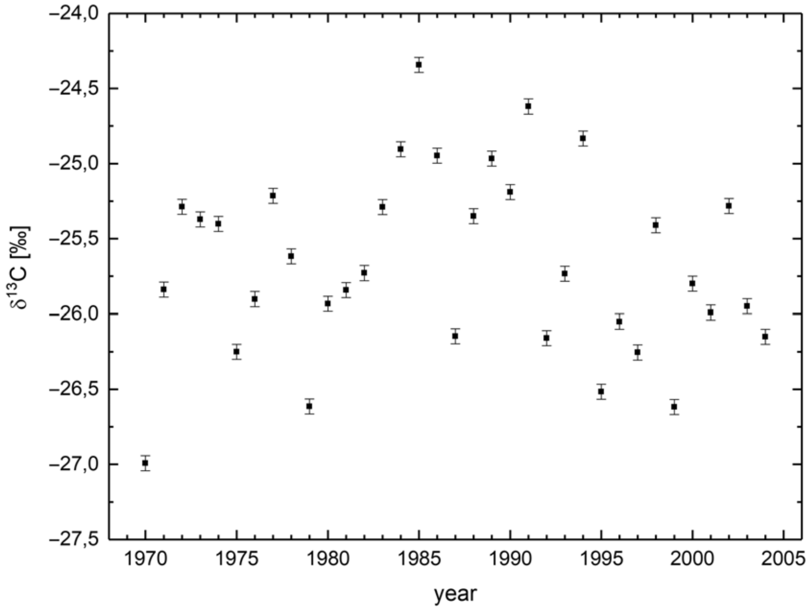

Figure 4 δ^{13}C in the analyzed tree-ring samples.

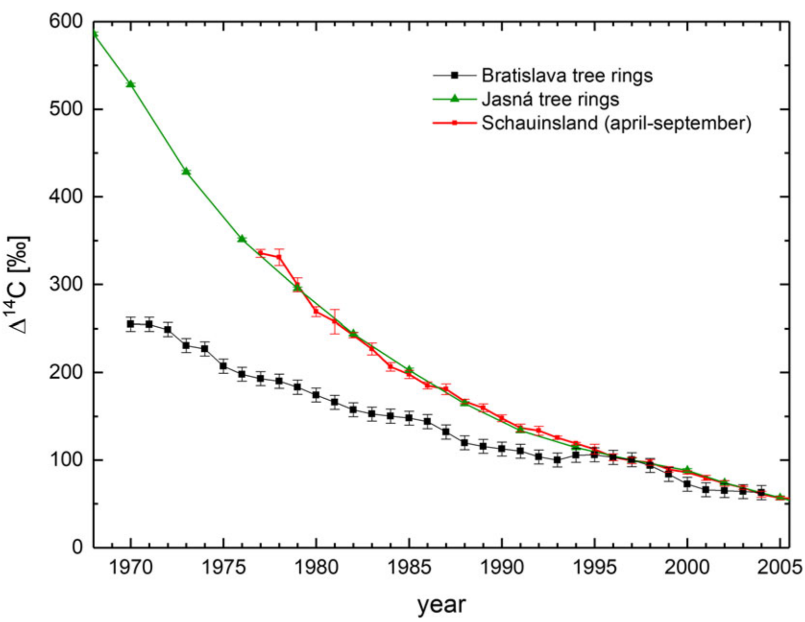

Figure 5 Comparison of ^{14}C activity measured in Bratislava tree rings with ^{14}C levels in tree rings from regional clean air reference sampling site in Jasná (Kontuľ et al. 2020).

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to determine the mixing ratio of fossil CO_2 in the total CO_2 in the sampled atmospheric air (expressed as percentage of fossil-derived CO_2 in the total CO_2 concentration) based on the method described by Levin et al. (2003). The mean mixing ratio of fossil-derived CO_2 was highest in 1970s (11.5%) and gradually decreased to 5.0% in 1980s and 1.3% in 1990s.

In 1994–1995 there is a small change in the decreasing trend of radiocarbon activity of tree-rings, the activity slightly increased and reached clean air values. A similar change has also been observed in a previously measured tree-ring record from a rural area ca. 30 km northwest from Bratislava (Kontuľ et al. 2017). This could be caused by a weaker Suess effect, an increase of anthropogenic ^{14}C releases or a combination of these two effects. Anthropogenic radiocarbon from nuclear power plants can indeed be a contributing factor, because given specific meteorological conditions there is a correlation between atmospheric radiocarbon activity at Žlkovce sampling station (close to the Bohunice nuclear power plant) and Bratislava sampling site (Povinec et al. 2008). But frequency of air mass transport from the direction of closest nuclear power plant is relatively low (several percent) and therefore weaker Suess effect is probably the dominant factor. This is also supported by CO_2 emission data for Slovakia showing a decreasing trend from year 1990 onward (MESR 2017).

CONCLUSIONS

Radiocarbon analysis of tree rings from Bratislava was used to extend the radiocarbon record for this sampling site further into the past and compare ^{14}C levels in the biosphere with the available monthly atmospheric data. Both the atmospheric and tree-ring radiocarbon levels are considerably lower than clean air background data. These extremely low values clearly indicate significant influence of fossil CO_2 released into the atmosphere. Data shows that this effect is not constant over the studied time period (1970–2004). The difference between clean air reference values and measured radiocarbon content of tree rings was slowly decreasing since the beginning of this tree-ring record. In the period before 1994 the difference is much larger than in the years following 1994, where the difference between Bratislava tree rings and clean air data is minimal. This is in all likelihood caused mainly by decreasing CO_2 emissions in the region during 1990s. Anthropogenic ^{14}C produced and released from Bohunice nuclear power plant in western Slovakia can also be a contributing factor in increasing ^{14}C activity to clean air levels, but its influence is much smaller than the effect of reduced fossil CO_2 emissions.

Comparison of tree-ring data with atmospheric $^{14}CO_2$ data shows that the studied tree did not efficiently record the high maxima or deep minima that occurred during the expected growing season. This is probably caused by the rapid nature of these ^{14}C-influencing occurrences—they are intense enough to influence monthly atmospheric data, but they do not have observable effect on a tree that integrates carbon from the atmosphere at a slower rate and during a several-times-longer time period.

Tree rings from the last part of the record (1994–2004) show a good agreement with the mean atmospheric values calculated for the expected growing season. The results indicate that the circumstances influencing radiocarbon levels in the atmosphere and biosphere changed in this period. Not only is the radiocarbon activity in the atmosphere much more stable, but the ^{14}C activity in both atmosphere and biosphere reaches almost clean air levels.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2022.95

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