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CALIBRATION ISSUES OF THE TREE RING RECORDS FROM THE BOMB PERIOD IN CROATIA

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Keywords:	Radiocarbon, NH1 and NH2 zone, tree rings, Croatia
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	Tijarovićeva street and V. Njegovana street in Zagreb for comparison. Average values of absolute differences between radiocarbon results ($\Delta^{14}C$) from both locations and NH1 and NH2 radiocarbon values were calculated. The average of absolute differences between zones and the location Crna Mlaka for zone NH1 is (13 ± 4) ‰, and for zone NH2 is (23 ± 10) ‰. The reduced $\chi 2$ values indicate a preference for NH1 zone for Crna Mlaka site, while the IRB location proved unsuitable for drawing conclusions because the impact of fossil fuels was observed.

SCHOLARONE MANUSCRIPTS

CALIBRATION ISSUES OF THE TREE RING RECORDS FROM THE BOMB PERIOD IN CROATIA

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ABSTRACT

Croatia is situated between 42°23′ and 46°33′ north latitude, and 13°30′ and 19°27′ east longitude. Due to its position within the boundary between NH1 and NH2 zones (Hua et al. 2022), the calibration of radiocarbon results for samples from the bomb peak period raises an issue regarding the choice of the calibration curve. To resolve this issue, radiocarbon analyses of tree rings from Croatian wood were performed. Wood was sampled at two main locations IRB (Zagreb, Croatia's Capital) (45°49' N, 15°59' E) and Crna Mlaka (45°34' N, 15°46' E), 30 km away from Zagreb. 23 tree ring samples were radiocarbon analysed from each location. Additionally, two tree ring samples were analysed from locations Tijarovićeva street and V. Njegovana street in Zagreb for comparison. Average values of absolute differences between radiocarbon results ($\Delta^{14}C$) from both locations and NH1 and NH2 radiocarbon values were calculated. The average of absolute differences between zones and the location Crna Mlaka for zone NH1 is (13 ± 4) ‰, and for zone NH2 is (23 ± 10) ‰. The reduced χ^2 values indicate a preference for NH1 zone for Crna Mlaka site, while the IRB location proved unsuitable for drawing conclusions because the impact of fossil fuels was observed.

INTRODUCTION

^{14}C occurs naturally in the Earth's upper atmosphere, where it rapidly oxidizes to $^{14}CO_2$ and enters the global carbon cycle. Under pre-industrial steady-state conditions, the atmospheric $^{14}C/^{12}C$ ratio fluctuated within relatively narrow natural boundaries controlled primarily by variations in cosmic ray intensity modulated by solar activity and geomagnetic field strength (Reimer *et al.* 2020; Stuiver and Quay 1980).

This equilibrium was disrupted during the 20th century by the fossil fuel production during industrialization and by the large-scale atmospheric testing of thermonuclear weapons. Between 1955 and 1963, approximately 600–700 Mt of fission products injected an estimated 10^{28} atoms of ^{14}C directly into the stratosphere and the troposphere (Turnbull *et al.* 2016). This caused a near-doubling of $^{14}C/^{12}C$ ratio of the atmospheric $^{14}CO_2$ reaching a peak (so-called

"the bomb peak") in 1963 (Naegler and Levin 2006). Nearly all tests were conducted above ground or in the lower atmosphere before the 1963 Partial Test Ban Treaty. The artificially produced ^{14}C mixed rapidly into the stratosphere and the troposphere and has been taken up by the biosphere and the ocean.

Regarding radiocarbon dating, it is important to know the spatial distribution of ^{14}C for developing of accurate calibration curves. Hua and Barbetti (2004) defined a special distribution of ^{14}C, NH (Northern Hemisphere) and SH (Southern Hemisphere), for a better understanding of the carbon cycle and accurate ^{14}C dating. The difference in spatial distribution of ^{14}C is especially pronounced within the bomb peak period and therefore, three zones are defined for the Northern hemisphere and two zones for the Southern hemisphere. The $^{14}C/^{12}C$ ratio is the highest in the NH1 and the lowest in the SH1-2 zone (Hua *et al*. 2013; 2022). Depending on the location of the sample to be radiocarbon dated, the selection of the proper zone for calibration of results is essential for obtaining reliable results. Calibration curves for the bomb peak period are included in calibration programs such as Oxcal (Bronk Ramsey 1995) or CaliBomb (Reimer *et al*. 2004) and can be easily selected. The problem may occur if the sampling area lies on the boundary of two zones, as is the case in Croatia. Croatia is situated between 42°23′ and 46°33′ N and 13°30′ and 19°27′ E. Due to its position within the boundary between NH1 and NH2 zones, the calibration of radiocarbon results for samples from the bomb peak period could raise an issue regarding the choice between zones, i.e., calibration curves. To resolve this issue, radiocarbon analyses of tree rings from wood from two main locations in Croatia were performed and compared to the NH1 and NH2 zones (Hua *et al.* 2022).

SAMPLING LOCATIONS

Trees were collected from multiple locations (Figure 1). Within the city of Zagreb, a region exposed to fossil fuel exploitation/emissions, trees were sampled from three different locations, one tree per location. The main location was IRB (abbreviation for the Ruđer Bošković Institute, 45°49′46.88″ N, 15°59′14.54″ E, altitude 186 m), while the other two, Tijardovićeva street (45°47'42.52" N, 15°54'7.02" E, altitude 118 m) and V. Njegovana street (45°47'24.10" N, 15°56'52.42" E, altitude 115 m), were used for comparison. The two locations are expected to have even more fossil fuel exposure than IRB because they are in more populated areas of the city. The other main location, Crna Mlaka (45°34′29.65″ N, 15°46′14.17″ E, altitude 110 m) is considered to be a location without local fossil fuel influence. It is located inside the bird sanctuary Crna Mlaka. The approximate distance between the main locations Crna Mlaka and Zagreb is 30 km. All locations are characterized by the Cfa climate type, moderately warm and humid with hot summers (Peel *et al.* 2007; Beck *et al.* 2018) with prevailing N and NE winds (Zaninović *et al*. 2008, Likso and Panžić 2012, Lisac 1984).

Figure 1.

SAMPLING, SAMPLE PREPARATION AND MEASURING TECHNIQUE

All sampled trees were deciduous species with growing period spring / summer: *Quercus robur* from Crna Mlaka location, and *Gymnodadus dioicus, Acer* spp. and *Sophora japonica* from IRB, V. Njegovana and Tijardovićeva St. locations, respectively. The year of the tree's death was known and it was attributed to the year of the last tree ring (Table 1).

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A wood slice (cross section) of approximately 5 cm thickness of each sampled wood was cut. The tree ring analysis was conducted at the Laboratory of Dendrochronology and Forest Resources Inventory, Faculty of Forestry and Wood Technology. To enhance the visibility of the tree rings, the analysed segment of the tree disc was sanded using a belt sander with various grit sizes. Tree-ring widths were measured using the TSAP-Win software suite for tree-ring measurement and analysis, coupled with a Lintab 6 measuring table and a Leica M50 stereomicroscope. Tree rings were counted, referring to the year of the last tree ring (Rede *et al.* 2022; Sinković *et al.* 2009) and samples for analysis were taken within straight line of the cross section ranging from the middle to the outer layer of wood. A sterile drill was used to take a sample of a particular tree ring, ranging from 50-300 mg of sampled material, taking care that only targeted ring is sampled. The drills used were 3 mm in diameter. The tree rings ranged from 3 mm to 8 mm (approximately). Whenever the tree ring was wider than the drill, drilling was made in the middle of the tree ring.

One sample per tree ring was analyzed. This unprocessed wood raw material was then subjected to chemical treatment. During the chemical treatment alpha-cellulose was extracted to obtain representative ^{14}C activity signal from an individual tree ring (Hoper *et al.* 1998). Soluble organic compounds (e.g., resins and oils) were first removed using solvents (soaking in ethanol: chloroform, 1:2 at 60 C, for 40 minutes, decanting and repeat three times, followed by soaking sample in 96 % ethanol at 70 C for 40 minutes, repeat three times and ultrapure water rinse three times). Solvents treatment was followed by bleaching with 1.5% sodium hypochlorite to oxidize and remove resins, lignin, and other mobile wood fractions, that can potentially migrate from adjacent tree rings and contaminate the sampled ring with ^{14}C originating from other years (Southon and Magana 2010; Cain and Suess 1976; Stuiver and Quay 1981). Finally, the standard ABA (acid–base–acid) procedure was applied to remove any residual acids and other contaminants. Dried samples were combusted and the CO_2 obtained was converted to graphite by zinc reduction (Krajcar Bronić *et al.* 2010; Sironić *et al.* 2013).

Totally of twenty tree ring samples were analysed at the two main locations, IRB and Crna Mlaka, covering the time span 1940 – 2018 and 1896 – 2016, respectively. A total of three samples were analysed from Tijardovićeva street and six samples from V. Njegovana street and the time periods covered were 1982 – 2008 and 1964 – 2018, respectively.

$^{14}C/^{13}C$ ratio of the graphite samples were measured by accelerator mass spectrometry (AMS) at the Center for Applied Isotope Studies, University of Georgia (Cherkinsky *et al.* 2010). Additionally, an aliquot of CO_2 from each sample was sealed in a glass tube for the determination of $\delta^{13}C$ value with an isotope ratio mass spectrometer (IRMS) at the same institution. The ^{14}C values are expressed to AD 1950 according to the radiocarbon convention as $\Delta^{14}C$ (‰) quantity, which is isotope fractionation normalised value ($\delta^{13}C$ to -25 ‰) and age-corrected deviation from the standard pre-industrial content of ^{14}C ($\Delta^{14}C$ = 0 ‰) (Mook and van der Plicht 1999; van der Plicht and Hogg 2006), so they can directly be compared to $\Delta^{14}C$ in Hua *et al*. (2022). $\Delta^{14}C$ is the Δ term of Stuiver *et al*. (1977).

RESULTS AND DISCUSSION

The obtained results were compared with those of Hua *et al*. (2022) and can be seen in Figure 2 and Table 1 (measurement results of analysed data). The results are in good agreement with the curves for NH1 and NH2 (Hua *et al.* 2022).

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128 Table 1. $\Delta^{14}C$ analyses of tree rings from the investigated locations

Year of tree ring growth	Locations			
	IRB	Crna Mlaka	V. Njegovana St.	Tijardovićeva St.
1896		-0.5 ± 2.7		
1906		-8.7 ± 2.7		
1916		-6.9 ± 2.7		
1926		-16.6 ± 2.8		
1936		-16.6 ± 2.7		
1940	-20.0 ± 2.7			
1942				
1946		-18.5 ± 2.7		
1951	-26.2 ± 2.7			
1952		-27.5 ± 2.8		
1956	-27.8 ± 2.9	36.4 ± 2.8		
1960	66.7 ± 3.1	238.6 ± 3.4		
1961	231.6 ± 3.1			
1962	296.7 ± 4.9	429.8 ± 3.7		
1963	795.6 ± 4.6			
1964		849.5 ± 4.8	881.3 ± 5.5	
1965	768.3 ± 4.5			
1966		695.4 ± 4.3		
1967	651.7 ± 4.2			
1969	568.5 ± 4.2			
1970		549.2 ± 4.1	543.7 ± 4.5	
1971	513.3 ± 3.9			
1972				
1975	379.6 ± 3.7			
1976		362.7 ± 3.5		
1981	260.9 ± 3.2			
1982		244.7 ± 3.3	218.9 ± 4.2	209.7 ± 3.4
1985	197.8 ± 3.3			
1986		198.6 ± 3.1		
1991	136.8 ± 3.0			
1992		134.0 ± 3.1		
1995	106.9 ± 3.1			
1996		113.4 ± 2.9	99.2 ± 4.2	99.4 ±3.2
2001	79.6 ± 3.0			
2005	52.8 ± 3.0			
2006		59.0 ± 2.8	46.2 ± 3.4	
2008				-0.2 ± 2.8
2011	28.9 ± 2.8			
2016		25.2 ± 2.7		
2018	2.0 ± 2.8		0.1 ± 3.6	

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Figure 2.

The $\Delta^{14}C$ measurements from the site Crna Mlaka cover the longest time span, from 1896 to 2016, and thus encompass the period when only anthropogenic influence on ^{14}C composition of atmospheric CO_2 was the Suess effect (Tans *et al*. 1979), all the way after the bomb peak. In the Crna Mlaka results, a decline in $\Delta^{14}C$ levels before the bomb onset is clearly observed, a large increase during the era of nuclear weapons testing and a quasi-exponential decrease starting around 1964, similar to data from Hua *et al*. (2022). The drop in $\Delta^{14}C$ before the bomb peak indicates that even locations that are not locally exposed to fossil-fuel sources are affected by the global influence of fossil-fuel CO_2 and that this global signal is superimposed on any local effects.

The results from the IRB location, a site exposed to fossil-fuel influence, also display all the key features (the Suess effect, sharp increase, quasi-exponential decline). At location IRB, however, we observe a delayed rise in $\Delta^{14}C$ that begins after 1956, later than at Crna Mlaka and the reference results for the NH1 and NH2 zones (Hua *et al.* 2022). $\Delta^{14}C$ from 1963 to 1985 fit well to the both reference curves and Crna Mlaka location. From 1985 $\Delta^{14}C$ values at IRB location shows decline which can be explained by increasing urbanization at IRB location and fossil fuel ^{14}C dilution. The delayed rise is somewhat harder to explain. One possible contribution could be from the "memory effect" in earlywood, which was predominantly sampled for the tree ring in ^{14}C analysis. The early wood can contain more components from earlier years if tree is recycling some of its molecules, (drawing non-structural carbon from branches and roots) during low photosynthesis period, i.e. early spring (Svarva *et al*. 2025). This memory effect is then shown as a "delay" in the ^{14}C-year curve. On the left side of the bomb onset, the differences from IRB location are much larger than on the right side. So, additional contributions are probably having an influence. The left side of the bomb onset curve has a steeper slope and is consequently more sensitive to the sampling procedure, i.e. smaller deviations in the sampling can give different results. The sampling of the whole ring in the case of narrow rings, and middle of the ring in the case of wider rings could affect the measured ^{14}C values, especially for the bomb peak period.

The comparison sites in the city of Zagreb, also affected by fossil fuels (Tijardovićeva St. and V. Njegovana St.), show relatively lower $\Delta^{14}C$ values than the location IRB, indicating an even stronger fossil-fuel influence, which is expected, as these sites are situated in the city-center of Zagreb.

The differences between our measurement sites and the NH1 and NH2 zones (Hua *et al.* 2022) are shown in Figure 3. Generally, the largest difference arises around the bomb peak due to sensitivity to the errors in sampling, i.e. small mismatch in the year of sampling has a large difference in $\Delta^{14}C$ value due to the nature of the curve.

Figure 3.

To quantify the difference between our main locations and the NH zones, the average value of the difference of absolute values between our measurements and NH zones is calculated with the following formula (Eq 1)

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$$\overline{X} = \frac{1}{N} \cdot \sum_i^N Abs(Value_i - NH_i) \quad \text{Eq 1}$$

where N is the number of our measurements for a particular location. NH_i is the corresponding $\Delta^{14}C$ value of the NH zone, and the $Value_i$ is the measured value.

The mean of the absolute values of the difference $\overline{X}$ between the NH1 zone and the main location IRB is (29 ± 10) ‰, while for the NH2 zone it is (26 ± 9) ‰. There is no a tendency for the location IRB to be closer to any zone.

A statistically non-significant tendency toward the NH1 zone is observed at the site Crna Mlaka, where the $\overline{X}$ is (13 ± 4) ‰ relative to the NH1 zone and (23 ± 10) ‰ relative to the NH2 zone. Overall, the IRB location in Zagreb follows the reference data of Hua *et al*. (2022) less closely than Crna Mlaka does.

The largest differences relative to the NH zones occur around the top of the bomb peak, which can be attributed to the fact that even small deviations in the time domain lead to large deviations in $\Delta^{14}C$, meaning the sensitivity of $\Delta^{14}C$ to the year of measurement around the bomb peak is high. In order to check goodness of fit between $\Delta^{14}C$ values obtained at analysed locations and NH1 and NH2 curves, a χ^2 value was estimated according to Raj *et al*. (2023) which described similar issue on the suitability of zones: although sampling area, Northern Israel, falls into a NH 2 zone, radiocarbon tree ring data for period of maximum ^{14}C activity (tree rings from 1964 – 1968) were closer to NH1 zone. χ^2 value was calculated from Eq 2 (Bronk Ramsey *et al*. 2001.):

$$\chi^2 = \sum \frac{(Value_i - NH_i)^2}{(\sigma^2_{Valuei} + \sigma^2_{NHi})} \quad \text{Eq 2}$$

The marks are the same as in Eq 1.

The reduced χ^2 values with 1σ values considered for all locations and both atmospheric curves are presented in Table 2. The closer the value to 1, the better is the fit.

Table 2. Reduced χ^2 values with 1σ values considered. N – number of measurements

Atmospheric curve	IRB N = 19	Crna Mlaka N = 14	V. Njegovana St.; N = 6	Tijardovićeva St., N = 3
NH1	1.41	3.67	3.50	95.53
NH2	1.39	9.43	5.20	95.53

Reduced χ^2 values imply that IRB values fit good to both atmospheric curves since reduced χ^2 values are very close to 1 based on 1σ values. Crna Mlaka shows discrepancy from NH curves, but reduced χ^2 value of 3.67 for NH1 curve and 9.43 for NH2 curve indicates better fitting to NH1 zone. If reduced χ^2 value is based on 3σ values, this would give reduced χ^2 of 1.48 for NH1 curve and 3.14 for NH2 curve clearly indicating better fitting of Crna Mlaka location to NH1 zone. Regarding the two additional sites V. Njegovana is similar to Crna Mlaka location, and fits better to NH1 than NH2, while for Tijardovićeva St. there are only three data that fit

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within the part in which atmospheric curves does not differ. It should be noted that for both additional sites the data sets are too small to achieve relevant statistics.

CONCLUSION

Croatia is located between zones NH1 and NH2. The calibration of radiocarbon results for samples from the bomb period raises an issue regarding the choice of the calibration curve. To resolve this issue, radiocarbon analyses of tree rings from Croatia were performed. Tree rings were sampled at two main locations IRB (Zagreb) and Crna Mlaka (30 km from Zagreb). Twenty tree ring samples were radiocarbon analyzed from the two locations, together with some additional comparison specimens. Average values of absolute differences between radiocarbon results, as well as reduced χ^2 from both locations and the NH1 and NH2 zones were calculated. It is shown that the location IRB was strongly affected by the fossil fuel emissions, so conclusions on preferences to any zone cannot be withdrawn from data collected at this location. The Crna Mlaka location, clean air site location, showed non-significant preference for the NH1 zone based on differences between radiocarbon results observed. Reduced χ^2 from Crna Mlaka and the NH1 and NH2 curves indicate that Crna Mlaka site fits better to NH1 zone. According to observed analyses, it may be concluded that samples from continental Croatia, sites north of Crna Mlaka, which belong to the bomb peak period, should be calibrated by NH1 atmospheric curve. This conclusion is also corroborated with wind direction at investigated area, as the prevailing N and NE winds bring air masses from NH1 zone. Additional investigations of tree rings from clean-air sites situated south of Crna Mlaka should be performed to establish suitability between NH1 and NH2 zones for samples from Southern and Mediterranean part of Croatia.

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CALIBRATION ISSUES OF THE TREE RING RECORDS FROM THE BOMB PERIOD IN CROATIA

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ABSTRACT

Croatia is situated between 42°23′ and 46°33′ north latitude, and 13°30′ and 19°27′ east longitude. Due to its position within the boundary between NH1 and NH2 zones (Hua et al. 2022), the calibration of radiocarbon results for samples from the bomb peak period raises an issue regarding the choice of the calibration curve. To resolve this issue, radiocarbon analyses of tree rings from Croatian wood were performed. Wood was sampled at two main locations IRB (Zagreb, Croatia's Capital) (45°49' N, 15°59' E) and Crna Mlaka (45°34' N, 15°46' E), 30 km away from Zagreb. 23 tree ring samples were radiocarbon analysed from each location. Additionally, two tree ring samples were analysed from locations Tijarovićeva street and V. Njegovana street in Zagreb for comparison. Average values of absolute differences between radiocarbon results ($\Delta^{14}C$) from both locations and NH1 and NH2 radiocarbon values were calculated. The average of absolute differences between zones and the location ~~IRB for zone NH1 is (29 ± 10) ‰, while for zone NH2 it is (26 ± 9) ‰. At the~~ Crna Mlaka ~~location, the average of absolute differences between zones and the location~~ for zone NH1 is (13 ± 4) ‰, and for zone NH2 is (23 ± 10) ‰. The reduced χ^2 values indicate a preference for NH1 zone for Crna Mlaka site, while ~~IRB location fits well to the both zones.~~ the IRB location proved unsuitable for drawing conclusions because the impact of fossil fuels was observed.

INTRODUCTION

^{14}C occurs naturally in the Earth's upper atmosphere, where it rapidly oxidizes to $^{14}CO_2$ and enters the global carbon cycle. Under pre-industrial steady-state conditions, the atmospheric $^{14}C/^{12}C$ ratio fluctuated within relatively narrow natural boundaries controlled primarily by variations in cosmic ray intensity modulated by solar activity and geomagnetic field strength (Reimer *et al.* 2020; Stuiver and Quay 1980).

This equilibrium was disrupted during the 20th century by the fossil fuel production during industrialization and by the large-scale atmospheric testing of thermonuclear weapons. Between 1955 and 1963, approximately 600–700 Mt of fission products injected an estimated

10^{28} atoms of ^{14}C directly into the stratosphere and the troposphere (Turnbull *et al.* 2016). This caused a near-doubling of $^{14}C/^{12}C$ ratio of the atmospheric $^{14}CO_2$ reaching a peak (so-called "the bomb peak") in 1963 (Naegler and Levin 2006). Nearly all tests were conducted above ground or in the lower atmosphere before the 1963 Partial Test Ban Treaty. The artificially produced ^{14}C mixed rapidly into the stratosphere and the troposphere and has been taken up by the biosphere and the ocean.

Regarding radiocarbon dating, it is important to know the spatial distribution of ^{14}C for developing of accurate calibration curves. Hua and Barbetti (2004) defined a special distribution of ^{14}C, NH (Northern Hemisphere) and SH (Southern Hemisphere), for a better understanding of the carbon cycle and accurate ^{14}C dating. The difference in spatial distribution of ^{14}C is especially pronounced within the bomb peak period and therefore, three zones are defined for the Northern hemisphere and two zones for the Southern hemisphere. The $^{14}C/^{12}C$ ratio is the highest in the NH1 and the lowest in the SH1-2 zone (Hua *et al*. 2013; 2022). Depending on the location of the sample to be radiocarbon dated, the selection of the proper zone for calibration of results is essential for obtaining reliable results. Calibration curves for the bomb peak period are included in calibration programs such as Oxcal (Bronk Ramsey 1995) or ~~Calib (Stuiver~~CaliBomb (Reimer *et al*. ~~2013~~2004) and can be easily selected. The problem may occur if the sampling area lies on the boundary of two zones, as is the case in Croatia. Croatia is situated between 42°23′ and 46°33′ N and 13°30′ and 19°27′ E. Due to its position within the boundary between NH1 and NH2 zones, the calibration of radiocarbon results for samples from the bomb peak period could raise an issue regarding the choice between zones, i.e., calibration curves. To resolve this issue, radiocarbon analyses of tree rings from wood from two main locations in Croatia were performed and compared to the NH1 and NH2 zones (Hua *et al.* 2022).

SAMPLING LOCATIONS

Trees were collected from multiple locations (Figure 1). Within the city of Zagreb, a region exposed to fossil fuel exploitation/emissions, trees were sampled from three different locations, one tree per location. The main location was IRB (abbreviation for the Ruđer Bošković Institute, 45°49′46.88″ N, 15°59′14.54″ E, altitude 186 m), while the other two, Tijardovićeva street (45°47'42.52" N, 15°54'7.02" E, altitude 118 m) and V. Njegovana street (45°47'24.10" N, 15°56'52.42" E, altitude 115 m), were used for comparison. The two locations are expected to have even more fossil fuel exposure than IRB because they are in more populated areas of the city. The other main location, Crna Mlaka (45°34′29.65″ N, 15°46′14.17″ E, altitude 110 m) is considered to be a location without local fossil fuel influence. It is located inside the bird sanctuary Crna Mlaka. The approximate distance between the main locations Crna Mlaka and Zagreb is 30 km. All locations are characterized by the Cfa climate type, moderately warm and humid with hot summers (Peel *et al.* 2007; Beck *et al.* 2018) with prevailing N and NE winds (Zaninović *et al*. 2008, Likso and Panžić 2012, Lisac 1984~~-~~).

Figure 1.

SAMPLING, SAMPLE PREPARATION AND MEASURING TECHNIQUE

All sampled trees were deciduous species with growing period spring / summer: *Quercus robur* from Crna Mlaka location, and *Gymnodadus dioicus, Acer* spp. and *Sophora japonica* from

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IRB, V. Njegovana and Tijardovićeva St. locations, respectively. The year of the tree's death was known and it was attributed to the year of the last tree ring (Table 1).

A wood slice (cross section) of approximately 5 cm thickness of each sampled wood was cut. The tree ring analysis was conducted at the Laboratory of Dendrochronology and Forest Resources Inventory, Faculty of Forestry and Wood Technology. To enhance the visibility of the tree rings, the analysed segment of the tree disc was sanded using a belt sander with various grit sizes. Tree-ring widths were measured using the TSAP-Win software suite for tree-ring measurement and analysis, coupled with a Lintab 6 measuring table and a Leica M50 stereomicroscope. Tree rings were counted, referring to the year of the last tree ring (Rede *et al.* 2022; Sinković *et al.* 2009) and samples for analysis were taken within straight line of the cross section ranging from the middle to the outer layer of wood. A sterile drill was used to take a sample of a particular tree ring, ranging from 50-300 mg of sampled material~~.~~, taking care that only targeted ring is sampled. The drills used were 3 mm in diameter. The tree rings ranged from 3 mm to 8 mm (approximately). Whenever the tree ring was wider than the drill, drilling was made in the middle of the tree ring.

One sample per tree ring was analyzed. This unprocessed wood raw material was then subjected to chemical treatment. During the chemical treatment alpha-cellulose was extracted to obtain representative ^{14}C activity signal from an individual tree ring (Hoper *et al.* 1998). Soluble organic compounds (e.g., resins and oils) were first removed using solvents (soaking in ethanol: chloroform, 1:2 at 60 C, for 40 minutes, decanting and repeat three times, followed by soaking sample in 96 % ethanol~~)~~, at 70 C for 40 minutes, repeat three times and ultrapure water rinse three times). Solvents treatment was followed by bleaching with 1.5% sodium hypochlorite to oxidize and remove ~~lignin~~resins, lignin, and other mobile wood fractions, that can potentially migrate from adjacent tree rings and contaminate the sampled ring with ^{14}C originating from other years~~.~~ (Southon and Magana 2010; Cain and Suess 1976; Stuiver and Quay 1981). Finally, the standard ABA (acid–base–acid) procedure was applied to remove any residual acids and other contaminants. Dried samples were combusted and the CO_2 obtained was converted to graphite by zinc reduction (Krajcar Bronić *et al.* 2010; Sironić *et al.* 2013).

Totally of twenty tree ring samples were analysed at the two main locations, IRB and Crna Mlaka, covering the time span 1940 – 2018 and 1896 – 2016, respectively. A total of three samples were analysed from Tijardovićeva street and six samples from V. Njegovana street and the time periods covered were 1982 – 2008 and 1964 – 2018, respectively.

$^{14}C/^{13}C$ ratio of the graphite samples were measured by accelerator mass spectrometry (AMS) at the Center for Applied Isotope Studies, University of Georgia (Cherkinsky *et al.* 2010). Additionally, an aliquot of CO_2 from each sample was sealed in a glass tube for the determination of $\delta^{13}C$ value with an isotope ratio mass spectrometer (IRMS) at the same institution. The ^{14}C values are expressed to AD 1950 according to the radiocarbon convention as $\Delta^{14}C$ (‰) quantity, which is isotope fractionation normalised value ($\delta^{13}C$ to -25 ‰) and age-corrected deviation from the standard pre-industrial content of ^{14}C ($\Delta^{14}C$ = 0 ‰) (Mook and van der Plicht 1999; van der Plicht and Hogg 2006), so they can directly be compared to $\Delta^{14}C$ in Hua *et al*. (2022). $\Delta^{14}C$ is the Δ term of Stuiver *et al*. (1977).

RESULTS AND DISCUSSION

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The obtained results were compared with those of Hua *et al*. (2022) and can be seen in Figure 2 and Table 1 (measurement results of analysed data). The results are in good agreement with the curves for NH1 and NH2 (Hua *et al.* 2022).

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131 Table 1. $\Delta^{14}C$ analyses of tree rings from the investigated locations

Year of tree ring growth	Locations			
	IRB	Crna Mlaka	V. Njegovana St.	Tijardovićeva St.
1896		-0.5 ± 2.7		
1906		-8.7 ± 2.7		
1916		-6.9 ± 2.7		
1926		-16.6 ± 2.8		
1936		-16.6 ± 2.7		
1940	-20.0 ± 2.7			
1942				
1946		-18.5 ± 2.7		
1951	-26.2 ± 2.7			
1952		-27.5 ± 2.8		
1956	-27.8 ± 2.9	36.4 ± 2.8		
1960	66.7 ± 3.1	238.6 ± 3.4		
1961	231.6 ± 3.1			
1962	296.7 ± 4.9	429.8 ± 3.7		
1963	795.6 ± 4.6			
1964		849.5 ± 4.8	881.3 ± 5.5	
1965	768.3 ± 4.5			
1966		695.4 ± 4.3		
1967	651.7 ± 4.2			
1969	568.5 ± 4.2			
1970		549.2 ± 4.1	543.7 ± 4.5	
1971	513.3 ± 3.9			
1972				
1975	379.6 ± 3.7			
1976		362.7 ± 3.5		
1981	260.9 ± 3.2			
1982		244.7 ± 3.3	218.9 ± 4.2	209.7 ± 3.4
1985	197.8 ± 3.3			
1986		198.6 ± 3.1		
1991	136.8 ± 3.0			
1992		134.0 ± 3.1		
1995	106.9 ± 3.1			
1996		113.4 ± 2.9	99.2 ± 4.2	99.4 ±3.2
2001	79.6 ± 3.0			
2005	52.8 ± 3.0			
2006		59.0 ± 2.8	46.2 ± 3.4	
2008				-0.2 ± 2.8
2011	28.9 ± 2.8			
2016		25.2 ± 2.7		
2018	2.0 ± 2.8		0.1 ± 3.6	

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Figure 2.

The $\Delta^{14}C$ measurements from the site Crna Mlaka cover the longest time span, from 1896 to 2016, and thus encompass the period when only anthropogenic influence on ^{14}C composition of atmospheric CO_2 was the Suess effect (Tans *et al*. 1979), all the way after the bomb peak. In the Crna Mlaka results, a decline in $\Delta^{14}C$ levels before the bomb ~~peak~~onset is clearly observed, a large increase during the era of nuclear weapons testing and a quasi-exponential decrease starting around 1964, similar to data from Hua *et al*. (2022). The drop in $\Delta^{14}C$ before the bomb peak indicates that even locations that are not locally exposed to fossil-fuel sources are affected by the global influence of fossil-fuel CO_2 and that this global signal is superimposed on any local effects.

The results from the IRB location, a site exposed to fossil-fuel influence, also display all the key features (the Suess effect, sharp increase, quasi-exponential decline). At location IRB, however, we observe a delayed rise in $\Delta^{14}C$ that begins after 1956, later than at Crna Mlaka and the reference results for the NH1 and NH2 zones (Hua *et al.* 2022). $\Delta^{14}C$ from 1963 to 1985 fit well to the both reference curves and Crna Mlaka location. From 1985 $\Delta^{14}C$ values at IRB location shows decline which can be explained by increasing urbanization at IRB location and fossil fuel ^{14}C dilution. The delayed rise is somewhat harder to explain. One possible contribution ~~coud~~could be from the "memory effect" in earlywood, which was predominantly sampled for the tree ring in ^{14}C analysis. The early wood can contain more components from earlier years if tree is recycling some of its molecules, (drawing non-structural carbon from branches and roots) during low photosynthesis period, i.e. early spring (Svarva *et al*. 2025). This memory effect is then shown as a "delay" in the ^{14}C-year curve. On the left side of the bomb ~~peak~~onset, the differences from IRB location are much larger than on the right side. So, additional contributions are probably having an influence. The left side of the bomb ~~peak~~onset curve has a steeper slope and is consequently more sensitive to the sampling procedure, i.e. smaller deviations in the sampling can give different results. The sampling of the whole ring in the case of narrow rings, and middle of the ring in the case of wider rings could affect the measured ^{14}C values, especially for the bomb peak period.

The comparison sites in the city of Zagreb, also affected by fossil fuels (Tijardovićeva St. and V. Njegovana St.), show relatively lower $\Delta^{14}C$ values than the location IRB, indicating an even stronger fossil-fuel influence, which is expected, as these sites are situated in the city-center of Zagreb.

The differences between our measurement sites and the NH1 and NH2 zones (Hua *et al.* 2022) are shown in Figure 3. Generally, the largest difference arises around the bomb peak due to sensitivity to the errors in sampling, i.e. small mismatch in the year of sampling has a large difference in $\Delta^{14}C$ value due to the nature of the curve. ~~It is interesting to note that from a peak value onward, the $\Delta^{14}C$ values at the IRB location are larger than those of Crna Mlaka up to 1993. That behavior suggests increased fossil usage from 1993 onward on the IRB location.~~

Figure 3.

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To quantify the difference between our main locations and the NH zones, the average value of the difference of absolute values between our measurements and NH zones is calculated with the following formula (Eq 1)

$$\overline{X} = \frac{1}{N} \cdot \sum_i^N Abs(Value_i - NH_i) \qquad \text{Eq 1}$$

where N is the number of our measurements for a particular location. NH_i is the corresponding $\Delta^{14}C$ value of the NH zone, and the $Value_i$ is the measured value.

The mean of the absolute values of the difference $\overline{X}$ between the NH1 zone and the main location IRB is (29 ± 10) ‰, while for the NH2 zone it is (26 ± 9) ‰. There is no a tendency for the location IRB to be closer to any zone.

A statistically non-significant tendency toward the NH1 zone is observed at the site Crna Mlaka, where the $\overline{X}$ is (13 ± 4) ‰ relative to the NH1 zone and (23 ± 10) ‰ relative to the NH2 zone. Overall, the IRB location in Zagreb follows the reference data of Hua *et al*. (2022) less closely than Crna Mlaka does.

The largest differences relative to the NH zones occur around the top of the bomb peak, which can be attributed to the fact that even small deviations in the time domain lead to large deviations in $\Delta^{14}C$, meaning the sensitivity of $\Delta^{14}C$ to the year of measurement around the bomb peak is high. In order to check goodness of fit between $\Delta^{14}C$ values obtained at analysed locations and NH1 and NH2 curves, a χ^2 value was estimated according to Raj *et al*. (2023) which described similar issue on the suitability of zones: although sampling area, Northern Israel, falls into a NH 2 zone, radiocarbon tree ring data for period of maximum ^{14}C activity (tree rings from 1964 – 1968) were closer to NH1 zone. χ^2 value was calculated from Eq 2 (Bronk Ramsey *et al*. 2001.):

$$\chi^2 = \sum \frac{(Value_i - NH_i)^2}{(\sigma^2_{Valuei} + \sigma^2_{NHi})} \qquad \text{Eq 2}$$

The marks are the same as in Eq 1.

The reduced χ^2 values with 1σ values considered for all locations and both atmospheric curves are presented in Table 2. The closer the value to 1, the better is the fit.

Table 2. Reduced χ^2 values with 1σ values considered. N – number of measurements

Atmospheric curve	IRB N = 19	Crna Mlaka N = 14	V. Njegovana St.; N = 6	Tijardovićeva St., N = 3
NH1	1.41	3.67	3.50	95.53
NH2	1.39	9.43	5.20	95.53

Reduced χ^2 values imply that IRB values fit good to both atmospheric curves since reduced χ^2 values are very close to 1 based on 1σ values. Crna Mlaka shows discrepancy from NH curves, but reduced χ^2 value of 3.67 for NH1 curve and 9.43 for NH2 curve indicates better fitting to

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NH1 zone. If reduced χ^2 value is based on 3σ values, this would give reduced χ^2 of 1.48 for NH1 curve and 3.14 for NH2 curve clearly indicating better fitting of Crna Mlaka location to NH1 zone. Regarding the two ~~control~~additional sites V. Njegovana is similar to Crna Mlaka location, and fits better to NH1 than NH2, while for Tijardovićeva St. there are only three data that fit within the part in which atmospheric curves does not differ. It should be noted that for both ~~control~~additional sites the data sets are too small to achieve relevant statistics.

CONCLUSION

Croatia is located between zones NH1 and NH2. The calibration of radiocarbon results for samples from the bomb period raises an issue regarding the choice of the calibration curve. To resolve this issue, radiocarbon analyses of tree rings from Croatia were performed. Tree rings were sampled at two main locations IRB (Zagreb) and Crna Mlaka (30 km from Zagreb). Twenty tree ring samples were radiocarbon analyzed from the two locations, together with some additional comparison specimens. Average values of absolute differences between radiocarbon results, as well as reduced χ^2 from both locations and the NH1 and NH2 zones were calculated. ~~The average value of absolute differences for~~ It is shown that the location IRB ~~and NH1 zone is slightly larger than that for~~ was strongly affected by the ~~NH2 zone, while~~fossil fuel emissions, so conclusions on preferences to any zone cannot be withdrawn from data collected at ~~the~~ this location. The Crna Mlaka location, ~~situation is opposite. The~~clean air site location, showed non-significant preference for ~~NH2 for IRB location and for Crna Mlaka location preference for zone the NH1~~ the NH1 zone based on differences between radiocarbon results ~~is~~ observed~~, but it is not significant.~~. Reduced χ^2 from ~~both locations~~ Crna Mlaka and the NH1 and NH2 curves indicate that ~~IRB site fits well to the both zones, while~~ Crna Mlaka site fits better to NH1 zone. ~~Based on~~According to observed analyses, it may be concluded that samples from continental Croatia, sites north of Crna Mlaka, which belong to the bomb peak period, should be calibrated by NH1 atmospheric curve. This conclusion is also corroborated with wind direction at investigated area, as the prevailing N and NE winds bring air masses from NH1 zone. Additional investigations of tree rings from clean-air sites situated south of Crna Mlaka should be performed to establish suitability between NH1 and NH2 zones for samples from Southern and Mediterranean part of Croatia.

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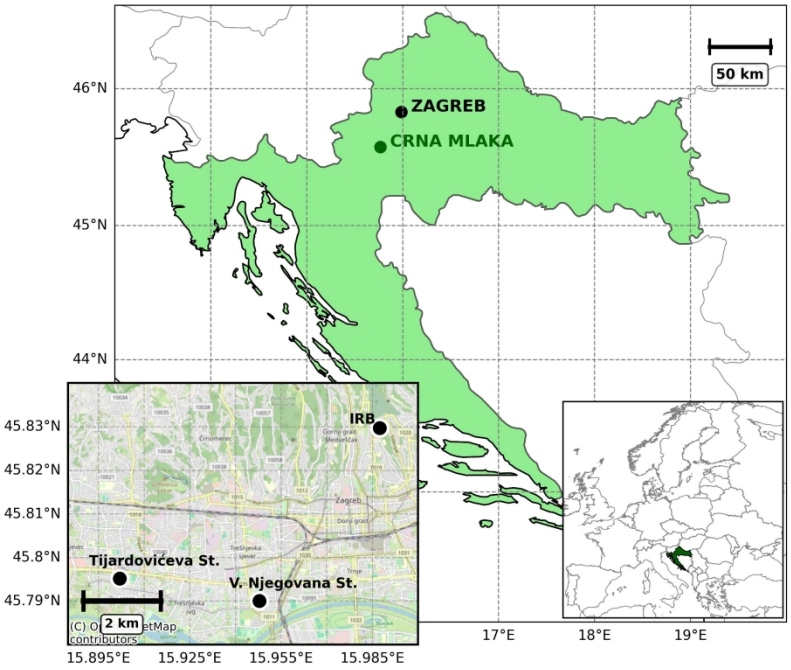

Figure 1. Locations of sampling sites. The main map shows the city of Zagreb and location Crna Mlaka. Three sublocation are shown detailed in the lower left map and the position of Croatia in Europe is presented in the bottom right corner.

254x203mm (300 x 300 DPI)

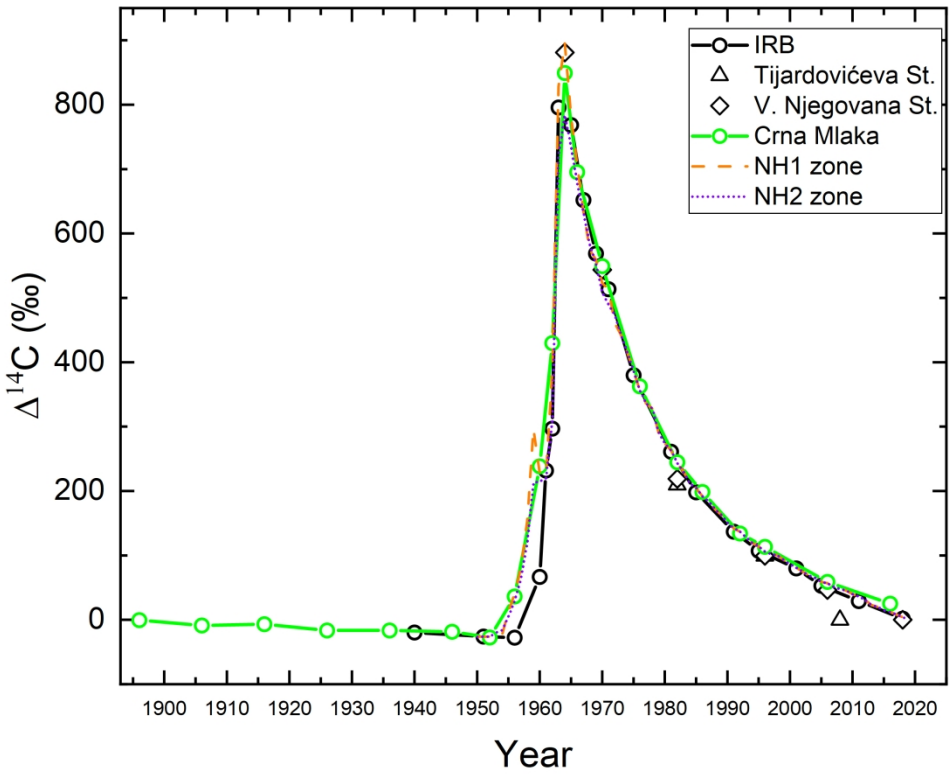

Figure 2. $\Delta^{14}C$ values in tree rings from the studied locations compared to the NH1 and NH2 zones (Hua et al. 2022).

229x185mm (300 x 300 DPI)

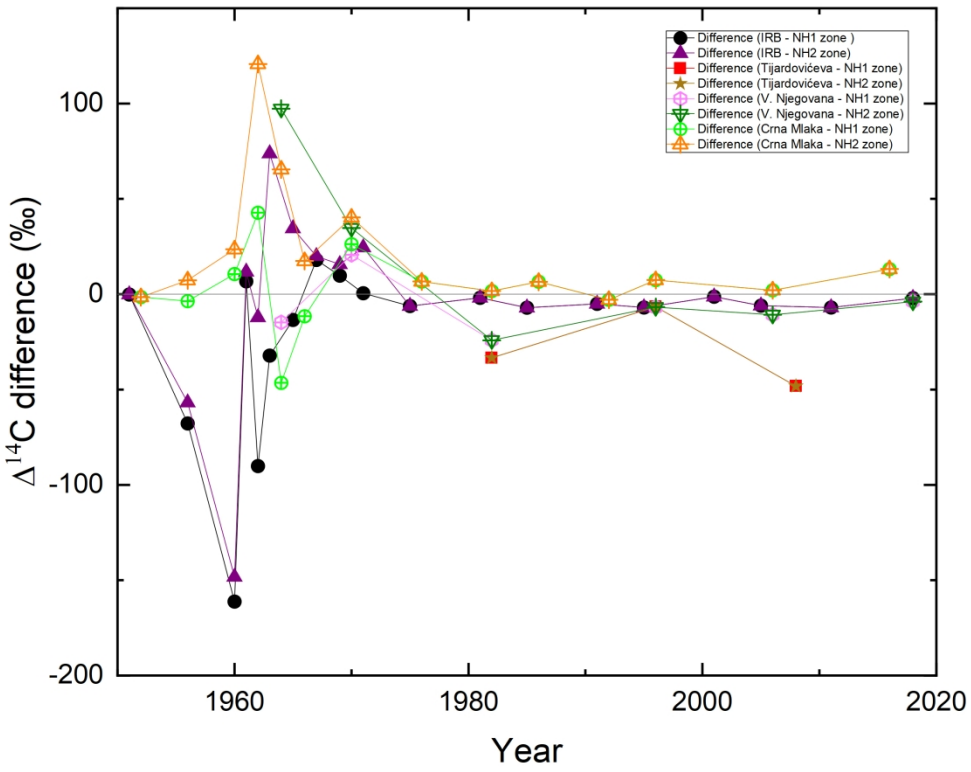

Figure 3. The difference of Δ14C between the studied locations and the NH1 and NH2 zones (Hua et al. 2022).

231x187mm (300 x 300 DPI)