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^{14}C AMS measurements in tree rings to estimate local fossil CO_2 in Bosco Fontana forest (Mantova, Italy)

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ABSTRACT

Radiocarbon concentration in atmosphere changes overtime due to anthropogenic and natural factors. Species growth preserves the local atmospheric radiocarbon signature over their life span in the annual tree rings and make it possible to use tree rings for the monitoring of changes in fossil-fuel emissions due to an increase of traffic exhaust, during the last decades.

In this paper, the CIRCE AMS system has been used to measure the ^{14}C concentration in tree rings of plants grown near an industrial area and a very busy State Road, in a forest in north Italy. Preliminary results related to tree rings of several years of plants respectively near and far the emitting sources are displayed, in order to estimate the local pollution effect. It is possible to find a dilution in years 2000 and 2006 in both the trees analysed, but not enough data have been analysed yet in order to distinguish the fossil dilution derived from the street vehicular traffic or that from the industries.

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1. Introduction

The nuclear bomb tests in troposphere of the late 1950s and early 1960s have doubled the natural ^{14}C concentration. Since 1964 this signal (bomb spike) is decreasing with an exponential trend due to the net radiocarbon flux to the oceanic and terrestrial reservoirs [1,2] and the fossil-fuel burning dilution [3,4]. Since the first industrial revolution, the burning fossil-fuels have produced an atmospheric CO_2 depleted in ^{14}C , compared to the original $^{14}\text{CO}_2$ concentration (Suess effect [3]). The ^{14}C content of CO_2 produced by petroleum utilization is equal to zero because of the age ($>>50$ ka) of the reservoir where it takes origin. This "dead" carbon, produced by anthropogenic activities, may locally influence the bomb spike signal diluting literature observed values. It is known that tree rings reflect the ^{14}C concentration of atmosphere during their formation [5,6] and many studies investigate radiocarbon concentration overtime from tree rings, other ones from the atmosphere or from both of them, in order to estimate local fossil-fuel introduction. For example, an analysis was performed in Japan about CO_2 and tree-ring measurements [7,8] or only tree rings [9]; in Poland on both sample types [9–11] or only on CO_2 [12,13]; in USA on tree rings [14]; in Croatia on both sample types [15]; in central Europe on CO_2 [16] and in Italy on tree rings [17].

In this study we investigate the possibility to utilize the radiocarbon abundances in tree rings to detect the local pollution in an industrial area near an intense vehicular traffic State Road. The CIRCE AMS facility was utilized to measure ^{14}C concentration in tree rings of *Quercus robur* L. grown in a forest at increasing distances from the vehicular traffic source in order to estimate the gradient effect of fossil carbon dioxide emitted by motorvehicles. Here, we show preliminary results about several tree rings, between 1966 and 2006, of two plants, one near the emitting source and the other far from that. As "clean air" we use the tree rings of the farther plant, to estimate vehicular traffic pollution, and CO_2 atmosphere values, to check the pollution related to other sources, like industries.

2. Materials and methods

2.1. Site and sample description

Bosco della Fontana forest is a Natural Reserve, situated in the municipal district of Marmirolo, in the province of Mantova (Italy, 45°N , 10°E). It spreads out on a plain of about 233 ha encircled by cultivated land. The climate is continental, with long, cold winters and hot, humid summers. The average annual temperature is 13.2°C ; the precipitation trend shows a maximum in October (76.5 mm) and a minimum in February (37.6 mm), with an average annual rainfall of 658 mm [18,19]. One side of the forest is located near a very busy State Road, the SS236.

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In March–April 2007 eight *Q. robur* L. trees were cored at an increasing distance from the street. In this preliminary work, only two trees were analysed, Qinq1 and Qinq7, located at about 200 and 1400 m from the pollution source, respectively. Four increment cores of 5 mm in diameter were sampled at breast height from each tree. For ^{14}C measurements individual tree rings which grew in 1966, 1989, 1995, 2000 and 2006 were analysed for both trees.

2.2. Sample preparation and investigation methods

After a preliminary dendrochronological analysis (performed at the Laboratory of Dendrodata s.a.s., Verona, Italy), each sampled core was sliced in annual tree rings, but only the latewood of rings was analyzed with the aim to isolate the nutritive substances assimilated during the corresponding growth year. For stable isotope and radiocarbon analysis we choose to extract α -cellulose from tree rings, because of its low mobility in the wood, obtaining an annual ^{14}C sign, in opposition respect to whole wood that reflects the carbon assimilated by the plant in a wider temporal range [20,21]. We extracted the cellulose from all the samples at the same time, but we put each sample in a single Teflon bag, which isolate each ring from the others, in order to avoid contaminations. In order to find the most suitable method of extracting α -cellulose, we tested two modified procedures from the James-Wise method [22]: A [23], B [24]. Initially, we choose the method A, replacing acetic acid with HCl, as the former one contains C atoms, that could introduce a possible contamination for radiocarbon analysis.

Because of the small sizes of raw samples (between 7 and 80 mg), the mass of extracted cellulose was not enough for radiocarbon analysis (less than 1 mg). Therefore we have decided to apply the other α -cellulose extraction procedure (B), previously tested at CIRCE [24], utilizing again HCl instead of acetic acid. This method omits resin extraction with soxhlet apparatus. The samples were treated in:

- 4% HCl solution at 80° for 1 h for the inorganic materials dissolution;
- a solution of 2 g of ClNaO_2 in 200 ml of HCl solution to remove lignin;
- 4% NaOH solution, weaker than method A (17% [23]), to isolate α -cellulose;
- 4% HCl solution for 1 h.

Finally, tree rings were dried in oven at 50 °C overnight.

The sample cellulose was oxidized to CO_2 via combustion in pre-cleaned quartz tubes with copper oxide in muffle furnace at 920 °C for 6.5 h. CO_2 was graphitized, with Fe as catalyst, using Zn and TiH_2 reagents in muffle furnace at 560 °C for 4 h and 550 °C for the another 4 h [25]. The graphite obtained was pressed in aluminium cathodes for ^{14}C analysis by the CIRCE AMS facility, which is based on a 9SDH-2 Pelletron Tandem accelerator with a maximum terminal voltage of 3 MV [26]. The $^{14}\text{C}/^{12}\text{C}$ isotopic ratio of each sample was corrected for fractionation using on line measured $^{13}\text{C}/^{12}\text{C}$ and normalized to that of the primary standard NIST OXII oxalic acid and of the control standards IAEA C3, IAEA C5 and IAEA C6. The background correction was then applied using AESAR graphite [26] and VIRI K sample, a wood blank tested for VIRI inter-comparison 2008 (III phase). VIRI K was processed using the same procedure applied for our tree-ring samples including cellulose extraction, combustion and graphitisation. Its ^{14}C content, representing the contamination introduced in each step, was used as background correction values for our samples.

3. Results and discussion

After α -cellulose extraction we found a variable percentage yield in the examined samples, between 5.75% and 37.07% of the

original sample mass. It is necessary to make further tests on cellulose extraction procedure to improve the method and to get a bigger yield in mass.

The $\Delta^{14}\text{C}$ [27] values obtained after background correction were compared to those of “clean air” (the Bomb curve is a mean of NH1 [5] and Jungfraujoch [28] series). The atmospheric values used here are a mean of only spring and summer measurements, corresponding to the growth season of study plants.

We also calculated the fossil-fuel CO_2 dilution percentage to estimate the fossil contribution in atmosphere (Table 1; Fig. 2).

From the following mass balances

$$\begin{cases} \Delta^{14}\text{C}_{\text{sample}}\text{CO}_{2\text{sample}} = \Delta^{14}\text{C}_{\text{atm}}\text{CO}_{2\text{atm}} + \Delta^{14}\text{C}_{\text{ff}}\text{CO}_{2\text{ff}} \\ \text{CO}_{2\text{sample}} = \text{CO}_{2\text{atm}} + \text{CO}_{2\text{ff}} \end{cases}$$

we deduce the equation:

$$X_{\text{ff}} = \frac{\Delta^{14}\text{C}_{\text{sample}} - \Delta^{14}\text{C}_{\text{atm}}}{\Delta^{14}\text{C}_{\text{ff}} - \Delta^{14}\text{C}_{\text{atm}}}$$

where X_{ff} represents the molar fossil-fuel fraction ($\text{CO}_{2\text{ff}}/\text{CO}_{2\text{sample}}$), $\Delta^{14}\text{C}_{\text{sample}}$ the $\Delta^{14}\text{C}$ measured in the sample, $\Delta^{14}\text{C}_{\text{atm}}$ the atmospheric $\Delta^{14}\text{C}$ and the fossil $\Delta^{14}\text{C}_{\text{ff}}$ component, equal to -1000 .

The dilution percentage was calculated in Qinq1 tree respect to Qinq7 tree, the one far from the street, our main pollution source, from which we expect no signal due to vehicular traffic, and in both the trees respect to atmospheric $\Delta^{14}\text{C}$ values to try to estimate also the effect produced by industrial activity overtime in the area (Fig. 2).

For years 1966, 1989 and 1995 the values of both trees, the nearer and the farther from the pollution source, show a good agreement (Table 1). It means that State Road didn't influence the tree growth in this period. For these years we can find also a good agreement of our results with the Bomb curve, indicating a negligible fossil dilution until 1995 in the area.

In year 2000 we can note a ^{14}C lower than the atmospheric value in both the trees, but in Qinq1, the nearer tree to the street, the dilution percentage is just a little bigger respect to the tree far from the SS236. It could indicate the presence of a fossil-fuel diffusion in the whole area (Table 1), due to the local industries and the little divergence between the two trees could be a normal oscillation in two different area derived from the industry source or a little effect of the traffic. But it is difficult to identify a possible signal due to the traffic pollution with a dilution divergence of only $0.89 \pm 0.69\%$ between Qinq1 respect to Qinq7 ^{14}C .

In year 2006 it is possible to note for Qinq1, the tree nearer to the pollution source, a $\Delta^{14}\text{C}$ lower than the atmospheric value,

Table 1

Results of ^{14}C measurements in annual tree rings from Bosco Fontana compared to those of contemporaneous “clean air” and estimated local fossil-fuel dilution percentages. In the first column there are the sample name and the relative year; in the second the $\Delta^{14}\text{C}$ value measured in the sample; in the third the $z - \mu$ value, indicating how much the sample $\Delta^{14}\text{C}$ differ from that of the “clean air” corresponding year; in the fourth column the dilution percentage with the error; in the last column it is indicated the “clean air” $\Delta^{14}\text{C}$ value, obtained averaging spring and summer values of Bomb curve [5,28] for each year.

Sample	$\Delta^{14}\text{C}$	$z - \mu$	Dilution%	$\Delta^{14}\text{C}$ Bomb curve
Qinq 1_1966	717.15 ± 5.64	0.86	-0.62 ± 0.72	706.60 ± 10.88
Qinq 7_1966	707.07 ± 5.86	0.038	-0.03 ± 0.72	706.60 ± 10.88
Qinq 1_1989	152.22 ± 5.33	-1.65	0.88 ± 0.53	162.40 ± 3.07
Qinq 7_1989	154.26 ± 3.17	-1.84	0.70 ± 0.38	162.40 ± 3.07
Qinq 1_1995	108.30 ± 4.84	-0.9	0.53 ± 0.60	114.27 ± 4.57
Qinq 7_1995	106.17 ± 4.39	-1.28	0.73 ± 0.57	114.27 ± 4.57
Qinq 1_2000	59.15 ± 5.12	-5.15	2.73 ± 0.53	88.92 ± 2.69
Qinq 7_2000	70.56 ± 5.18	-3.14	1.68 ± 0.53	88.92 ± 2.69
Qinq 1_2006	37.51 ± 2.82	-5.17	1.68 ± 0.32	55.23 ± 1.95
Qinq 7_2006	54.06 ± 3.28	-0.31	0.11 ± 0.36	55.23 ± 1.95

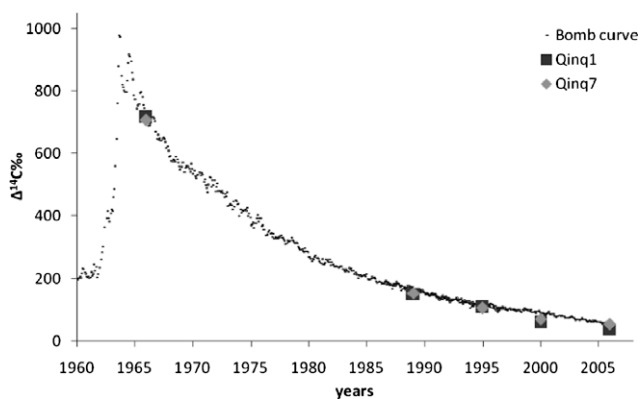


Fig. 1. $\Delta^{14}\text{C}$ of Bosco Fontana tree-ring samples compared to the Bomb curve.

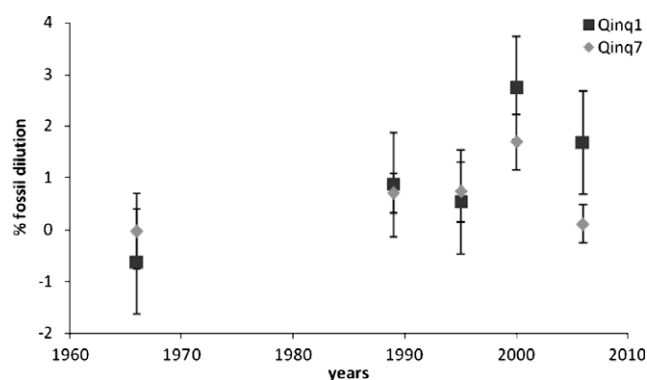


Fig. 2. Fossil-fuel dilution percentage estimated from ^{14}C in local tree rings.

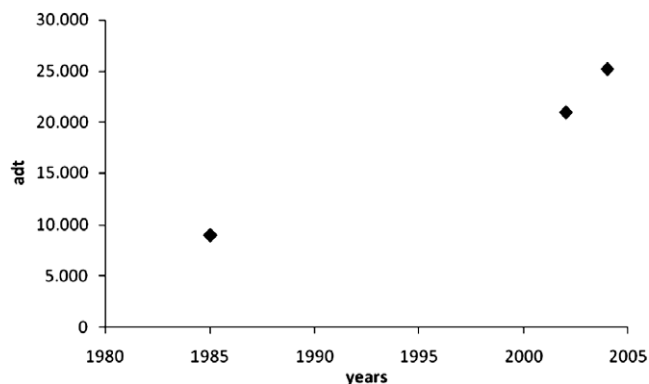


Fig. 3. Data and tendency of vehicular traffic growth in SS236 (1985 is ANAS – Azienda Nazionale Autonoma Strade Statali datum; while 2002 and 2004 are Provincia di Mantova, settore viabilità, data). “Adt” is the average daily traffic.

while Qinq7 tree, the one far from the pollution spring, has a $\Delta^{14}\text{C}$ concordant with atmosphere, suggesting an assumption of fossil CO_2 by trees grown near the State Road (Figs. 1 and 2; Table 1). Traffic data seem to confirm this results (Fig. 3), showing an increase of the average daily traffic in the last years. We have the average daily traffic data relative only to 1985, 2002 and 2004, taken by stations near Bosco Fontana (Fig. 3). Nevertheless the presence of dilution in both the trees in 2000 make it difficult to relate the dilution of 2006 only to the street component, while a combination of both the pollution sources is rather probable.

We compared the biggest dilution percentages found in our samples (2.73% for 2000 in Qinq1 tree and 1.68% for 2000 in Qinq7

and for 2006 yr in Qinq1 tree) with the dilution value in the industrial area of Brindisi, in South Italy, where the higher dilution percentage found is 2.6% in 2005 [17], while near Cracow (Poland) the maximum dilution percentage is of 8.7% [11]. So it is possible to recognize in the studied area a moderate dilution %. But the presence of other plants between the trees sampled and all the pollution sources could interfere with the fossil-fuel diffusion in the forest trees, attenuating the dilution signal.

4. Conclusions

In this study we have investigated the presence of traffic pollution in an area measuring ^{14}C in tree rings and comparing it with Bomb curve. Our preliminary results indicate that in 1966, 1989 and 1995 we did not find a fossil-fuel dilution, while in 2000 we found a dilution concerning both the trees analysed. This indicates the presence of a pollution source in the area not related to the vehicular traffic, but probably due to the industries present in the area.

In 2006 we found a fossil dilution only in Qinq1 tree, the plant grown near the SS236. It means that the pollution source could be now the street vehicular traffic. Probably we can see this signal only in this year as the vehicular traffic shows a great growth only in the last years. But it is difficult suppose the presence of dilution related only to the street, because of the presence of a fossil-fuel component also in previous years, not related to the street.

The analysis of industry activity overtime and the radiocarbon measurements of the other rings of Qinq1 and Qinq7 and the rings of the other trees could clarify this preliminary results.

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