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PIXE and µ-PIXE Analysis of Biological Records in Environmental Studies

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Abstract. We present the results of the PIXE analysis of tree ring cores sampled from living pines (*Pinus Pinea*) growing in two of the most industrialised areas in Southern Italy: Brindisi and Taranto. Large variations of elemental concentrations were determined as well as significant differences between the two areas. The results obtained by PIXE have been also compared with those resulting from the analysis of the radiocarbon concentration in tree rings measured by AMS and by µ-PIXE analyses performed on particulate air matter.

Keywords: PIXE, Environmental Pollution, Tree rings

INTRODUCTION

Dendro-dated tree ring sequences can be regarded as a powerful tool for the reconstruction of the environmental history of the site of the tree growth [1,2]. In particular, the easiness of sampling and the possibility to obtain an accurate age for each ring allow to use tree ring cores as qualitative and quantitative bio-indicators of the past levels of environmental pollution, recorded by trees by either a direct or an indirect mechanism. The direct mechanism consists of the uptake and fixation of contaminants in the wood through roots, leaves and stem while the indirect mechanism results in changes in the concentration of trace or major elements, normally present in the wood cells, as a response to environmental changes [3]. Among the other techniques used for the analysis of the chemical composition of tree-rings such as XRF (X-Ray Fluorescence), ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry), LA-ICP-MS (Laser Ablation Inductively Coupled Mass Spectrometry), SRXFA (Synchrotron Radiation X-ray Fluorescence Analysis), the role of PIXE (Particle Induced X-Ray Emission) is becoming more and more important [4]. This is mainly related to its multi-elementarity, sensitivity, spatial resolution and to the possibility to combine PIXE with other IBA techniques such as µ-PIXE, PIGE (Particle Induced Gamma Ray Emission) and RBS (Rutherford Backscattering Spectrometry) for the determination of the light elements content and density of the ring matrix.

We present here the results of analysis of tree ring sequences taken from pines grown in two of the most industrialized areas in Southern Italy: the industrial districts of Brindisi and Taranto.

We show also how, the information on elemental concentration obtained by PIXE can be combined with the results of the analysis of the wood carbon isotopic content performed by AMS (Accelerator Mass Spectrometry) and with µ-PIXE analysis of particulate air matter .

SAMPLING AREAS AND SAMPLE SELECTION

Tree ring cores were sampled from living pines (*Pinus Pinea)* trees located in the industrial areas of Taranto and Brindisi (Figure 1). Brindisi and Taranto are two of the most industrialized areas in Southern Italy with several highly polluting sources such as large steel smelting industries and oil refineries in Taranto, and three power plants and large-scale chemical factories in Brindisi. In fact, both the districts are classified by local authorities as "areas with high risk of environmental crisis" having, overall, more than nine industries classified as "plants of relevant risk".

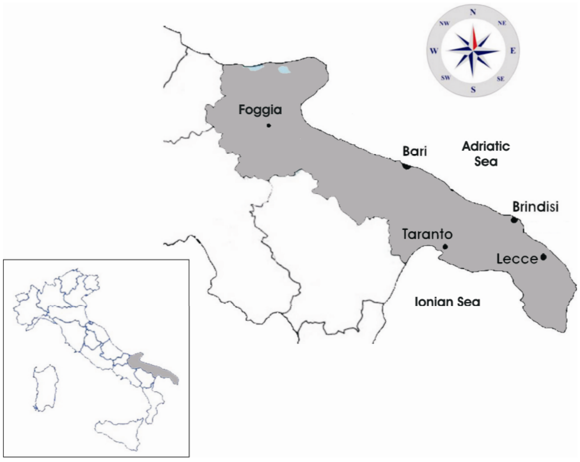

FIGURE 1. Map of the studied areas.

The climate in the area is Mediterranean with the maximum temperature ranging from 13-15°C (January and February) to 26-29 °C (June-September) and the minimum temperatures from 6-7 °C (January and February) to 18-21°C (June- September). The total rainfall ranges over the year from 10-20 mm in June-July to 70-75 mm in October-November with a quite high relative humidity between 70 and 80 %.
The samples were taken by a 5 mm diameter and 50 cm long increment borer at breast height (1.5 m).
In Taranto a single ring core was taken from a pine (Tree T1, trunk diameter ~80 cm) growing in the industrial area while in Brindisi cores were obtained from two trees: the first one (Tree B1, trunk diameter ~80 cm) to be used for the PIXE elemental analysis and the second one (Tree B2) for the AMS analysis.
The thickness of each ring was measured by visual observation at the optical microscope identifying the early and late wood portion of each ring whose position was then marked in the plastic frame holding the cores during the PIXE measurements. The age of each ring was determined by direct counting.

BRINDISI TREES: AMS ISOTOPIC ANALYSIS

One of the two ring cores selected from Brindisi (Tree B2) was used to obtain information about the carbon isotopic composition of each ring by performing AMS analyses. In fact in Brindisi all the main industries (chemical industries, coal and oil fired power plants) are expected to release in the atmosphere carbon dioxide resulting from the combustion of carbon-based products of fossil origin (coal and hydrocarbons) with a total emitted CO_2 of more than 18 x 10^6 tons per year. The fossil-derived compounds are completely depleted in ^{14}C and thus the carbon dioxide produced by their combustion has a characteristic isotopic signature ($^{14}C/^{12}C = 0$) completely different from the isotopic composition of the “clean” atmospheric CO_2. Thus, when CO_2 of fossil origin is released a variation of the isotopic composition in the surrounding atmosphere can be expected and these variations are recorded by the biosphere. This is in particular the case of trees which fix the CO_2 during photosynthesis. This makes of tree rings a powerful proxy record of the past carbon isotopic composition of the atmosphere they lived in.
In fact by imposing the isotopic mass balance the concentration of fossil-derived CO_2 (C_f) can be expressed by:

$$C_f = \frac{R_a - R_m}{R_a}$$

where R_a, R_m indicate the $^{14}C/^{12}C$ ratios measured in a clean atmosphere and in the studied tree ring [5]. The large difference (~100 %) in the isotopic signatures of clean and CO_2 of fossil origin and the precision levels achieved by modern AMS systems (0.3-0.4 %) results in the possibility to detect concentrations of fossil-derived CO_2 at the level of 0.5-0.6 %. By using this approach and by comparing the ^{14}C content in five rings of the Tree B2 (from Brindisi) with that of contemporaneous tree rings taken from a tree of the same species in an agricultural open-field area 100 Km from the industrial district, it was possible to reconstruct the variations of the C_f term (Figure 2).

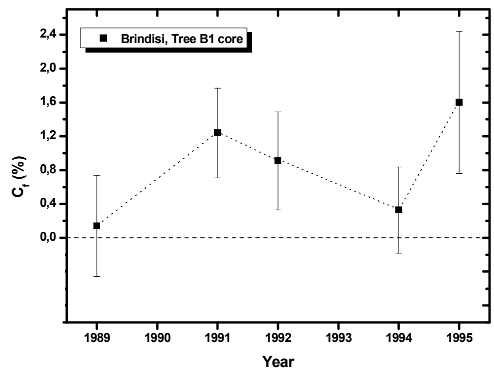

FIGURE 2. Variation of the C_f term with time for the core sampled from the tree B2 in the industrial area of Brindisi.

Figure 2 shows that in 1989 and 1994 the ^{14}C content in the tree rings can not be distinguished from the clean air reference (C_f~0) while in the years 1991, 1992 and 1995 a depletion of the ^{14}C content in the atmosphere is present reaching its maximum value in 1995 (C_f= 1.6 ± 0.8 %).

PIXE ANALYSES

The two tree ring sequences were analyzed by PIXE at the external ion beam line at CEDAD (Centro di Datazione e Diagnostica), University of Salento, Lecce, Italy.

Ring samples were irradiated, without any processing, by using 3 MeV protons, extracted in air through a 8 μm thick Kapton foil and impinging perpendicularly on the sample surface. In order to attenuate the contribution of low-energy X-Rays a "funny" 100 μm thick polyethylene collimator with a 1 mm hole was placed in front of the 80160 Si(Li) detector (active area 80 mm^2) placed at 45° relative to the proton beam. The cores were scanned under the beam by using a step-motor system and irradiating alternatively the early and late portion of each ring, whose positions were marked on a plastic frame used to fix the cores allowing to obtain reproducible irradiation condition. The Ar Kα line was used for normalization and the spectra were elaborated by using the GUPIX code [6] . Thirteen (from 1983 to 2006) and ten (from 1996 to 2006) years long cores were measured for Brindisi and Taranto, respectively.

RESULTS

Figure 3 shows a typical PIXE spectrum obtained for one of the rings: S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn and Sr were determined.

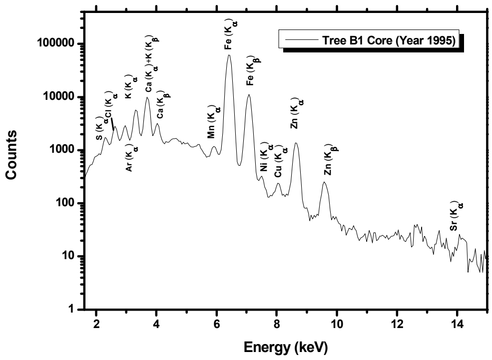

FIGURE 3. PIXE spectrum obtained for the ring corresponding to year 1995 from Brindisi.

A relevant effect which has to be properly taken into account when using PIXE for the analysis of tree rings is related to the difference in matrix composition and density from one ring to the other or from the early and late portion of the same ring. In fact different methods have been suggested for matrix correction such as RBS [7].

Nevertheless, it has been demonstrated that, at least for heavy elements (X-rays with energies higher than 6-7 keV) the analytical error associated to variation of matrix is relatively small (~0.5-1 %) [8]. For this reason our analysis is limited to elements heavier than iron. Figure 4 shows that both the trees (from Brindisi and Taranto) have a similar dependence, increasing towards outer rings, of the Fe concentration as a function of the year, with comparable absolute concentrations.

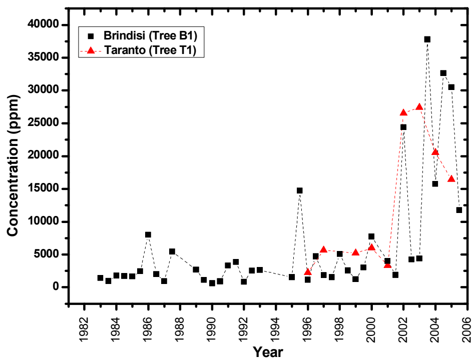

FIGURE 4. Fe concentration as a function of the growth year for the two trees in Brindisi (black squares) and Taranto (red triangles).

This pattern of Fe concentration is consistent with what was observed by others [7,9].

In fact, preliminary μ-PIXE investigations performed on particulate air matter collected by exposing cellulose filters in the industrial area of Taranto for two days, showed the presence of micro-particles (diameter ~ 20μm) mainly composed of Fe together with particles with a high Si concentration, probably soil dust (Figure 5). Besides this, however, no relevant differences were measured between the Taranto and the Brindisi trees.

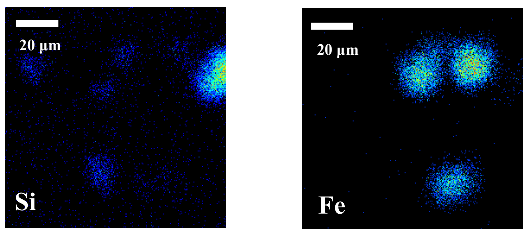

FIGURE 5. Fe and Si micro-map of cellulose filter exposed for two days in the industrial area of Taranto (E_p=3 MeV).

A dependence similar to that observed for Fe was measured also for Ni and Cu for the Brindisi tree (correlation factors $r_{Fe,Cu}$=0.89, $r_{Fe,Ni}$=0.95, $r_{Ni,,Cu}$=0.92) except for a large spike in the Cu concentration measured in 1992 (Figure 6).

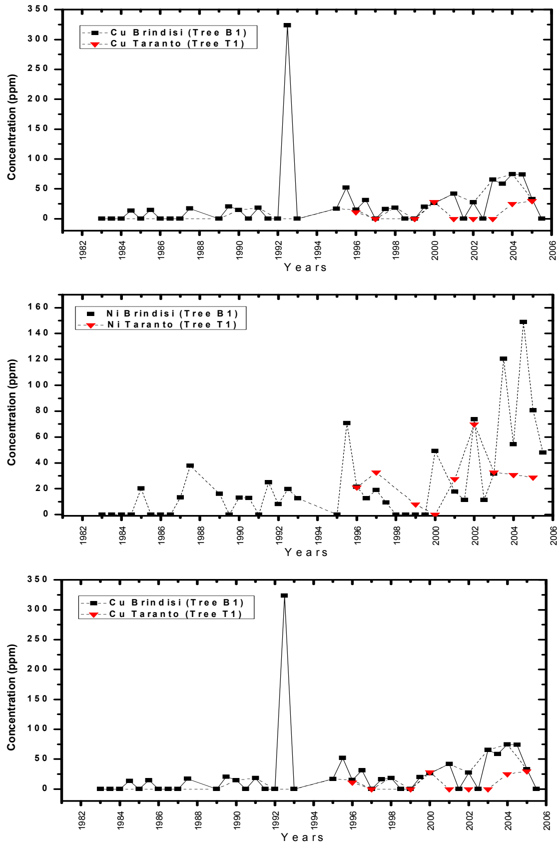

FIGURE 6. Cu, Ni and Zn concentrations as a function of the growing year.

On the other hand, when comparing the two trees relevant differences exist in the shape of the Ni and, mainly, Zn concentrations. For Ni while till 2003 the two trees show a similar behavior, starting from 2004 the Ni concentration in the Brindisi tree shows a significant increase. An even more marked difference between the two trees is that measured in the Zn concentration which is always significantly higher (up to a factor of 170) for the Brindisi tree with large spike in 1992, 1995 and 2003.
The reason for this high Zn concentration and for the large oscillations observed in Brindisi is not yet completely explained and more studies are in progress. In fact if it is true that variations in the Zn concentration have been reported between summer and winter [10] these are the order of 1.5-2.5 and a simply seasonal variation seem not to be a good explanation in this case where the variations are much higher. Furthermore it has been shown by other authors [3] that high Zn variations are indicative of the response of tree metabolism to external factors being either a direct or indirect indication of environmental contamination. At the actual stage of the work we thus suggest that the increase in the Zn concentration and its variations over time could be explained as the response of the tree to air pollution in the studied site. Nevertheless, according to the data of the European Pollutant Emission Register [11], the three power plants in Brindisi are accounted for a total release, overall, of ~2.8 t of Zn and its compounds in the air.

CONCLUSIONS

Tree ring cores were sampled from living pines in Brindisi and Taranto, two of the most industrialized areas in Southern Italy and submitted to ^{14}C-AMS and PIXE analyses. The AMS ^{14}C data showed, for the site of Brindisi, a depletion of the atmospheric ^{14}C concentration corresponding to the release in the atmosphere of carbon dioxide derived from the combustion of fossil-derived compounds. The PIXE data show characteristic shapes of the concentration of heavy elements with relevant differences between the two studied sites. In particular high Zn concentrations were observed for the tree grown in Brindisi with large spikes.

Further investigations will be carried out in order to increase the number of studied trees and trying to relate the observed variations of the elemental composition with the nature and magnitude of the polluting sources.

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