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Oak tree-rings record spatial-temporal pollution trends from different sources in Terni (Central Italy)☆

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Monitoring atmospheric pollution in industrial areas near urban center is essential to infer past levels of contamination and to evaluate the impact for environmental health and safety. The main aim of this study was to understand if the chemical composition of tree-ring wood can be used for monitoring spatial-temporal variability of pollutants in Terni, Central Italy, one of the most polluted towns in Italy. Tree cores were taken from 32 downy oaks (*Quercus pubescens*) located at different distances from several pollutant sources, including a large steel factory. Trace element (Cr, Co, Cu, Pb, Hg, Mo, Ni, Tl, W, U, V, and Zn) index in tree-ring wood was determined using high-resolution laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). We hypothesized that the presence of contaminants detected in tree-rings reflected industrial activities over time. The accumulation of contaminants in tree-rings was affected by anthropogenic activities in the period 1958–2009, though signals varied in intensity with the distance of trees from the industrial plant. A stronger limitation of tree growth was observed in the proximity of the industrial plant in comparison with other pollutant sources. Levels of Cr, Ni, Mo, V, U and W increased in tree-ring profiles of trees close to the steel factory, especially during the 80's and 90's, in correspondence to a peak of pollution in this period, as recorded by air quality monitoring stations. Uranium contents in our tree-rings were difficult to explain, while the higher contents of Cu, Hg, Pb, and Tl could be related to the contaminants released from an incinerator located close to the industrial plant. The accumulation of contaminants in tree-rings reflected the historical variation of environmental pollution in the considered urban context.

1. Introduction

Monitoring atmospheric pollution in the proximity of industrial plants and urban areas is essential to infer past levels of contamination and to evaluate the impact of environmental regulations. Unfortunately, stations monitoring air pollutants have been installed during the 1980's and, therefore, only short time series are available. However, trees may help in reconstructing past pollution episodes and levels. In fact, pollutants deposited over aerial plant surfaces (Schreck et al., 2012) can, eventually, be transported via phloem to cambium zone at different tree heights (Lepp, 1975), and assimilated by roots (Watmough et al., 2004). A number of studies has shown the ability of trees to take up and incorporate pollutants into their annual growth rings (Nabais et al., 2001a; Robitaille, 1981; Rolfe, 1974), so that the accumulation of pollutants in tree-rings may reflect to some degree the variation of pollutant concentrations in the environment at the time of tree-ring formation (Watmough, 1999). The possibility of using element profiles in tree-ring series represents a powerful approach to biomonitor retrospectively pollution events and trends (Jensen et al., 2014). Indeed, tree-rings have been used to provide annual records of pollution over decades, tracing pollutants on a spatial and temporal scale in relation to their sources (Cocozza et al., 2016; Danek et al., 2015;

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Odabasi et al., 2015).

High coherence between the chemical composition of tree-rings and the chemistry of the surrounding environment, in space and time, was previously found in *Quercus* spp. (Cutter and Guyette, 1993; Eklund, 1995; Jonnson et al., 1997), showing that oak trees are suitable indicators of sources of metal contamination. This is based on the permeability of ring porous wood of these species, as well as their low number of rings in the sapwood, ecological amplitude, longevity, and wide geographical distribution. Downy oak (*Quercus pubescens* Willd.) seedlings were found to absorb Cd in roots, leaves and stems, with negative impact on photosynthetic capacity varying progressively with increasing Cd concentration in the soil (Cocozza et al., 2012). Thus, accurate dendrochemical indicators may integrate information collected from traditional passive and active sampling devices (Lin, 2015), determining large scale patterns of pollutant distribution over time and providing a tool to forecast the impacts of pollution on green infrastructures in relation to human activities (Haase et al., 2014; Watmough, 1999).

Nevertheless, the use of dendrochronological techniques for a retrospective biomonitoring of pollutants have been questioned (Cheng et al., 2007; Garbe-Schonberg et al., 1997; Nabais et al., 2001b, 1996), and the debate on whether elemental concentration changes in tree-rings are reliable indicators of environmental alteration through time is still open and topical (Baes and Mclaughlin, 1984; Bindler et al., 2004; Pearson et al., 2005). Several studies found no correlation between element concentrations in tree-rings and changes of their amount in the air, possibly due to the translocation of elements across tree-ring boundaries (at least) in the sapwood (Kennedy, 1992) and their accumulation in the outermost rings (Poulson et al., 1995), as well as the lack of confidence on rough analytical approaches (Brabander et al., 1999). This controversy illustrates the need to carefully choose appropriate sampling design, tree species and analytical methods (Cutter and Guyette, 1993). Furthermore, analytical methods were recently improved, enabling the determination of very low concentration (ppm to ppb levels) and reducing the quantity of material needed for the analysis, avoiding the necessity of using more than one growth ring and thus enhancing analytical resolution.

The most powerful analytical methods in dendrochemistry are the GC/MS (Gas Chromatography/Mass Spectrometry), GC/FID (Gas Chromatography/Flame Ionization Detection), XRF (X-Ray Fluorescence), and LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) (Hoffmann et al., 1994; MacDonald et al., 2011). LA-ICP-MS is a sophisticated analytical technique with high level of accuracy that precisely allows the description of the elemental composition of solid samples, including biological tissues (Limbeck et al., 2015). Such as, LA-ICP-MS is potentially suited to investigate contaminants that generally are present at very low concentrations in plant material. In particular, LA-ICP-MS is promising for the determination of trace elements in individual tree-rings and in their portions (Witte et al., 2004), allowing high-resolution analysis of element distribution in early and late wood (Monticelli et al., 2009).

We hypothesized that trace elements taken up by trees are fixed in the growth ring produced in a particular year, providing a spatial-temporal pollution record. A strongly polluted town in central Italy was selected as study area. The main aim of the study was to demonstrate the feasibility to detect changes in environmental contamination across space and time by measuring pollutant levels in tree-rings, corresponding to a period for which monitoring data were not available, using updated LA-ICP-MS method. Downy oak trees, growing in the proximity of a steel factory and at distal sites in the town of Terni, were sampled and elements in tree cores were measured using LA-ICP-MS. High levels of metals were emitted into the environment by the industrial plant through time, specifically particulate matter (Sgrigna et al., 2016, 2015). In particular, we verified whether: (1) these oak trees took up and stored pollutants in the annual tree-rings; (2) element levels in tree-rings indicated spatial-temporal distribution of pollutants; and (3) climate and pollution had interactive effects on tree growth.

2. Materials and methods

2.1. Site description

The study area is located in the town of Terni in central Italy (42° 34′ N; 12° 39′ E, elevation 130 m a.s.l., 112′000 inhabitants). The area is within a valley, surrounded by three main mountain chains, Sabina mountain (NS direction), Martana chain (ESE-WNW direction) and the Narnese-Amerina mountain (NNW-SSE direction) (Cattuto et al., 2002) (Fig. 1), and winds are mainly blowing from N-NE (Sgrigna et al., 2015). The morphology of the town leads to the persistence of atmospheric pollutants and the area is one the most polluted in Italy, especially for particulate matter (PM), in winter and summer months (Sgrigna et al., 2016, 2015) (www.arpa.umbria.it). There is a huge industrial pole mostly located in the town center (Capelli et al., 2011) characterized by one of the largest stainless steel production site in Europe (Moroni et al., 2013) (around 150 ha), established at the end of 19th century. The industrial plant produces 1 million tons/year of manufactured steel (communication of factory). The emission is daily monitored by environmental stations around the steel factory, which detect particulate matter and heavy metals (Pb, Cd, As, Ni, Cr). At around 7 km from the steel factory, there is an area contaminated and identified as a remediation site by a project aimed to implement environmental restoration and monitoring activities, which started in 2003 - area of national interest (SNI): "Terni-Papigno" (DM 468/2001 and DMA 08/07/02). "Terni-Papigno" includes a treatment plant of wastewaters of the steel factory and two storage sites: one for waste and special waste, and another for dangerous waste have been active since 1982 and 2006, respectively. Close to "Terni-Papigno" and near the d8 site, there is another waste disposal. Three incinerators of solid waste are also located in the area of "Maratta" (Fig. 1). In 2008, an incinerator was closed due to environmental laws related to suspected harmful and radioactive substances in waste (Mosca, 2008). In 2007, during the excavations for the construction of a tunnel, a dense underground lake of hexavalent Cr (VI) was found below the landfill. Moreover, a large hospital with nuclear medicine department and other industries are also located near the city center (Fig. 1), contributing to very complex environmental conditions.

Eight sites in urban and peri-urban area were selected: four sites (p1, p2, p3, p4) at a distance of 0.5 km from the steel factory, indicated as proximal sites (P-chronology), and four sites (d5, d6, d7, d8) at 1 km from the plant, indicated as distal sites (D-chronology) (Fig. 1).

Air quality of the area is monitored through environmental stations that supply a real-time air quality (PM level, dioxins, ozone, sulphur and nitrogen dioxide and heavy metals in urban airborne). The PM levels were detected by 6 different monitoring stations located in the urban and peri-urban area (Fig. 1). PM_{10} levels of 40 ± 1.60 μg/m^3 in station 1, 28 ± 1.35 μg/m^3 in station 2, 34 ± 1.64 μg/m^3 in station 3, 30 ± 1.68 μg/m^3 in station 4, 32 ± 1.62 μg/m^3 in station 5, and 33 ± 2.23 μg/m^3 in station 6 were calculated as annual mean values in the period 2004–2011 (www.arpa.umbria.it). The highest PM level was detected by the monitoring station number 1 (N 42° 34′ 20.78″, E 12° 40′ 32.68″), located in p2, the area closest to the steel factory. According to the WHO (2016), 20 μg/m^3 annual was chosen as mean annual level of PM