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

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ABSTRACT

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

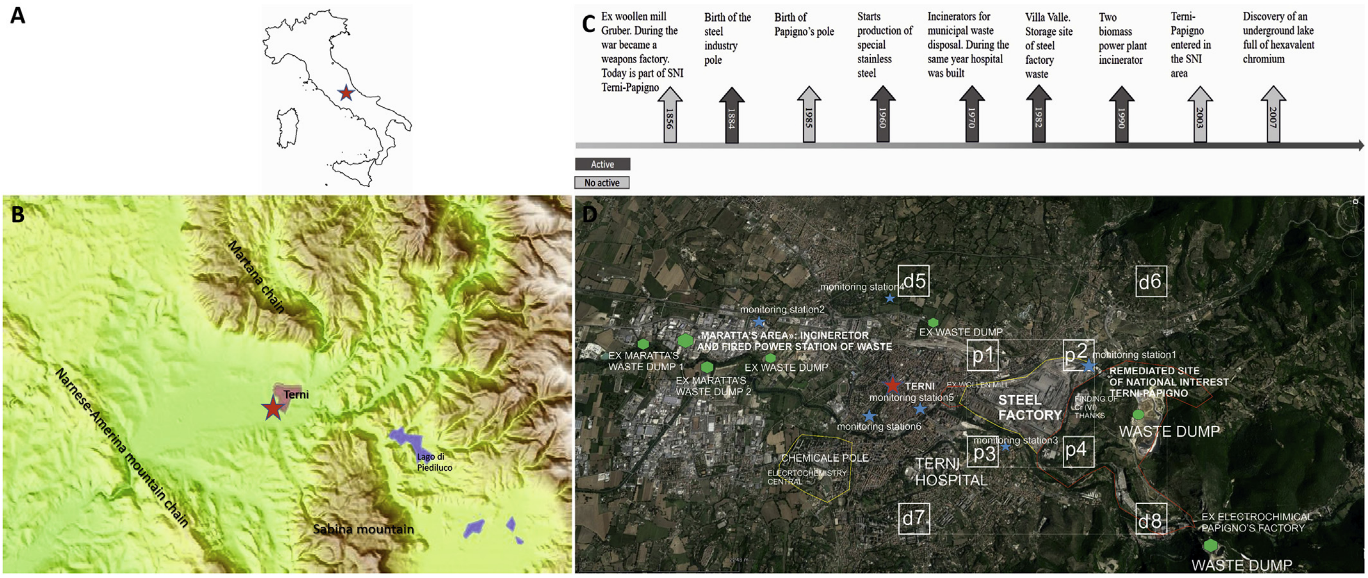

Fig. 1. (A) Location map of the study area in Central Italy. (B) Orographic map of the Terni area. (C) Reconstruction of the temporal trends of industrial activity. The arrows indicate the start of specific activities in the area. (D) Location map of sampling sites (p1, p2, p3, p4, d5, d6, d7 and d8), factories, landfills and monitoring stations (star symbols).

in the long-term guideline value to avoid health problem. This value represents the minimum of the range over which significant effects on survival rate were observed, causing air pollution-related deaths by around 15% (WHO, 2016). This issue had attracted media and legal attention for the "real dangers to the citizen health, linked to the spread of pollutants in water and air" (Moroni et al., 2013).

2.2. Tree-ring core collection and sampling procedure

Tree cores of downy oak, the most common tree species in the study area, were sampled. Downy oak was previously used for dendrochemical studies with positive results, as correlation between pollution level of the environment and observed metal content in tree-ring profile was observed (Cocozza et al., 2016). To avoid the effect of any wood alteration, only trees without abrasion scars or other visible evidence of injury were selected. Four healthy downy oak trees were randomly identified in each site, at both proximal and distal sites. Trees were chosen with diameter at breast height (DBH) ranging from 30 to 80 cm and height around 10–15 m. Two cores for each tree were sampled using an incremental borer of 50 cm length and an inner diameter of 5.15 mm (Haglof Sweden AB). Coring was performed at breast height (1.30 m).

Tree cores were collected in winter (December, 2015), in dormancy season when no significant mobility of the elements should occur once stored (Hagemeyer et al., 1994). Later, the samples were prepared for LA-ICP-MS analysis. The cores were fixed on hemicylindrical-grooved plastic supports with wood vessels perpendicularly oriented with respect to the support surface. The cores were sectioned with a microtome and mounted for insertion into the LA-ICP-MS instrument. The core sections were reduced to half of their original diameter, thus exposing the inner part.

2.3. Ring-width measurement

Tree-rings were dated and then measured with a resolution of 0.01 mm, using the LINTAB-measurement equipment (Rinntech, Heidelberg, Germany), coupled with a Leica MS5 stereoscope (Leica Microsystems, Germany), and TSAP Win 0.55 software (Rinn, 1996). Cross-dating is one of the fundamental principles of dendrochronology. Each ring-width chronology should be cross-dated within and between trees and among all trees within the same site. Raw ring-width chronologies should be first cross-dated visually and then statistically (Cherubini et al., 2002). Usually the visual cross-dating is validated statistically using Student t-test, Pearson correlations and more dendrochronologically suited statistical tests, i.e., the Glk (the *Gleichläufigkeit*), to determine the significance of the correlation between the curves (Cherubini et al., 2002). Statistical crossdating was performed through the software COFECHA to assess the quality and accuracy of tree-ring series measurement (Holmes, 1983). The ARSTAN program was used to remove variability due to age, size and other non-climatic factors affecting tree growth, and to standardize ring width data into final chronologies producing tree-growth indices (Cook et al., 1990). To preserve the long-term fluctuations in the series, a conservative method of detrending was used. Only the negative exponential curves and/or linear regressions with negative or zero slopes were used and a 20-year smoothing spline.

The standardization produced two-chronologies, one for proximal sites and one for distal sites. Standardized tree-ring index series are combined into a mean value of all series to obtain a standardized chronology (STD). Means of each year are computed as either the bi-weight robust estimate or the arithmetic mean (Cook, 1985). The bi-weight mean is an integral part of the ARSTAN methodology and strongly recommended to remove effects of endogenous stand disturbances and to enhance the common signal contained in the data. Standardized tree-ring chronologies were statistically characterized by: raw mean ring width, calculated as the arithmetic average of the raw data of each elementary series; mean ring width of STD chronology; mean sensitivity (MS); standard deviation (SD) to assess the high-frequency variations (Fritts, 1976); and expressed population signal (EPS) as threshold indicating an acceptable level of coherence in dendrochronology (Wigley et al., 1984).

The ring widths of P- and D-chronologies were converted in tree growth index (TGI). This index is a ratio calculated as follows:

$$TGI = 3 \text{ consecutive rings width data} / (\text{means of a series}^{1/n}) - 1$$

for P- (TGI P) and D-chronologies (TGI D).

Each point represents the annual average growth rate, based on the procedure of Robitaille (1981), calculated as the ratio between the mean of the values measured on 3 consecutive annual rings and the mean of the series for a specific interval time (n). Higher or lower values for a given year represent proportionally higher or lower tree growth for that year. The index is useful to interpret the growth variations in terms of climate or other environmental factors.

2.4. Climatic data

The role of climatic variables in influencing tree growth was analysed with the R Statistical Software version 3.0.2 (Dalgaard, 2010), package "bootRes", using moving correlation function (MCF) for detecting stationarity and consistency of correlation functions over time. The MCF considers air temperature and precipitation, the main parameters to assess the climatic long-term effect on radial growth (Żywiec et al., 2017). Moving correlation function analysis is a valuable statistical method for the assessment of the influence of climate on tree growth (e.g., Carrer et al., 2007; Reynolds-Henne et al., 2007; Palombo et al., 2014). The calculation is performed year by year. Each square represents a climatic response (correlation coefficients) in 20-yr time windows on the basis of a linear regression analysis of year by year data set. Correlations were calculated separately for each month, allowing the observation of seasonal sensitivity of correlations, for the period from March of the year prior to ring formation to October of the year of growth (according to Zang and Biondi, 2015). This technique is useful to summarize large amount of data and the colour scale corresponds to both the sign and strength of the correlations. The standardized tree-ring chronologies were used to correlate tree growth with mean temperature and total precipitation. The climatic data used for the correlations were downloaded from ftp://palantir.boku.ac.at/Public/(Moreno and Hasenauer, 2016). The resolution of climatic data is 0.0083° (about 1 × 1 km grid) obtained combining the gridded climate data set of E-OBS (European Observations) version 8.0 at 0.25° resolution (approximately 30 km) and WorldClim climate surfaces. Mean temperature and total precipitation, with monthly detail in the period from 1951 to 2012, were considered. The coordinates of the center of the steel plant (42°46′39″ N; 12°22′31″ E) were used to extract climatic data from the grid.

2.5. Trace elements in tree: LA-ICP-MS determination

Trace elements were detected in tree cores using LA-ICP-MS at the laboratory of the Institute of Geochemistry and Petrology (ETH, Zürich, Switzerland). Standard operating conditions of LA-ICP-MS were set up (Table 1). LA-ICP-MS analysis was carried out on 2 cores of 3 trees in each site. The analysis was performed along the tree cores.

Helium carrier gas transported the ablated material to the ICP-MS at a flow rate of 0.7 L/min. Argon makeup gas was mixed within the funnel of the 2-volume ablation cell at a flow of 1–1.1 L/min. To optimize the ICP-MS system and ensure high sensitivity and stability, the glass standard reference material (SRM) NIST 612 was ablated using single line patterns (laser settings: energy 3.5 J/cm^2; spot size 43 μm; scan speed 3 μm/s; shot frequency 10 Hz). One large spot (257 μm crater) was ablated in each tree-ring. The spot dimension was similar to that used by Märten et al. (2015) (200 μm spot dimension). The spot dimension, the method of spot ablation, and the type of wood (e.g., wood density and pore dimension) depend on tree species. The spot ablation technique has the advantage to associate the result to a specific tree ring (age assignment of ablation results). All oak wood samples were ablated orthogonally to the tree-rings in the drilling direction. The analysis was done in late wood, because during dormancy no significant mobility of the elements should occur once stored (Hagemeyer et al., 1994). Moreover, in ring porous species (as in the case of oak), late wood has smaller vessels and a denser and more uniform structure than early wood (Danek et al., 2015). This ensured that the spot size chosen was quantitatively sufficient for the combustion of the ablated particulate. For data reduction, Sills software (Guillong et al., 2008) was used to select integration intervals, remove spikes and calculate net count rates (cps) for all measured elements. For better comparability, all count rates were normalized to ^{13}C to correct for differences in ablation yield, beside the fact that carbon is difficult to accurately measure (Frick and Günther, 2012). Due to the lack of a suitable reference material, absolute concentration was not calculated and the element/^{13}C ratios were taken as proxy for the element level. Each analysis consisted of about 30 s of gas blank data; used for background correction and 40 s of sample ablation. The following isotopes were measured to obtain the elemental contents in the tree-rings: Cobalt (^{59}Co), Copper (^{65}Cu), Chromium (^{53}Cr), Lead (^{208}Pb), Mercury (^{202}Hg), Molybdenum (^{95}Mo), Nickel (^{62}Ni), Tungsten (^{182}W), Thallium (^{205}Tl), Uranium (^{238}U), Vanadium (^{51}V), and Zinc (^{66}Zn).

Table 1
Laser Ablation ICP-MS parameters.

Instrumental parameters	Dendrochemical analysis
Instrument Host	LA-ICP-MS ETH Zurich
Type	RESOLUTION 155S (asi)
ICP-MS	Element XR (Thermo Fischer)
Laser Type	193 nm excimer
Setting	10 Hz, 3.5 J/cm^2 single hole, 400 pulses
Spot size	257 micron diameter
Normalized	^{13}C intensity

2.6. Element levels

Data of three trees were averaged to obtain a single time series for each site and for each element.

The level of each element was determined by normalization procedures (Bukata and Kyser, 2007). The normalization defined common temporal levels of element in tree-rings of different sites. An index value was assigned for year (I_x), using the following equation:

$$(I_x) = (level_x - level_{lowest}) / (level_{highest} - level_{lowest})$$

where, $level_x$ refers to the level of a specific year, $level_{lowest}$ and $level_{highest}$ refer to the lowest and the highest levels, respectively, measured in tree-rings of each site.

Finally, normalized levels of each element in tree-rings of the sites near the steel factory (p1, p2, p3, p4) and far from that (d5, d6, d7, d8) were averaged for the characterization of element levels, and the two series in P- and D-chronologies were plotted.

2.7. Statistical analysis

The trend of Cr, Cu, Hg, Mo, Ni, Pb, Tl, U, V, W, and Zn contents in P- and D-chronologies was assessed using the non-parametric Man-Kendall test (MK test) (McLeod, 2005; Tognetti et al., 2014). According to Man-Kendall test, the null hypothesis H0 assumes that there is no trend (the data are independent and randomly ordered) and this is tested against the alternative hypothesis H1, which assumes that there is a trend (Önöz and Bayazit, 2003). Each element was compared between P- and D-chronologies. The initial value of the Mann-Kendall statistic, S (Mann-Kendall score), is assumed to be zero (i.e., no trend; null hypothesis). If a data value in a later time period is higher than a data value in an earlier time period (i.e., a trend is detected; alternative hypothesis), S is higher than one. On the other hand, if the data value in a later time period is lower than a data value in an earlier time period, S is lower than one. The incremental and decremental values define the final value of S. This test allows to investigate long-term trends of data without assuming any particular distribution. Then, the rank correlation coefficient, Kendall's tau, was calculated to compare the strength of the correlation between two data series; tau ranges between −1 and 1, measuring the degree of similarity between ranks of pairs of chronologies. The tau coefficient corresponds to: value 1, when the agreement between the two rankings is perfect (i.e., the two rankings are the same); value −1, when the anticorrelation between the two rankings is perfect (i.e., one ranking is the reverse of the other); value 0, when the rankings are completely independent. The resultant MK test statistic was performed using XLSTAT-Time statistical analysis software.

The trends in P- and D-chronologies were tested using the non-parametric Levene's *t*-test. This test evaluates the significant difference between the means of two independent samples in order to define the relationship between two variables and the trends of the relationship. The Levene's *t*-test correlation coefficients were determined by linear regression. Differences between groups were considered to be significant when *p-value* $\leq$ 0.05. The Levene's test verifies two hypotheses. The null hypothesis indicates that the variance between series is equal. The null hypothesis is rejected when the p-value of Levene's test is less than 0.05, assuming the hypothesis that series are different. The analysis was performed using the SPSS 20.0 software package (SPSS Inc., Chicago, IL, USA).

3. Results

3.1. Ring-width chronologies

The longest chronologies of downy oak for the investigation were 68 years old (1947–2015) in P-chronology and 122 years old (1893–2015) in D-chronology (Fig. 2A). The raw mean ring width showed higher growth rates in P- than D-chronologies. Values of STD, MS, SD, and EPS did not show differences between P- and D-chronologies (Table 2). The low MS indicated that downy oak is relatively complacent at this site (Douglass, 1919; Fritts, 1976). The high STD expressed consistency between the values of the time series analysed. The EPS value showed a good level of coherence of the chronologies, indicating consistency of the studied chronologies (Wigley et al., 1984).

The tree-ring widths were converted into a growth index and plotted (Fig. 2B). The chronologies revealed a growth decrease of 0.04 unit/year in P-chronology, whereas, a growth decrease of 0.02 unit/year was observed in D-chronology, in the period 1985–2015. Overall, after 1985, tree growth exhibited a 58% decrease in D-chronology, and a 158% drop in P-chronology.

3.2. Growth-climate relationships

Tree growth in P- and D-chronologies correlated weakly with climatic factors. Correlations between tree growth and climatic variables (temperature and precipitation) in P- and D-chronologies were generally weak (strength of correlation), although resulting in statistically significant correlations (Fig. 3). The bootstrap graph showed positive correlation between radial growth and precipitation in November of the previous year in P-chronology (Fig. 3). Whereas, correlations between plant growth and precipitation were negative in October of the previous year and January (1968–1987), and October of the current year (1988–2007) in P-chronology (Fig. 3). In summer, negative correlations between radial growth and precipitation occurred in July (1993–2012) and in August from 1973 to 2002 in P-chronology (Fig. 3). In D-

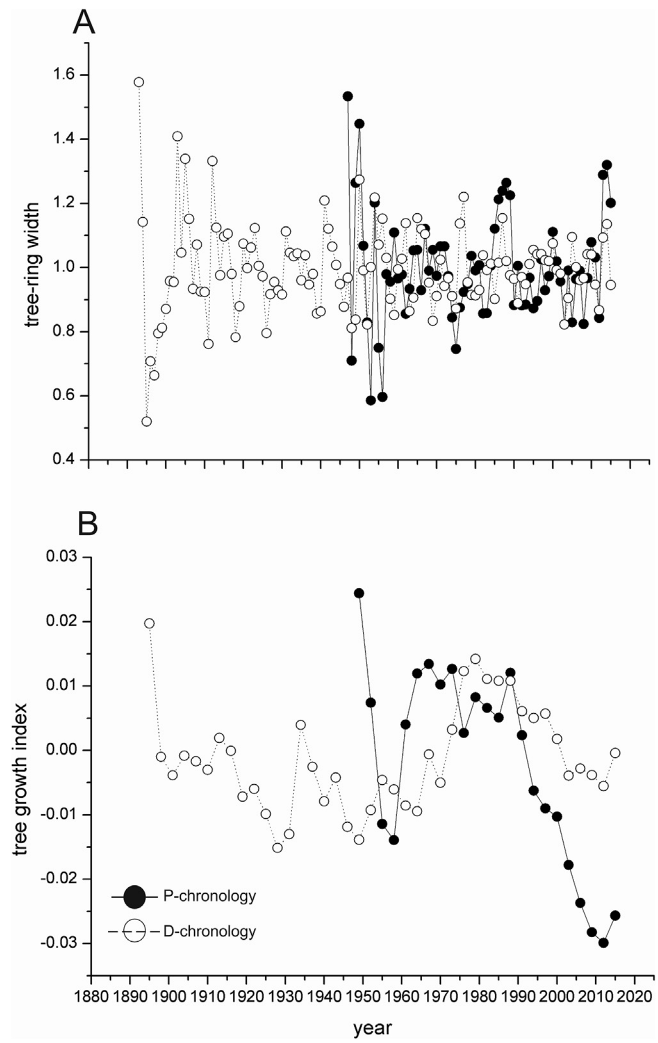

Fig. 2. (A) Tree-ring width of P-chronology (black circles) and D-chronology (white circles). The tree-ring index is produced through the ARSTAN programme applying a conservative method of detrending with negative exponential curves and/or linear regressions with negative or zero slopes; (B) Tree growth index (TGI) of *Q. pubescens* in D and P-chronologies was calculated as the ratio between the mean of the values measured on 3 consecutive annual rings and the mean of the series for a specific time interval (n). The index is useful to interpret the growth variations in terms of climate or other environmental factors.

Table 2
Descriptive statistics of two chronologies (P- and D-chronologies): mean tree-ring width calculated on the raw chronology and the STD chronology; tree-ring standard deviation (SD), which estimates the variability of measurements for the whole series; mean sensitivity (MS), which is an indicator of the mean relative change between consecutive ring widths; and EPS, the expressed population signal to indicate the level of coherence of the constructed chronology (ARSTAN analysis).

Statistical value	P-chronology	D-chronology
Measured years (n)	69	123
Raw mean ring width (mm) of chronology	4.05	2.46
Mean ring width of STD chronology	0.995	0.992
Mean sensitivity (MS)	0.117	0.121
Standard deviation (SD)	0.14	0.17
Expressed Population Signal (EPS)	0.81	0.81

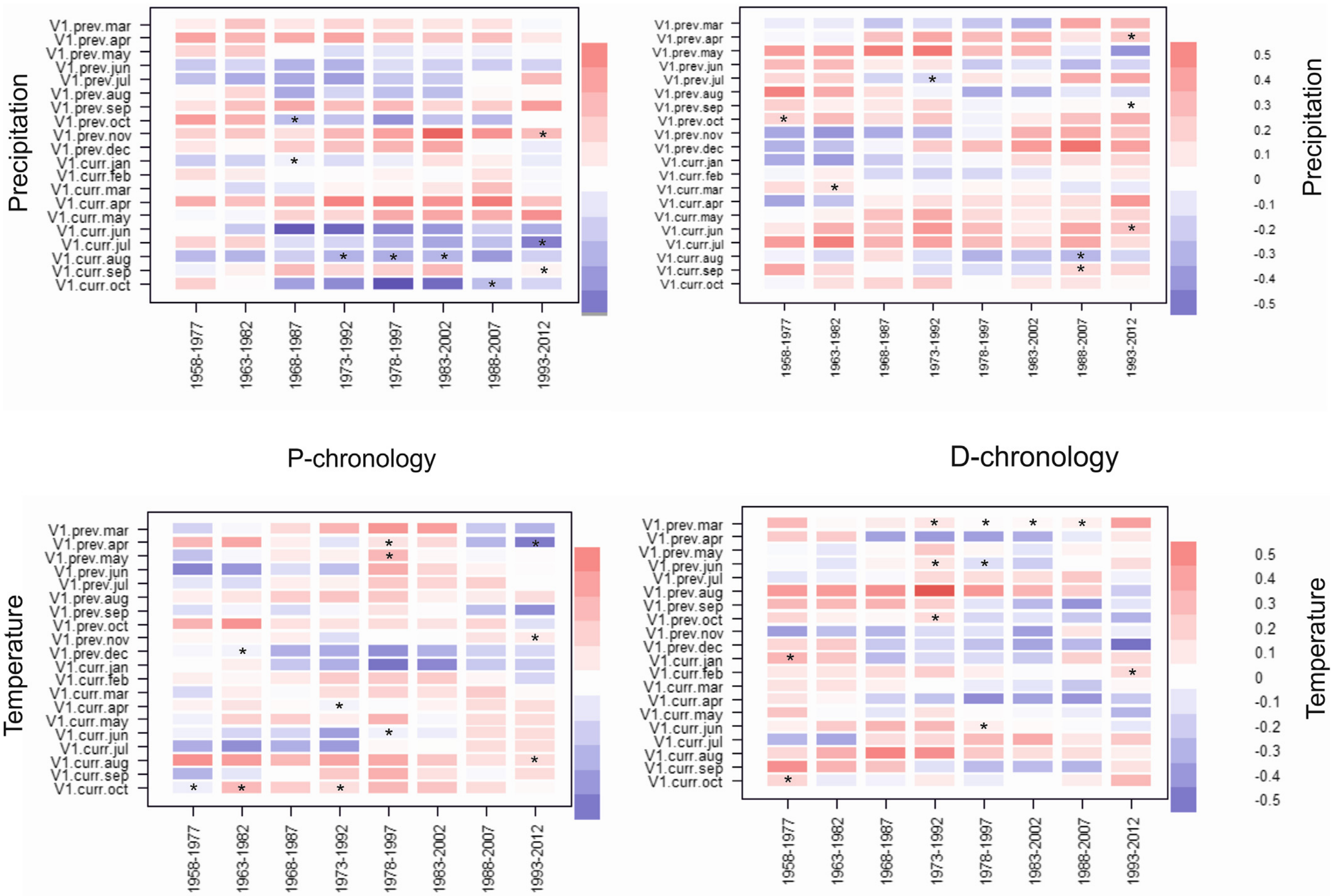

Fig. 3. Running means of bootstrapped statistically significant correlation coefficients between climate data and tree-ring indexed chronologies (MCF) in P- and D-chronologies. Correlations were calculated separately for each month for the period from March of the previous year to October of the current year. Each rectangle represents a correlation calculated over a 20-yr period plotted in the last year of each 20-yr period. Colour scale corresponds to the sign and strength of the correlations, asterisks refer to significant correlation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

chronology, growth-climate analysis revealed positive significant correlations of precipitation, in October of the previous year (1958–1977), in March (1963–1982), in April and September of the previous year (1993–2012), in June (1993–2012) and September (1988–2007) of the current year. Whereas, negative correlations between growth and precipitation in D-chronology were found in July of the previous year (1973–1992) and in August (1988–2007) of the current year of analysis (Fig. 3).

In P-chronologies, the relationships between air temperature and radial growth were significantly positive in April and May of the previous year (1978–1997), in November of the previous year (1993–2012), in August (1993–2012), and in October (1963–1982; 1973–1992) of the current year. Whereas, negative correlations between growth and air temperature in P-chronology were found in April (1993–2012) and December (1963–1982) of the previous year, April (1973–1992), June (1978–1997) and October (1958–1977) of the current year (Fig. 3).

Significantly positive correlations between tree-growth and temperature in D-chronology were observed in March (from 1973 to 2007), June and October of the previous year (1973–1992), January (1958–1997), February (1993–2012), June (1978–1997) and October (1958–1977) of the current year (Fig. 3). Negative correlation was found between radial growth and air temperature in January of the previous year (1978–1997) (Fig. 3).

3.3. *Spatial and temporal variation patterns of elements levels and sources*

Higher levels of Co, Cr, Mo, Ni, U, V, W, and Zn were detected in P- than D-chronologies, within the analysed period 1958–2009 (Fig. 4). Data in the period 1967–1974 are missing due to unclear signal of the ablation analysis in these years.

The levels of Co, Mo, Ni, Pb, and U over time (*p-value* ≤ 0.05) (MK test rejected the null hypothesis, $H0 \leq 0.01$) increased significantly in both P- and D-chronologies. Vanadium and Cu levels showed an increasing trend only in D-chronology. Chromium, Tl, Zn and W levels did not show any temporal pattern (*p-value* ≥ 0.05, accepting the null hypothesis H0) (Table 3), whereas, Hg and Pb levels showed a decreasing pattern over time (Table 3).

Moreover, Cu, Hg and Tl were unevenly distributed in tree-rings in P- and D-chronologies. The normalized levels of these elements (I_x) varied in D-chronology in the period 1958–2009: Cu in d7 > d5 > d8 > d6 (0.3 ± 0.039, 0.3 ± 0.010, 0.11 ± 0.034, 0.1 ± 0.014, respectively); Hg in d5 and d7 > d6 and d8 (0.4 ± 0.016, 0.3 ± 0.014, respectively); Pb in d7 and d8 > d5 and d6 (0.04 ± 0.001, 0.03 ± 0.003, respectively); Tl in d5 > d8 > d6 and d7 (0.06 ± 0.002, 0.05 ± 0.001, 0.04 ± 0.003, respectively).

Significant differences in temporal trends of each element were found between P- and D-chronologies (*p-value* ≤ 0.01), except for Cu levels (Table 4).

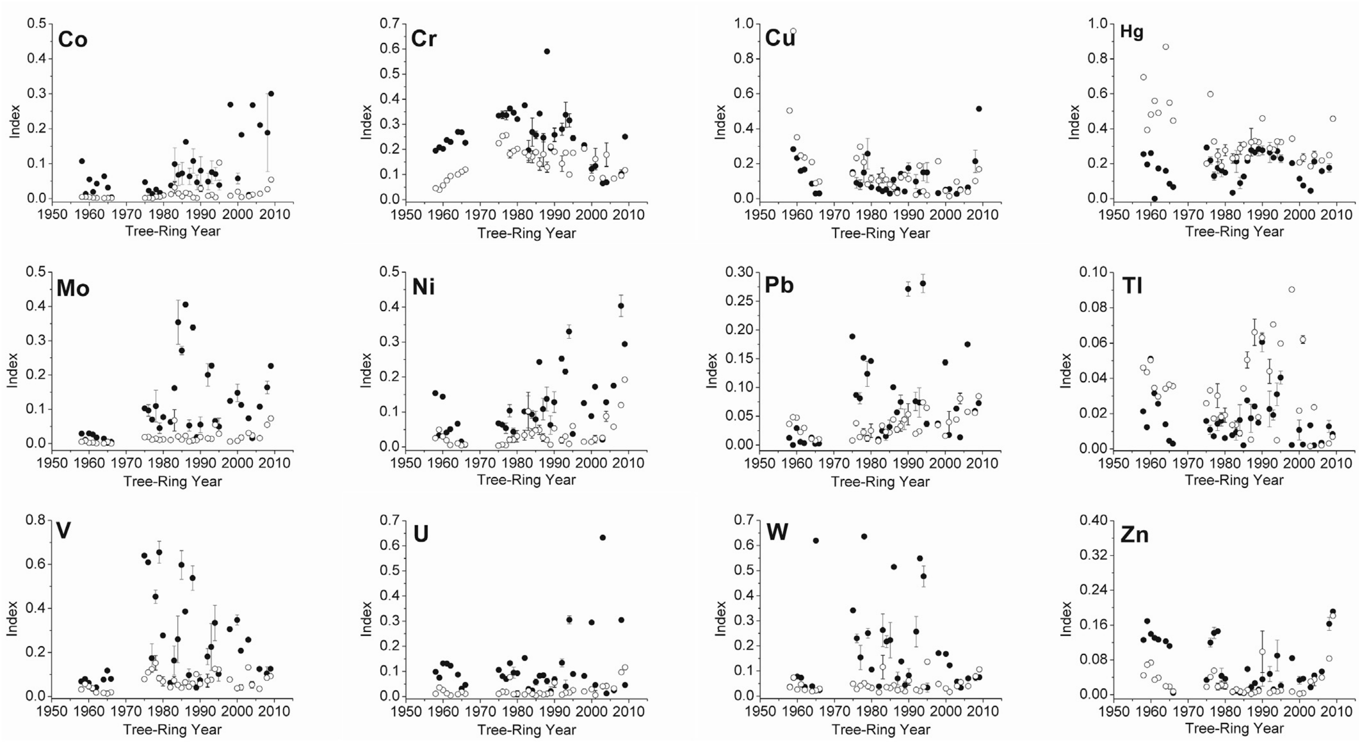

Fig. 4. Tendency of elements distribution (mean normalized data) in tree-rings of P-chronology (black circles) and D-chronology (white circles).

4. Discussion

4.1. Impact of urban environment on tree growth

Growth-climate analysis (weak relationships) highlighted that climatic effects do not completely explain the reduction of tree growth in plants grown at increasing proximity to the steel factory (P-sites). Whereas, pollution probably played a progressively negative effect on plant growth, as shown by the tree growth index in proximal sites (Fig. 2), in the 1950s, from 1973 and from 1990, in correspondence with the start of steel production, waste incinerator and biomass incinerator, respectively (Fig. 1). The periods of lowest precipitation in Terni were those from 1967 to 1975 and from 1988 to 2002, with cumulative annual precipitation ranging from 570 to 800 mm (Meloni and Carpine, 2004). This precipitation pattern did not fully explain the observed reduction of tree growth in the '80s.

Precipitation somewhat affected tree growth in D- and P-chronologies differently. Site-specific environmental conditions were probably the cause of a different microclimate between P- and D-chronologies, though at a short distance to each other. P-chronology is in the urban context with compacted soils and more heat (urban heat island), while D-chronology refers to the peri-urban area with less drastic transformations affecting soil conditions and moisture availability. The intensified warming caused by altered land surface properties and the lowered evapotranspiration-induced cooling due to sealed surfaces added to detrimental pollution levels, posing challenges to the growth of urban trees (e.g., Gregg et al., 2003; Robitaille, 1981; Svensson and Eliasson, 2002).

Although a stronger limitation to tree growth was observed in the proximity of the industrial plant, the impact exerted by other pollution sources could not be ruled out. The timing of the reduction of tree growth coincide with the development of a landfill in the same area during the end of '80s. Results obtained here pointed to higher levels of pollutants in P- compared to D-chronology. A marked reduction in tree growth due to the interactive effects of climatic conditions and industrial activities (paper manufacturing, aluminium-refining and phosphate fertilizer factories) was also observed in *Picea abies* Karst. (Tomakomai forest), near a major industrial district in Hokkaido, Japan (Kobayashi et al., 1997). However, in the present case, the unfavourable urban context probably enhanced the environmental pollution effect in limiting tree growth more in P- than D-chronology (Barniak and Krąpiec, 2016; Fischer et al., 1994; Robitaille, 1981). More thorough examinations of elemental index profiles in stem wood and tree ecophysiological responses to stress factors are, therefore, needed before drawing unambiguous conclusions about the impact of environmental conditions on downy oak or other tree species as derived from dendrochemical analyses.

4.1.1. Trace elements in tree-rings

Different trace element profiles in tree-rings were detected with annual resolution in trees grown at different distance from the potential pollutant source, in the period 1958–2009, reflecting industrial activities in the urban area. Levels of Co, Cr, Mo, Ni, Pb, V, W, and Zn were higher in annual rings of trees closest to the steel factory (Fig. 4). Moreover, the levels of Cr, Mo, Ni, V, and W in growth rings increased during the '80s and '90s, in agreement with a high peak of pollution history in Terni. During those pollution peaks, a waste disposal of the steel factory was implemented in "Terni-Papigno" (Umbria, 2010), causing an increase in particulate matter index. These findings were detected by monitoring stations. Yet, high depositions of particulate matter on leaves of downy oaks were observed in the same area (Sgrigna et al., 2016). The use of Cr, Mo, Ni, V, Zn, and W is common during the productive processes of steel manufacture (Santonen et al., 2010), for the corrosion resistance of flat-rolled stainless steel, and W, in the welding procedure

Table 3
Mann–Kendall rank correlation test of trace elements in P- and D-chronologies. Values of Tau of Kendall, S (Kendall score, expressed as negative or positive value indicating decreasing or increasing trend, respectively), p-value and trend function, defined by arrows, are reported. Significant elements were marked in grey.

		P-chronology pattern		*D-chronology pattern*
Co	Tau di Kendall	0.398	Tau di Kendall	0.425
	S	237	S	253
	p-value (bilateral)	≤0.01	p-value (bilateral)	≤0.01
	trend	↗		↗
Cr	Tau di Kendall	-0.173	Tau di Kendall	-0.045
	S	-103	S	-27
	p-value (bilateral)	-	p-value (bilateral)	-
	trend	no		no
Cu	Tau di Kendall	-0.2	Tau di Kendall	-0.466
	S	-119	S	-277
	p-value (bilateral)	-	p-value (bilateral)	≤0.01
	trend	no		↗
Hg	Tau di Kendall	-0.324	Tau di Kendall	-0.237
	S	-193	S	-141
	p-value (bilateral)	≤0.01	p-value (bilateral)	≤0.05
	trend	↘		↘
Mo	Tau di Kendall	0.331	Tau di Kendall	0.435
	S	197	S	259
	p-value (bilateral)	≤0.01	p-value (bilateral)	≤0.01
	trend	↗		↗
Ni	Tau di Kendall	0.371	Tau di Kendall	0.314
	S	221	S	187
	p-value (bilateral)	≤0.01	p-value (bilateral)	≤0.01
	trend	↗		↗
Pb	Tau di Kendall	-0.096	Tau di Kendall	-0.24
	S	-57	S	-143
	p-value (bilateral)	-	p-value (bilateral)	≤0.05
	trend	no		↘
Tl	Tau di Kendall	-0.119	Tau di Kendall	-0.2
	S	-71	S	-119
	p-value (bilateral)	-	p-value (bilateral)	-
	trend	no		no
U	Tau di Kendall	0.257	Tau di Kendall	0.361
	S	153	S	215
	p-value (bilateral)	≤0.05	p-value (bilateral)	≤0.01
	trend	↗		↗
V	Tau di Kendall	0.113	Tau di Kendall	0.227
	S	67	S	135
	p-value (bilateral)	-	p-value (bilateral)	≤0.05
	trend	no		↗
W	Tau di Kendall	-0.018	Tau di Kendall	0.143
	S	-11	S	85
	p-value (bilateral)	-	p-value (bilateral)	-
	trend	no		no
Zn	Tau di Kendall	-0.129	Tau di Kendall	-0.197
	S	-77	S	-117
	p-value (bilateral)	-	p-value (bilateral)	-
	trend	no		no

(Santonen et al., 2010). These elements are, consequently, potential tracers of the industrial activity in the studied area, their elemental index varying with the level of pollution. Distinctively, concentrations of Cl and Cu were consistent in the area particularly exposed to the vehicular traffic.

Although U is a naturally occurring element found in low levels within rock, soil and water (UNSCEAR, 1993), it was difficult to explain the presence of U in our tree-rings, exceeding the

Table 4
Levene's *t*-test of element patterns in P- and D-chronologies. The test evaluates the significant differences between the means for each element index in P- and D-chronologies (p-value ≤ 0.05). Significant elements were marked in grey.

		F	*p-value*
Co	Equal variances assumed		
	Equal variances not assumed	29.466	0.000
Cr	Equal variances assumed		
	Equal variances not assumed	3.670	0.060
Cu	Equal variances assumed	0.717	0.400
	Equal variances not assumed		
Hg	Equal variances not assumed		
	Equal variances assumed	6.648	0.012
Mo	Equal variances not assumed		
	Equal variances assumed	34.890	0.000
Ni	Equal variances assumed		
	Equal variances not assumed	15.516	0.000
Pb	Equal variances not assumed		
	Equal variances assumed	21.573	0.000
Tl	Equal variances not assumed		
	Equal variances assumed	8.658	0.004
U	Equal variances assumed		
	Equal variances not assumed	11.032	0.001
V	Equal variances assumed		
	Equal variances not assumed	44.811	0.000
W	Equal variances not assumed		
	Equal variances assumed	34.890	0.000
Zn	Equal variances assumed		
	Equal variances assumed	18.849	0.000

background noise in P-chronology. The occurrence, source, distribution, level, mobility, and speciation of U in the soil environment might depend on both natural and anthropogenic factors. A potential pollution source of U accumulation in tree-rings could be found in the radioactive waste of the hospital, where the depleted U and radioactive isotopes are used, for example, for sterilization of medical equipment and for cancer therapy (Davidovits, 1994). The multiplicity and variability of possible pollution sources (in space, time, type, and level) added to the complexity of the pollution issue caused by the steel factory.

The uneven distribution of Cu, Hg, and Tl found in tree rings of P- and D-chronologies, with higher contents in the latter (Fig. 4), may be explained by the accumulation of pollutants emitted by the incinerator in the peri-urban area of "Maratta"and the waste disposal areas around the D-chronology (Fig. 1). According to recent researches, Hg, Pb and Tl (Crowley et al., 2003; Ruck et al., 1989) are trace metals commonly used to fingerprint emissions from waste incinerators (Font et al., 2015) and waste disposal (National Research Council, 2000). The area of Terni is interested by different pollution sources, such as incinerator and waste dump. A report of Regione Umbria (2008) identified, in the area of Terni, activities of burning or dumping of urban waste, hospital waste and electronic materials, which contain toxic metals, such as Hg, Pb and Tl. In fact, D-chronology showed higher values of Hg and Tl indexes compared to P-chronology. It is worth noting that trees grown in the sites closer to the incinerator in "Maratta" (d7 and d5) and waste disposal (d8) showed higher accumulation of elements differently distributed in the external site, within the period 1958–2009.

Lead and Cu showed an erratic and unclear spatial and temporal distribution, probably due to other unspecific and/or multiple urban sources of pollution, such as local vehicular traffic and other industrial processes (Cansaran-Duman et al., 2014). However, Cu naturally occurs in the earth's crust, in rocks, soils, and waters (Manahan, 2010). It is interesting to note also that the decreasing patterns of Pb and Hg could be due to Pb replacement policies, and the replacement of Hg with non-toxic liquid metal alloy (NewMerc, e.g., gallium and indium), also in medical devices (Rice et al., 2014). Copper did not show a specific temporal pattern in P- and D-chronologies, probably due to the varying sources of contamination (industrial and waste pollution), or the common background presence in the soil.

Although some difficulties in identifying the exact source were encountered, the investigation of tree-ring elemental index variability over time allowed the assessment of temporal patterns of pollutant accumulation and the comparison of differences among different sites. The increasing pattern of Co, Cr, Mo, Ni, U, V, W, and Zn levels in tree-rings within the monitored time span suggests a continuous contamination in the town of Terni (Corona and Serneri, 2007; Terni, 2004).

Elements can be translocated through the xylem, phloem or ray cells, or can be mobile across tree-ring boundaries, radially or vertically translocated in the stem (Hagemeyer et al., 1994), which may complicate their analytical detection. Some elements are more mobile and actively translocated within the plants through metabolic processes (e.g., Cl, K, Mg, P, S, etc.), than others (e.g., B, Ba, Ca, Cu, Fe, Li, Mn, Mo, Sr, and Zn, either immobile or restricted in their mobility within the phloem; Bukovac and Wittwer, 1957), which may provide controversial results. Instead, As, Cd, Cr, Cu, Fe, Hg, Mo, Ni, Sb, Sn, V, and Zn are not highly mobile within the stem (Odabasi et al., 2015). Therefore, a complication of the analytical detection can be determined by the migration of elements between individual tree-rings or by the different mobility of elements, that determine the elemental index in tree-ring series. The interpretation of temporal patterns is difficult and the possibility to use dendrochemistry for reflecting historical changes in the environment limited (Garbe-Schonberg et al., 1997).

5. Conclusion

The ring width growth decreased in trees grown in the proximity of sites impacted by pollutant sources, whereas the accumulation of trace elements increased. Although there were no simple correlations between the contents of trace elements in tree-rings and the index of pollutants in the surrounding environment, the LA-ICP-MS spot analysis was successful in describing historical variation in this highly polluted urban context. Determining the variability of trace element levels in tree-rings with annual resolution is of crucial importance when assessing contamination episodes and trends to identify the legacy of environmental contamination associated with industrial activities and subtle pollutants. The use of LA-ICP-MS spot analysis proved to be useful in providing systemic information regarding changes in historical pollutant loading, making the reconstruction of temporal trends of environmental contamination possible. However, a clear understanding of how elements become physiologically incorporated into tree-rings is still needed to have a precise interpretation of temporal trends in tree-ring elemental contents.

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