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Urban and industrial contribution to trace elements in the atmosphere as measured in holm oak bark

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HIGHLIGHTS

- Tree bark has been used to study trace element concentrations in the atmosphere.
- Two urban environments affected by different pollution sources have been studied.
- High levels of As, Co, Fe, Mn, Ni, V and Zn are measured in industrial areas.
- Maps can highlight both a particular point and diffuse sources of metal pollution.

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ABSTRACT

The concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, Pb, V and Zn were measured by ICP-OES in samples of bark of the holm oak (*Quercus ilex* L.) collected from trees in different urban environments (residential and mixed residential/industrial).

The use of tree bark as a bioindicator makes it easy to create maps that can provide detailed data on the levels and on the spatial distribution of each trace element.

For most of the elements considered (As, Co, Fe, Mn, Ni, V and Zn), the concentrations in the industrial sites are about twice (from 1.9 to 2.8 times higher) of those in the residential area. Arsenic, Fe and Zn show the highest concentrations near a steel plant (operational until 2005), but for the other elements it is not possible to identify any localized source, as evident from the maps. In areas where urban pollution is summed up by the impact of industrial activities, the population is exposed to significantly higher amounts of some metals than people living in residential areas.

1. Introduction

Air quality is a global concern (WHO, 2013), and many efforts are continuously devoted to its improvement. Among the air pollutants belonging to different groups of chemicals, metals may present a serious health threat, even at trace levels; for this reason, their presence in the atmosphere, related both to natural and anthropogenic non-point and point sources (industrial emissions, disposal of municipal waste, traffic-related activities, etc.) has been extensively studied during the last decades (Nriagu, 1979; Pacyna and Pacyna, 2001). Recently, several authors have discussed the association between health effects and exposure to particulate matter (PM) (especially PM2.5 and PM10), not only in terms of mass but also in terms of composition, relating metal concentrations with development of cardiovascular and pulmonary disease (Bell et al., 2010; Franklin et al., 2008; Gehring et al., 2015; Schwarze et al., 2006). The number of monitoring stations measuring the PM levels and the chemical composition of PM has increased over the last years; however, due to the necessity of expensive technical equipment, these stations are placed only in some big cities, usually at critical sites, and they remain dedicated to the assessment of the impact of specific sources at a certain time (Baulig et al., 2004; Faggi et al., 2011).

The use of bioindicators, i.e. organisms exposed to the different environmental contaminants, can be an interesting alternative (or complementary) strategy, allowing wider monitoring programs, involving a larger number of sampling sites at affordable costs by means of simpler instrumental equipment.

In the literature, many studies showed that tree bark is a simple

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and useful bioindicator that is able to provide information on the levels of trace elements in the atmosphere (Cucu-Man and Steinnes, 2013; Faggi et al., 2011; Fujiwara et al., 2011; Roganovic et al., 2013).

In the present study, the concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, Pb, V and Zn were measured in samples of bark of the holm oak (*Quercus ilex* L.) collected from trees in different areas of Genova (northwestern Italy). The trace elements analyzed were chosen according to: i) their relevance for human health; ii) the availability of literature data for possible comparison; iii) the sensitivity of the analytical equipment used; and iv) good performance (accuracy and reproducibility) of the analytical method (mineralization and analysis).

The aim of this study is to provide information about the trace element deposition in urban environments affected by various pollution sources. In particular, considering the strict closeness between industries and residential houses in Genova, the main objective is to show the influence that industrial activities may have on the population living nearby and to differentiate between urban contributions and industrial sources. Moreover, one of the important advantages of this approach consists in the capability of drawing maps allowing one to visualize in considerable detail the presence of several contaminants.

2. Materials and methods

A total of 56 samples of holm oak (*Quercus ilex* L.) bark were collected in 2014 and 2015 from the trunks of trees in Genova, the capital city of the Liguria region (northwestern Italy). The city, which has approximately 582,000 inhabitants, lies on a narrow coastal strip about 30 km long, with almost equal width from west to east, delimited to the north by hills ranging from 400 to 1100 m a.s.l. situated between 6 and 10 km from the sea.

For this study, the city was divided into two parts, representing two different urban environments. The central-eastern area (22 samples) is characterized by residential and office settlements; commerce and tourist activities are also concentrated in this area. Thus, the main sources of trace elements in the atmosphere are vehicular traffic and domestic heating. There are no major industrial activities; even though this area includes a portion of the port, the maritime traffic takes place in the western part. The western area (34 samples) is characterized by a close residential proximity to important industrial activities. In fact, this part of the city includes a power plant (coal and heavy fuel oil, 295 MWatt) and some industrial facilities (electrical engineering and electronics, petrochemicals, ship construction and repairs), together with intense port activities (oil and cargo terminals) and related transport infrastructures (railway, highways, airport). Genova is one of the most important ports of the Mediterranean and ranks 15th in Europe, with over 2 million containers and 52 million tons of goods exchanged in 2014. Moreover, the western area includes the district of Cornigliano, characterized by strong industrial development since 1950s, when a steel plant was built in the area, with a consequent increase of population. The steel crisis and the consequent decline of related industrial activities determined the closure of the coke oven in 2002 and of the blast furnace in 2005. In the meantime, several studies regarding pollution in the area (Prati et al., 2000) and its impact on the health of the population were published (Parodi et al., 2005), and the area became the object of one of the most important requalification projects of disused industrial settlements in Italy. Fig. 1 shows the sampling sites in the two urban areas, together with the main industrial and port activities.

In the Mediterranean area, the holm oak has a wide natural distribution, and it is frequently used in the landscaping of urban environments (streets, gardens and parks). Its finely squared-fissured bark has already proven to be a useful bioindicator (Minganti et al., 2015, 2016).

Bark samples (thickness of 2–6 mm) were collected from the trunks of trees along streets (within 5 m from the edge of the street) and in urban parks, at a height of 1.50–1.80 m from the ground, in order to limit the presence of soil dust (Schelle et al., 2008) and they were stored in polyethylene bags at −25 °C. The geographical coordinates of each tree sampled were recorded using GPS equipment. The age of each tree sampled was estimated using the method of Panaïotis et al. (1997), based on the measurement of the diameter of the stem at the height of the bark sample collection and applying a second order polynomial equation. All trees showed an estimated age in the interval of 50–100 years.

After manually removing any extraneous material, the individual samples were freeze-dried and homogenized in 25 mL Teflon grinding jars containing 10 mm zirconium oxide grinding balls using a MM2 Mixer Mill (Retsch GmbH, Germany), which was used without sieving. All concentrations are reported on a dry weight (d.w.) basis. Reporting the results as dry weight is important because a great variability in the water content of the samples was observed. A series of samples (n = 6) collected during a dry period showed a mean water content of 10%, while another series (n = 13) taken during a rainy period had 33% of mean water content; the overall range was from 4% to 54%.

About 0.10–0.15 g of the samples were mineralized using 5 mL of 65% (m/m) nitric acid (for trace metal analysis, from Scharlau, Spain) in closed Teflon PFA vessels heated in a microwave digestion system MDS 2000 (CEM Corporation, USA). After cooling, the solutions were transferred into 25 mL volumetric flasks and diluted to volume using ultra-pure (>18 MOhm cm) water (Elgastat UHQ, Elga

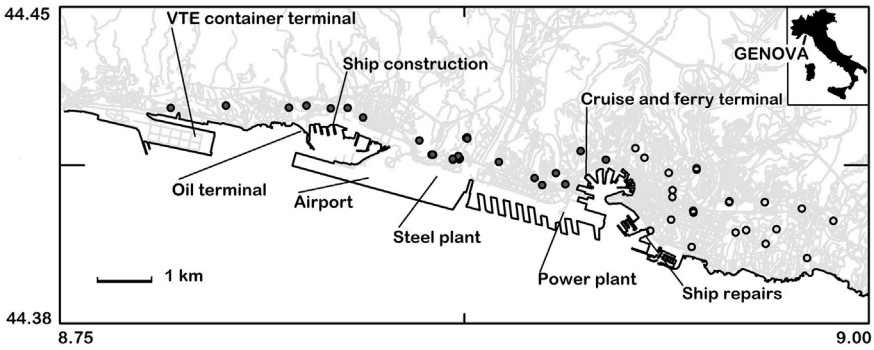

Fig. 1. Sampling sites of holm oak bark in Genova. Filled circles correspond to industrial-residential sites; empty circles correspond to residential sites. The main industrial activities are also indicated.