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# Wood and bark of *Pinus halepensis* as archives of heavy metal pollution in the Mediterranean Region

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ABSTRACT

Natural levels of heavy metals (HM) have increased during the industrial era to the point of posing a serious threat to the environment. The use of tree species to record contamination is a well-known practice. The objective of the study was to compare HM levels under different pollution conditions: a) soil pollution due to mining waste; b) atmospheric pollution due to coal-fired power plant emissions. We report significant HM enrichment in *Pinus halepensis* tissues. Near a burning power plant, Pb content in a tree wood was 2.5-fold higher that in natural areas (no pollution; NP). In mining areas, Cd content was 25-fold higher than NP. The hypothesis that HM contents in tree rings should register pollution is debatable. HM uptake by pines from soil, detoxification mechanisms and resuspended local soil dust is involved in HM contents in wood and bark.



## 1. Introduction

Pollution is one of the current problems that the environment faces. Heavy metals (HM) are related to different sources of pollution, such as mining (Martínez García et al., 2001; Odumo et al., 2014), industry and energy production (Agrawal et al., 2010; Lv et al., 2015; Rodríguez Martín and Nanos, 2016; Wang et al., 2010), population growth (Argyraki and Kelepertzis, 2014; Jiménez-Ballesta et al., 2017; Petrotou et al., 2012) and fossil fuel burning (Karbassi et al., 2015; Rodríguez Martín et al., 2015). These anthropic activities are an important source of HM, particularly Cd, Cu, Cr, Hg, Ni, Pb and Zn. Atmospheric HM tend to accumulate in soil. Many studies have confirmed that human activities have dramatically increased natural concentrations in the last century. Soil can provide a record of HM contamination in the environment and can indirectly detect sources of pollution (Nanos et al., 2015; Nanos and Rodríguez Martín, 2012; Rodríguez Martín et al., 2013b). Soil is also one of the most important reservoirs of HM and one of the principal routes of metals uptake in plants (Carbonell et al., 2011; Rizwan et al., 2017). However, HM soil contents do not reflect the evolution of pollution.

In line with this, the use of trees, particularly conifers, as bioindicators of contamination has been well-known since the 1970s (Smith, 1972). The tree-wood can be used to evaluate anthropogenic pollutants from the atmosphere or from deposition on soil and the subsequent uptake by trees (Cocozza et al., 2016; Lageard et al., 2008). Tree rings have been used to monitor pollution and show changes in the concentration of HM over time (Robitaille, 1981; Xu et al., 2014). Some authors have studied temporal volcanic activity using elements associated with tree rings (Rodríguez Martín et al., 2013a; Sheppard et al., 2008; Watt et al., 2007). It is now accepted that analyses of plants and tree rings indicate the temporal evolution of HM availability in the environment. However, there are controversial findings regarding the use of tree rings in pollution chronology (Watmough and Hutchinson, 2003; Witte et al., 2004). It cannot always be directly measurable since different factors such as soil HM contents (Witte et al., 2004) or radial mobility in the stem wood (Nabais et al., 1999) may limit the usefulness of dendrochemistry in monitoring temporal changes in metal deposition (Watmough and Hutchinson, 2003). In addition, the HM contents and their availability in soil, the micronutrient limitations in these soils (Fuentes et al., 2007), the roots' capacity to uptake HM from soils (Sheppard and Funk, 1975) and the mobility

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of HM in the xylem and phloem (Robitaille, 1981) are all inherent problems when using trees as bioindicators of pollution. Many recent studies have confirmed that HM may accumulate in tree woods. Nevertheless, the direct path introducing HM into growth rings remains unknown (Chiarantini et al., 2016). In dead plant tissues, like tree bark, atmospheric HM accumulate on the outermost surface due to air deposition (Chiarantini et al., 2016; Sawidis et al., 2011). Nonetheless reconstructing environmental pollution over time is more complicated in bark and its accumulation there is still poorly understood (Cocozza et al., 2016; Rodríguez Martín et al., 2013a).

In the Mediterranean basin, Aleppo pine (*Pinus halepensis* Mill.) is one of the most widely distributed species covering approximately 2,500,000 ha, including islands. Aleppo pine represents an accessible bioindicator in the Mediterranean region that can be used to evaluate degraded ecosystems and to analyse historical trends in trace element deposition. The study objectives were to: (1) evaluate the use of *Pinus halepensis* as bioindicators of HM pollution employing different tissues (wood and bark); (2) compare HM levels with different soil HM contents and two human activities: a) soil pollution due to mining waste and b) atmospheric pollution due to coal-fired power plant emissions; (3) compare the past and the present-day in the tree rings at sites with differing degrees of contamination.

## 2. Materials and methods

### 2.1. Study areas and sampling

The forest study areas are located at three sites in Spain, where two sites (A and B. Fig. 1) were established on the Island of Majorca (The Balearics). It is formed mainly by calcareous lithologies of a marine origin. On the whole, climate is purely Mediterranean with annual rainfall of 350–650 mm. Ecologists in Action reported that The Balearics has higher air pollution levels than those recommended by the World Health Organization (WHO). Moreover, some 150,000 people (13% of the islands' population) live in areas where air pollution exceeds the limits legally permitted in Spain (https://majorcadailybulletin.com/news/local/2016/10/27/45790/majorca-pollution-above-recommended-levels.html). According to the island's orography, two plots were established in the Sierra de Tramuntana, in the north-western part of the island (Site B plot 54 and 55). Plots 54 and 55 are located at a distance of 25.2 and 31.4 km, respectively, from the nearest coal-fired power plant of the island, as "sentinel sites", which were assumed clean of pollution (NP). In contrast, two other plots were established in the Alcudia

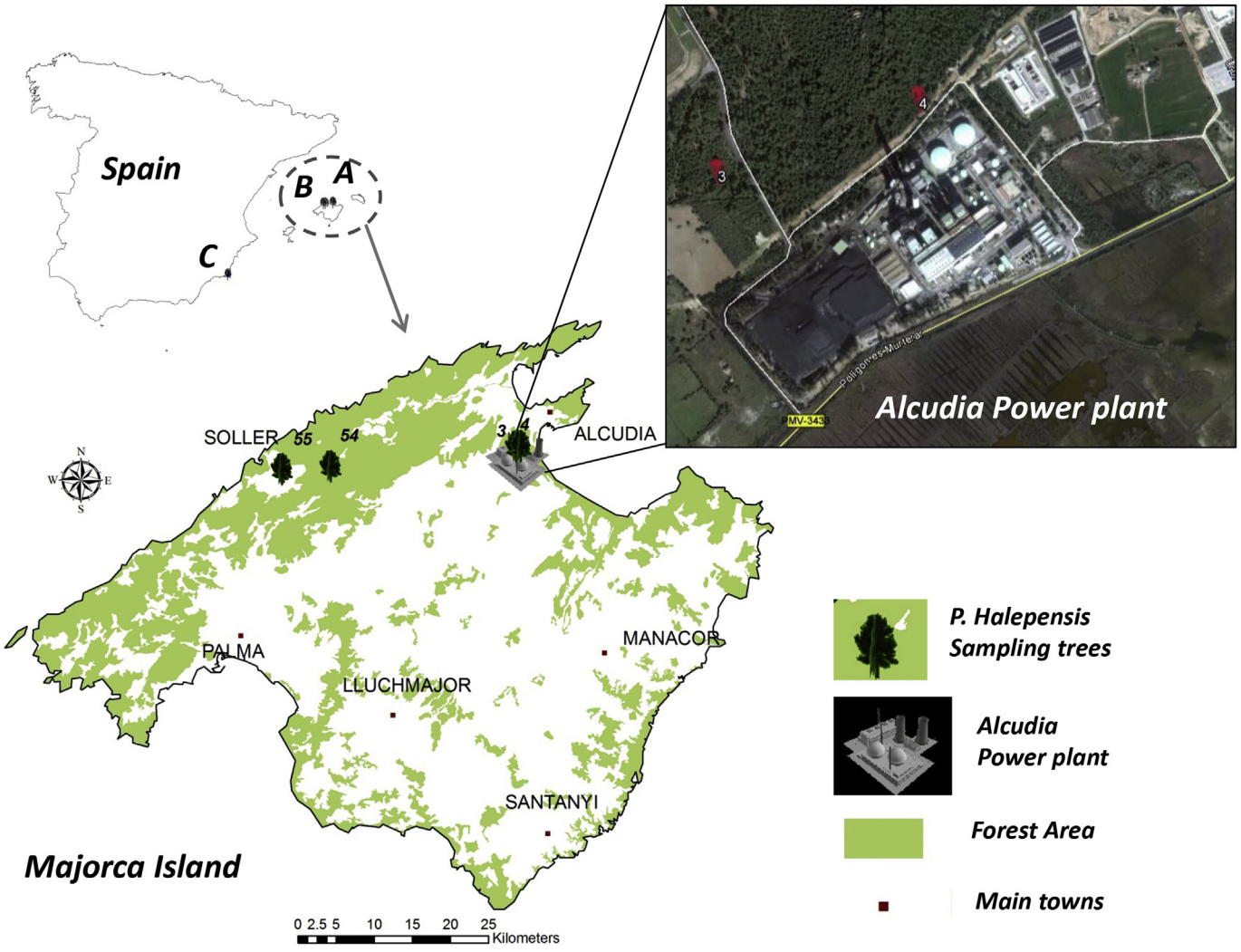


**Fig. 1.** Location of the study trees on the Island of Majorca and the position of the Alcudia coal-fired power plant. P3 and P4 in area A (AP) near the power plant and P54 and P55 at Sierra de Tamuntana on the northern backbone of Majorca (Area B: NP). Area C (SP) showing the position samples in the Cartagena–La Unión mining district (Murcia, Spain).