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ISSN : 0254-8704
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J. Environ. Biol.
30(5), 831-834 (2009)
info@jeb.co.in

Biomonitoring of zinc and manganese in bark of Turkish red pine of western Anatolia

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(Received: February 02, 2008; Revised received: August 10, 2008; Accepted: September 29, 2008)

Abstract: *Turkish red pine (Pinus brutia) is a widespread evergreen tree in Mediterranean and Aegean regions of Turkey. The barks of Pinus brutia were tested as a possible biomonitor of Zn and Mn accumulation studied in Western Anatolia, Turkey. Samples collected from industry, roadside, suburban and rural areas from thirty locations in the study area were investigated. The concentration of zinc and manganese were determined in the bark of the red pine by atomic absorption spectrometry. As a result of this study, the following mean concentrations were determined: for Zn between min 8.4 and max 14.1 $\mu g\ g^{-1}$, and for Mn between min 19.1 and max 24.0 $\mu g\ g^{-1}$. It was found that there is no affect of location on the element concentration of both Mn and Zn.*

Key words: *Acumulation, Biomonitor, Trace element, Turkish pine bark, Western Anatolia*
PDF of full length paper is available online

Introduction

All compartments of the biosphere are polluted by a variety of inorganic and organic pollutants as a result of anthropogenic activities and alter the normal biogeochemical cycling (Prasad and Freitas, 2003). Although heavy metals are natural components of the environment, they are emitted into the environment in different ways, *i.e.* transportation, industry, fossil fuels, agriculture, and other anthropogenic activities (Aksoy *et al.*, 2000; Baslar *et al.,* 2003; Baslar *et al.,* 2005; Butkus and Baltrenaite, 2007; Cayir *et al.,* 2008).

Higher plants have been used to detect the deposition, accumulation and distribution of metal pollution. Lower plants, especially mosses, algae and lichens are probably the organisms most frequently used for monitoring metal pollution in urban environments (Aksoy *et al.*, 1999; Deo, 2004).

In literature, there are many studies focusing on using barks of different tree species as biomonitor. However, in some studies only pine species were investigated to decide whether pine species can be used as a biomonitor for the determination of heavy metals. Results of such studies identified that the barks of the pine trees are good adsorbents of airborne pollutants, including anthropogenic heavy metals. Among the studied barks of pine tree are Turkish red pine (*Pinus brutia* Ten.) (Dogan *et al.*, 2007); Italian stone pine (*Pinus pinea* L.) (Oliva and Mingorance, 2006); Austrian pine (*Pinus nigra* Arnold.) (Coskun, 2006); Masson pine *(Pinus massoniana* Lamb.) (Kuang *et al.*, 2007) and scots pine (*Pinus sylvestris* L.) (Laaksovirta *et al.*, 1976; Swieboda and Kalemba, 1979; Takala *et al.*, 1994, Huhn *et al.*, 1995; Lippo *et al.*, 1995; Poikolainen, 1997; Schulz *et al.*, 1999; Harju *at al.*, 2002; Mattsson *et al.*, 2005; Poykio *et al.*, 2005; Samecka-Cymerman *et al.*, 2006).

Since the barks of the pine trees are good adsorbents of airborne pollutants, the aim of this study is to determine the accumulation levels of zinc (Zn) and manganese (Mn) by using the bark of *P. brutia* as bioindicator in Western Anatolian part of Turkey.

Materials and Methods

The Turkish red pine is a native pine to the eastern Mediterranean region. It is dominantly distributed in Turkey, at lower altitudes from sea level to 600 m, it can also be seen up to 1200 m in the southern parts. The species is also extends to the East Aegean Islands and Greece, the Crimea, Georgia, Azerbaijan, northern Iraq, Jordan, western Syria, Lebanon and Cyprus.

It is a medium–size tree, reaching 20–35 m tall and with a trunk diameter of up to 1 m, exceptionally 2 m. The bark is orange–red, thick and deeply fissured at the base of the trunk, and thin and flaky in the upper crown. The needles are in pairs, slender, mostly 10-16 cm long, bright green to slightly yellowish green. The cones are stout, heavy and hard, 6-11 cm long and 4-5 cm broad at the base when closed, green at first, ripening glossy red–brown when 24 months old. The seeds are 7-8 mm long, with a 15-20 mm wing, and are mainly wind-dispersed (Frankis, 1999).

The barks of *P. brutia* were collected from different sites during July-August, 2005. The number of sites from each category sampled was as follows: Industrial 8, roadside 6, suburban 6, rural area 6 and control 4. The trees used for sampling were of the same age (approximately 35-40 years old). The barks were carefully removed with a stainless steel pen knife at an average height of about 2 m above the ground. About 200 g of upper part of the bark of *P. brutia* from each direction of the trees were collected. The samples were dried in oven at 80°C for 24 hr, milled in a micro-

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hammer cutter and fed through a 2 mm sieve. Bark samples were stored in clean self-sealing plastic bags under silica gel desiccant. Contamination from the micro–hammer cutter was negligible during the grinding because it was washed after every grinding, first with absolute alcohol then with triple distilled water.

The bark digestion method used in this study was described by Perkin Elmer Corporation (Anonymous, 1996). The metals were determined by Perkin Elmer Analyst 700 model flame atomic absorption spectrometry (FAAS). The reproducibility of the method used in decomposing the bark samples was checked by carrying out a triplicate analysis. All samples were analyzed as soon as possible after preparation.

One way ANOVA was used to determine whether there is a location affect on the element concentration of both Mn and Zn.

Results and Discussion

In this study, the bark samples of *P. brutia* collected from 30 different stations, in industrial, suburban, roadside, rural and control areas throughout Western Anatolian Region, in Turkey were investigated to identify the pollution level of the region by analyzing the density of some heavy metals.

As a result of this study it was detected that the mean zinc concentration found in the study area ranges between 8.4 and 14.1 µg g^{-1} (Table 1). The minimum mean zinc value was determined as 8.4 µg g^{-1} in control areas, and the maximum mean value was determined as 14.1 µg g^{-1} in both industrial areas and roadsides. Accumulation of Zn in areas where there are less anthropogenic activities is less than in industrial areas and roadsides. This result leads us to reach a conclusion that in such areas the origin of Zn accumulation is anthropogenic activities.

Heavy metals occur regionally in natural soils. Of particular concern is, however, soil pollution with heavy metals introduced by human activities (Ducic and Polle, 2005). For example, zinc occurs naturally in air, water and soil (Lindroos *et al.*, 2007), but as a result of human activities its concentrations are rising unnaturally. Most zinc is added during industrial activities, such as mining, and waste combustion and steel processing in automotive and electrical industries. Moreover, recent developments in hardware industries make their contribution to zinc deployment in the environment. Some soils are heavily contaminated with zinc, and these are to be found in and around industrial areas, or where sewage sludge from industrial areas has been used as fertilizer (Nies, 1992).

Table - 1: Mean concentrations of manganese (Mn) and zinc (Zn) in the bark of *Pinus brutia* in the study area

Site	Numbers	Element (µg g^{-1} dry weight)			
		Mn		Zn	
		Mean	SE*	Mean	SE*
Control	4	19.1	5.12	8.4	1.70
Rural	6	22.9	6.42	8.8	2.08
Suburban	6	21.4	6.11	12.9	2.04
Roadside	6	19.9	3.28	14.1	5.09
Industry	8	24.0	5.22	14.1	2.82
F statistics		0.136		0.776	

*Standard error (SE) of mean

The results of this study showed that from the zinc pollution point of view, the least pollution levels were determined in the control and the rural study stations, than suburban, and the most polluted stations were in industrial areas and roadsides. The level of Zn accumulation in the industrial areas and roadsides were close to each other.

According to Bowen (1979), land plant intervals for zinc are between 20-400 µg g^{-1}, dry weight. In this study, as a result of investigating the bark samples collected from 30 stations, only a few results taken from some stations in industrial areas and roadsides were in between Bowen's limits. The zinc concentrations of the rest of the stations were below these limits. That means that in our study area, there is no considerable zinc pollution.

The results of Manganese trace element investigated in this study revealed that the accumulation of Mn ranges between 19.1 and 24 µg g^{-1} (Table 1). Mn accumulation values in five study stations were not considerably different from each other.

Like many trace elements, a grey-white, chemically-reactive heavy metal, manganese and manganese compounds exist naturally in the environment as solids in the soil and as small particles in water. Manganese may also be present in small dust-like particles in the air. It is a valuable element for the human beings. For example, it is used in the production of batteries, in dietary supplements, and as ingredients in some ceramics, pesticides, and fertilizers. However, its principal value is derived from its role in steel production.

It is also an essential micronutrient throughout all stages of plant development. It is important for vital plant functions (Marschner, 1995), but can be toxic when present in excess in the environment. Humans, as a result of industrial activities and burning fossil fuels, are the source of unnatural manganese in the environment. Among the sources of airborne manganese, iron-and steel-producing plants, power plants, coke ovens, and dust from uncontrolled mining operations can be counted (Anonymous, 1997; Butkus and Baltrenaite, 2007).

Bowen (1979) stated that acceptable Mn content limits for plants are between 20-700 µg g^{-1}. Evaluation of the results taken from this study showed that our results were close to the Bowen's minimum limit. Therefore, we can reach a conclusion that our study area is not polluted by Mn.

Mulgrew and Williams (2000) stated that coniferous trees indicate pollution over a longer time period, and since bark is exposed to air pollutants either directly from the atmosphere or from stemflow, tree bark is appropriate in indicating longer term air pollution. Moreover, depend upon the type of the tree, the deployment of heavy metal content and ways of accumulation show a great variety. For example, in some trees heavy metals are filtered out by the leaves from the air, while in others they are taken up by their crown or by their roots. According to Rademacher (2001), Mn or Zn are mainly taken up by the root system and are than transported from there to the crowns, since they are highly mobile elements. Therefore, it is better to investigate its deposition in the crowns.

One way ANOVA were applied to the data and it was found that there is no affect of location on the element concentration of both Mn and Zn. In the related literature, Zn and Mn accumulation levels in different plant species were investigated throughout the world. For example, Gaudry *et al.* (2003) investigated the Zn and Mn accumulation in the bark of cedar (*Cedrus libani* var. *atlantica* (Endl.) Hook.f.) in Morocco and the values were determined as 61.8 and 92.90 μg g^{-1}, respectively. Recently, Rusu *et al.* (2006) studied Zn and Mn accumulation in the bark of hornbeam (*Carpinus betulus* L.) in Romania. Their Zn and Mn values were reported as 13-240 and 122-538 μg g^{-1}, respectively. More recently, Kuang *et al.* (2007) investigated the Zn and Mn concentration in the bark of Masson pine (*Pinus massoniana* Lamb.) in China and identified that the mean concentrations of Mn (59.94±7.15 μg g^{-1}), Zn (52.96±7.27 μg g^{-1}). When we compare the results of the studies given above with our results, it is clearly seen that the results determined in our study area is well below with those of others. That implicates that the study areas in Morocco, Romania and China are highly contaminated by Zn and Mn.

In some other studies, although they studied different trace element accumulation in different plant species, only one of them can be compared with our results, since either Zn or Mn was included their studies. For example, Schulz *et al.* (1999) studied on the bark of the scots pine (*Pinus sylvestris*) in northern Europe and found out that Zn element values were between 4.5-189 μg g^{-1}. It was understood from their results that some of the study areas in their study are more contaminated than those of ours. While Pacheco *et al.* (2001) studied the Mn deposition in the bark of olive tree (*Olea europaea* L.) in Portugal. The Mn value was reported as 7.25 μg g^{-1} dry weight. In this case, it is again revealed from their results that our study area is more contaminated by Mn than those of theirs, though both results were under the accepted levels for Mn contamination. In other words, their study area is not accepted as a contaminated area by Mn. We can conducted that this study demonstrates that barks of Turkish red pine can be used as a biomonitor for detecting the heavy metal accumulation in a specific area**.**

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