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# The use of Aleppo pine needles as a bio-monitor of heavy metals in the atmosphere

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**Abstract**

The needles of Aleppo pine (*Pinus halepensis* L.) tree were tested as a possible bio-monitor of heavy metal pollution in Amman City, Jordan. Concentrations of Pb, Cd, Cu and Zn were determined in soils, unwashed and washed needles collected from different sites of the city, viz. industrial, residential and on the roadside of a busy high way. The analyte concentrations were compared with that of samples from the control site (uncontaminated area that was 60 km away from Amman City).

The results of the investigation indicate that the industrial site has high levels of the metal pollutants except for Pb and Cu which is much higher on samples from the roadside. The highest concentrations were registered for Pb and Zn where 10 and 1210 $\mu g\,g^{-1}$, respectively, were found in soil, thereby leading into the contamination factor of 13 and 17 as compared with samples from the control site. The results obtained indicate that *P. halepensis* L. needles are useful bio-monitor of the heavy metals in the arid environment.


*Keywords:* Aleppo pine; Bio-monitor; Heavy metals; Needles; Pollution

## 1. Introduction

The industrial activities of man have resulted in the contamination of soil, water, and air with heavy metals. Heavy metals are the most dangerous groups of anthropogenic environmental pollutants with high toxicity and persistence in the environment. Independent of the origin of the source, heavy metals can accumulate in crops or plants and may lead to the damage and alteration of animal or human physiological functions through the food chain [1].

The industrial uses of cadmium are the largest sources of environmentally hazardous amounts of cadmium. Cadmium and lead are amongst the elements that have adverse effects on animal and human health as they are readily transferred through food-chains and are not known to serve any essential biological function [2]. Cadmium accumulates in the liver, and therefore acute exposure to toxic doses of Cd produces apoptosis and necrosis in the liver [3].

High Pb concentration in air and soil in urban areas has been attributed to increasing number of automoboles, especially leaded petrol [4]. Lead poisoning in humans is a public health problem that affect mostly children in which the major impact produced by lead is in the brain [5].

Concern over the potential ecotoxicological hazards posed by elevated levels of metals in the environment has prompted a search to find reliable, low cost methods of assessing the extent of metal contamination at local environment and the exposure risk to both plants and animals. One avenue of research has been to identify organisms that could potentially be utilized as biological monitors for estimating levels of metal pollution.

Biological monitors are organisms that provide quantitative information on some aspect of their environment, such as how much of a pollutant is present [6]. Botanical materials such as fungi, lichens, tree bark, tree rings and leaves of higher plants, have been used to detect the deposition, accumulation and distribution of metals. Higher plants are mostly suitable for monitoring metal pollution in industrial and urban areas as lichens and mosses are often missing. There is much information available on the concentrations of trace elements in the leaves and needles of trees commonly used as bio-monitors, such as:

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*Pinus sylvestris* [7], *Picea abies* [8] and *Quercus ilex* [9]. Pine needles have been used in the monitoring of airborne pollutants as their waxy surfaces accumulate gaseous pollutants and polluting particulates [10].

The aim of this study was to apply Aleppo pine (*Pinus halepensis* L.) tree as a bio-monitor for Pb, Cd, Cu and Zn pollution in Amman City, Jordan. Aleppo pine trees were preferred as they are available in large numbers in this city and easily accumulate heavy metals.

## 2. Experimental

### 2.1. Apparatus

An ICP-AES (Jobin Yvon 38–Plasma Source JY3832) was used for all analysis. The nebulizer flow-rate was 0.8 l $min^{-1}$ and other parameters were default conditions recommended by the manufacturer. The analytical lines used were Pb 217.0 nm, Cd 228.8 nm, Cu 324.7 nm and Zn 213.9 nm. Four replicates were usually taken during analysis.

### 2.2. Reagents and standard solutions

Standard stock solutions containing 1000 mg $l^{-1}$ of the analyte (Merck) were used for the preparation of working standards for Pb, Cd, Cu and Zn. Ultra-pure water (resistivity, 18.2 MΩ cm), obtained from a Milli-Q water purification system (Millipore Corp., USA), was used for all dilutions and sample preparation. Ultra-pure $HClO_4$ (Merck), HF (Merck) and HCl (Merck) were used during the digestion of samples. A certified reference tissue sample, BCR 62 olive leaves (Community Bureau of Reference, Brussels), was analyzed to validate the method of determination.

### 2.3. Sample collection

The needles of Aleppo pine (*P. halepensis* L.) tree and soil samples were collected from different sampling sites, in Amman City, Jordan, during July–August 2005. These sites are Sahab, industrial site were samples were collected 10 m around the factories Down Town, sites located on the busy traffic roads and Wadi Sir, residential area on the outskirts of the City. The reference area was a background site at 60 km away from major anthropogenic activities outside Amman City. The number of samples collected from each site was 15. The soils collected represent 10 cm of the top soil layer and were air-dried and sieved through a 2-mm stainless steel sieve.

About 200 g of adult leaves from each direction (west, east, south and north) of Aleppo pine (*P. halepensis* L.) tree were collected to eliminate the factor of wind directions. The leaf samples were then divided into two sub-samples. One sub-sample was thoroughly washed with running distilled water to remove dust particles, and the other remained untreated. All leaves were dried in an oven at 80 °C for 24 h, milled in a micro-hammer cutter and fed through a 0.2-mm sieve. The samples were then stored in clean self-sealing plastic bags.

#### 2.3.1. Determination of analytes in leaves

Approximately 2 g ground leaf samples in a platinum crucible were placed in a muffle furnace. The temperature of the furnace was slowly increased from room temperature to 600 °C for over an hour. The samples were ashed until a white or gray ash residue was obtained. The resultant ash was allowed to cool, and 5 ml of a mixture of 1:1 concentrated $HNO_3$ and HCl was added to dissolve the product. The solution was transferred to a 50.0 ml volumetric flask and made to volume with deionized water.

#### 2.3.2. Determination of total concentrations of analytes in soil

To approximately 2 g soil sample, accurately weighed into a platinum crucible, 50 ml conc. HF and 10 ml conc. $HClO_4$ were added and heated to evaporate excess acid. To eliminate the remaining organic matrix, 10 ml of $HClO_4$ were added and heated to dryness. The residue was then dissolved with 10 ml of 6 M HCl and diluted to 100.0 ml.

### 2.4. Statistical analysis

Analytical results have evaluated by statistical analysis system (SAS). The standard error values of the means were calculated to compare the site categories. To determine significance of washing the leaves, a paired *t*-test was performed, comparing heavy metal contents of washed and unwashed plants, for each type of site.

## 3. Results and discussion

### 3.1. Results of the determination of analytes in certified reference material

The methods that were used for the determination of Pb, Cd, Cu and Zn in needles and soil were validated by the analysis of certified reference materials. The results shown in Table 1 indicate that there is no difference between the found and certified values for all elements at 95% level of confidence thereby confirming the validity of the method of determination.

### 3.2. Levels of metal pollutants in different sites

The mean analytes concentrations found in Aleppo needles are shown in Table 2. As shown, all elements were found at high levels in samples collected from industrial sites, except for Pb and Cu which were higher in samples collected from roadside

Table 1
Results for the determination of metals in certified reference material, BCR 62

| Analyte | [a]Measured value (μg $kg^{-1}$) | Certified value (μg $kg^{-1}$) |
|---|---|---|
| Pb | 24.3 ± 1.5 | 25 ± 1.5 |
| Cd | 0.095 ± 0.01 | 0.10 ± 0.02 |
| Zn | 15.6 ± 0.4 | 16 ± 0.7 |
| Cu | 45.5 ± 0.8 | 46.6 ± 1.8 |

[a] Average of six determinations at 95% level of confidence: mean ± $t_{0.05} \times (s/\sqrt{n})$.

Table 2
Mean Pb, Cd, Zn and Cu concentrations (μg $g^{-1}$ dry weight) in needles of Aleppo pine (*Pinus halepensis* L.) collected from different sites of Amman City

| Site | Pb | | | Cd | | | Zn | | | Cu | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Unwashed | Washed | *t*-Test | Unwashed | Washed | *t*-Test | Unwashed | Washed | *t*-Test | Unwashed | Washed | *t*-Test |
| Industry | 90.0 ± 10 | 45.0 ± 5.0 | *** | 3.50 ± 0.20 | 1.50 ± 0.10 | *** | 262 ± 20 | 118 ± 15 | *** | 29.5 ± 3.0 | 15.5 ± 1.5 | *** |
| Roadside | 196 ± 18 | 75.5 ± 4.0 | *** | 2.10 ± 0.16 | 0.50 ± 0.06 | *** | 95.0 ± 9.0 | 55.0 ± 2.0 | *** | 37.0 ± 3.0 | 16.0 ± 1.5 | *** |
| Suburban | 40.0 ± 5.0 | 15.0 ± 2.0 | ** | 0.55 ± 0.05 | 0.20 ± 0.03 | ** | 55.0 ± 4.0 | 36.0 ± 3.0 | ** | 16.50 ± 1.5 | 7.50 ± 1.0 | ** |
| Control | 19.0 ± 2.0 | 11.0 ± 1.0 | * | 0.25 ± 0.06 | 0.12 ± 0.01 | * | 25.0 ± 1.0 | 10.0 ± 0.90 | * | 10.0 ± 2.0 | 5.32 ± 0.95 | * |

***$p < 0.001$, **$p < 0.01$ and *$p < 0.05$ significance. Average of six determinations at 95% level of confidence: mean ± $t_{0.05} \times (s/\sqrt{n})$.

that is associated with the road traffics. The roadside samples were collected 2 m away from the main road where the traffic density was estimated to be 847 vehicles per hour.

In general, the industrial site has high levels of analytes as compared to other sites. It can therefore be concluded that the industrial plant is a large source of metal pollution to its surroundings. This industrial plant produced significant levels of metallic Zn, Cd, Cu and Pb emissions due to the lack of a filter system in its chimneys. Certainly, a filter system for the flues of the plant might reduce these levels and is thus necessary to bring down this load of heavy metal pollution considerably.

The high metals concentrations along or close to the roadside environment are obviously attributed mainly to aerial deposition of the metal particulates emissions from motor vehicles and not as a function of soil type as reported Jaradat and Momani [11]. It is a well-known fact that Alkyl Pb compounds (tetra-ethyl lead, $[Pb(C_2H_5)_4]$) are very often added to petrol as antiknock additives for boosting the octane levels in large numbers of cars in Jordan. Consequently, the combustion of leaded petrol leads to the release of large amount of Pb into the environment thereby polluting the atmosphere with Pb [12]. It is worth mentioning that leaded petrol is the predominant fuel used by automobiles in Jordan and this make contamination of the environment with Pb inevitably high. While the probable source of Cu and Pb in pine bark is the combustion petrol products which contain Pb and Cu [13], Cu is also derived from engine wear [14].

### 3.3. Results of the determination of analytes in soil

Table 3 is a summary of the comparison of the levels of metal pollutants in the contaminated and uncontaminated area that is 60 km from Amman City. The results show that industrial site had the highest contamination with Cd and Zn where 10 and 1210 μg $g^{-1}$ were found in soil samples, respectively. This concentration translates into the contamination factor of 13 and 17 times higher than the control site (uncontaminated area) for Cd and Zn, respectively. The roadside has the third most contamination factor of 11 with Pb. Overall, the concentration of Pb in soil ranges between 80 and 500 μg $g^{-1}$.

### 3.4. Effects of washing Aleppo needles before analysis

The purpose of comparing washed and unwashed Aleppo needles was to distinguish between airborne and soil borne contamination. The results of the determination of heavy metals in washed and unwashed needles (Table 2) shows that washing the needles significantly reduces the concentrations of contaminants in Aleppo pine needles from all sites. This indicates that there was substantial aerial deposition of the four analyte elements on the needles thereby confirming that the significant heavy metals pollution originated from anthropogenic activity and not a function of soil type.

The washing effect was most noticeable in industrial and roadside site (as indicated by *t*-test results) where there was greatest aerial deposition. Similar results were reported by Aksoy et al. [15] who also found that washing the leaves significantly reduced the Pb, Cu, Zn and Cd concentrations in urban environment due to greater aerial deposition. In contrast, the washing of the leaves of *Ficus microcarpa* [16], *Inula viscosa* [17] and *Citrus limon* [18] reduces the concentration of Pb while the concentrations of Zn, Cu and Cd between washed and unwashed leaves remains the same.

It can be concluded that the contents of heavy metals after the washing of needles depend on the plant species that is used as a bio-monitor. This also shows that plant species that retain constant metal concentration in washed and unwashed needles could be a more suitable bio-monitor of metal pollution.

According to Markert [19] and Wittig [20], the basic criteria for the selection of a species as a bio-monitor are that it should be represented in large numbers all over the monitoring area, have a wide geographical range, should be able to differentiate between airborne and soil borne heavy metals, be easy to sample, inexpensive to sample and there should be no identification problems. Aleppo pine (*P. halepensis* L.) due to the higher avail-

Table 3
Results of the determination of Pb, Cd, Zn and Cu in soils from different sites of Amman City

| Site | [Pb] (μg $g^{-1}$) | [Cd] (μg $g^{-1}$) | [Zn] (μg $g^{-1}$) | [Cu] (μg $g^{-1}$) |
|---|---|---|---|---|
| Industrial | 160 ± 16 | 10 ± 0.6 | 1210 ± 60 | 40 ± 5 |
| CF | 4 | 13 | 17 | 3 |
| Roadside | 500 ± 50 | 3.2 ± 0.4 | 215 ± 17 | 85 ± 6 |
| CF | 11 | 4 | 3 | 7 |
| Residential | 80 ± 5 | 2.1 ± 0.2 | 115 ± 12 | 18 ± 3 |
| CF | 2 | 3 | 2 | 2 |
| Control | 44 ± 5 | 0.80 ± 0.05 | 70 ± 6 | 12 ± 2 |

Average of six determinations at 95% level of confidence: mean ± $t_{0.05} \times (s/\sqrt{n})$.

ability in Amman City, Jordan, embodies all these criteria and this study fully supports the view.

## 4. Conclusions

The needles of Aleppo pine (*P. halepensis* L.) were found to be a good bio-indicator for Pb, Cd, Zn and Cu pollution in the arid environment of Amman City and surely this model could be used in other cities populated with these plant species. The samples obtained from an industrial area and urban roadsides had the highest accumulation of the heavy metals due to the higher human activity and vehicular density. This study demonstrates that industry is the main source of heavy metal pollution. The reason for the higher Pb content in urban roadside is leaded petrol consumption by cars. Washing the needle of Aleppo pine (*P. halepensis* L.) reduces Pb, Zn, Cu and Cd concentrations significantly thereby confirming that aerial deposition of these metals.

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