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Determining the Heavy Metal Pollution in Mascara (Algeria) by Using Casuarina equisetifolia

Lakhdari Aissa*, Benabdeli Kéloufi

University of Djilalli Liabes, Faculty of Sciences, B.P.89, Sidi Bel Abbes, 22000. ALGERIA
* Corresponding author: a_kakhdari@yahoo.fr

Abstract. In this study, *Casuarina equisetifolia* needles were evaluated as the possible biomonitors of heavy metal air pollution in Mascara (Algeria). The needles were sampled from seven locations with different degrees of metal pollution (near roads) and from a control site. The concentrations of lead, zinc, copper and nickel were measured by using a flame atomic absorption spectrophotometer. The maximal values of these four metals were found in the samples collected near the roads and the minimal values were found in the control site. Furthermore, sites with high traffic density and frequency of cars stoppage showed high heavy metal concentrations. However, the comparison of concentrations of all metals showed that the zinc one had the highest concentration of all. The cluster analysis divided the selected sampling sites in three distinct clusters. With regard to the results of this study, *Casuarina equisetifolia* can be successfully applied in biomonitoring of air pollution.

Key words: *Casuarina equisetifolia*, Mascara, biomonitors, pollution, heavy metals.

Introduction

Heavy metal pollution represents an important environmental problem due to toxic effect of metals, and their accumulation throughout the food chain leading to serious ecological and health problems. In developing countries an estimated 0.5-1.0 million peoples die prematurely each year as a result of exposure to urban air pollution (KOJIMA, 2001). The emission of toxic substances into the environment has spread mainly from industrialized countries. However, many industrial plants and especially road traffic may emit heavy metals into the atmosphere. LEYGONIE (1993) noted that, fossil fuels contain many kinds of heavy metals which are emitted during the combustion of those fuels. Furthermore, the wear of auto tires, degradation of parts and especially paint, and metals in catalysts are all suspected as potential sources of heavy metal pollution (SADIQ *et al.*, 1989; WEI & MORRISON, 1994; MONACI *et al.*, 2000; OZAKI *et al.*, 2004; SUZUKI *et al.*, 2009). Generally, traffic related pollutants include toxic metals like lead, cadmium, copper and zinc (VIARD *et al.*, 2004). On the other hand, some trace metals are essential in plant nutrition, but plants growing in a polluted environment can accumulate them at high concentrations (HOVMAND *et al.*, 1983; HUCKBEE *et al.*, 1983; KABATA-PENDIAS & PENDIAS, 1984; ALLOWAY, 1990; VOUSTA *et al.*, 1996; SHARMA *et al.*, 2004).

The first attempts for (in the early 1960s) biomonitoring and assessment of environmental pollution coming from exhaust gases of automobiles in road traffic were based on the analyses of different trees, grasses and vegetables that grow near highways and in the cities. Since then, phytomonitoring is increasingly used as an alternative to the traditional methods, for studying the regional deposition of natural and anthropogenic pollutants from the atmosphere to the terrestrial environment (PACHECO *et al.,* 2001; DOGAN *et al.,* 2007). An advantage of plants as biomonitors is that they are effective collectors which reflect the summarized effect of environmental pollution and accumulation of toxicants from the atmosphere (deposition, binding and solubility of metals on the leaf surface).

Recently, different bio-indicators are used in monitoring of the air pollution especially in urban areas. Botanical materials such as fungi, lichens, tree rings and leaves of higher plants have been used to detect pollution level (HUSEYINOVA *et al.,* 2009). The use of higher plants, especially different parts of trees, for air monitoring purpose is becoming more and more widespread. Tree leaves have been widely used as indicator of atmospheric pollutions (KOVÁCS, 1992; PETROVA, 2011), and they are effective alternatives to the more usual monitoring methods, including mosses and lichens. Trees are long-lived organisms, which can take up trace elements from the soil, water, or air, and retain them for a long time (MADEJON *et al.,* 2006). However, the foliage of tree species from contaminated regions can be considered as an accumulation monitor where significant amount of chemical elements is cumulated on the leaf surface (MANKOVSKÁ *et al.,* 2004). According to SRINIVAS *et al.* (2009) atmospheric metals are deposited on plant surfaces by rain and dust. On the other hand, airborne pollutants can retain on leaf surfaces and some elements could enter via the stomata and accumulate in leaf tissues.
The aim of this study was to assess *Casuarina equisetifolia* needles as possible biomonitors of heavy metal pollution in Mascara city (Algeria).

Material and methods

Study area and sampling sites

This study was carried out in the city of Mascara which is located in the North-West (NW) part of Algeria at N 35°26', E 02°11' (Fig.1). It is one of the most populated cities of Algeria (over 365 000 inhabitants), with Mediterranean climate and a mean annual precipitations of about 450mm. The average annual temperature is 13.1°C.

Nowadays, *Casuarina equisetifolia* covers the majority of urban trees in Mascara and it has a very wide range of horticultural use. The needles of *Casuarina equisetifolia* were collected in June 2011 from seven locations (sites S1 to S7), near the roads and from one control site (St) located far from road traffic and other anthropogenic sources of metal contamination (Fig.1). Cars were the dominant vehicles in all the seven sites. No other sources of pollutants were noted. At each site needles samples were taken from the lower part of the tree crown at the 2-3m height in all directions. They were cut directly from the branch, at about 1cm from needle base. All the samples were stored separately in clean cellulose bags to avoid further contamination and were transported to laboratory in the same day.

Chemical analysis

In laboratory, about 1g of dried and milled plant material was put into Erlenmeyer's flasks with 6 ml mixture of 65 % Nitric acid (HNO_3) and 70% Perchloric acid ($HClO_4$). Later, they were incubated in hot water (52°C) for at least 2 hours. Then these digests were filtered by a Whatman filter paper. The obtained filtrates were completed by deionized distilled water and the new solutions were stored in glass bottles and used to determine heavy metals concentrations (MAATOUG *et al.*, 2007). The concentrations of Pb, Zn, Cu and Ni were measured by a flame atomic absorption spectrophotometer (Perkin-Elmer, 280 model).

Statistical analysis

Pearson correlation coefficient was used to analyze and establish inter-metal relationship. Cluster analysis was performed to classify and identify relatively homogenous groups with similar properties. For all statistical analysis the STATISTICA 6.0 statistical package was used (STATSOFT, 2001).

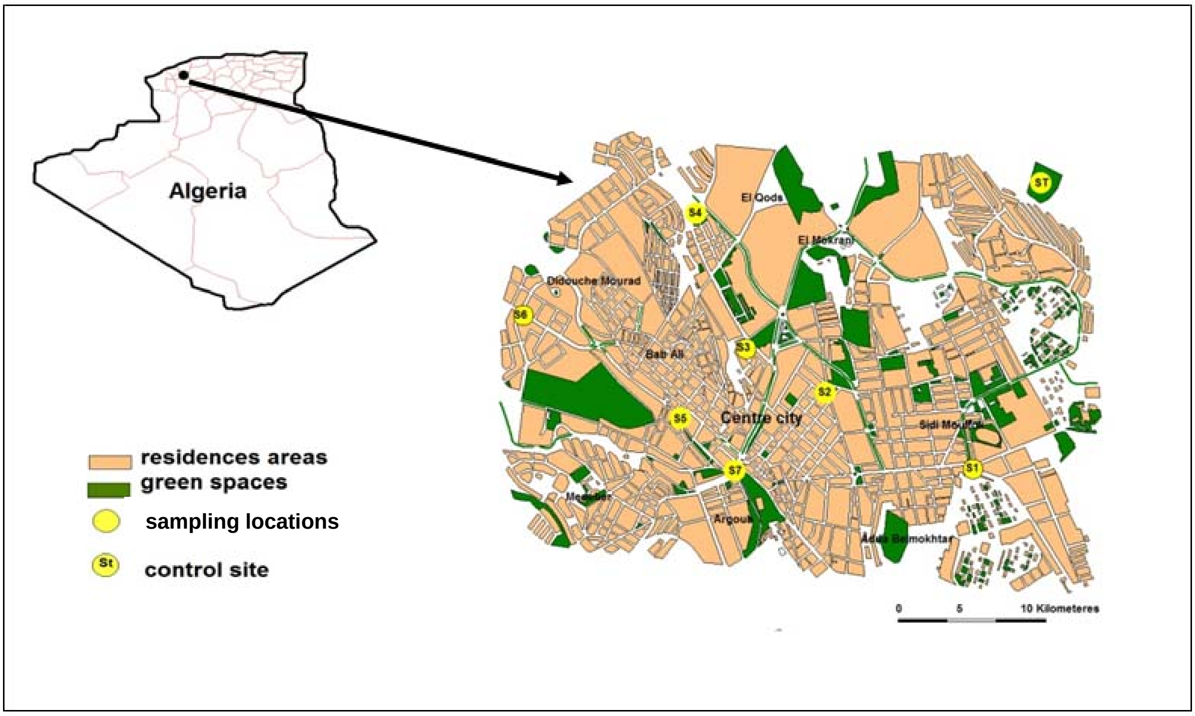

Fig.1. Geographical location of the study area and sampling sites.

Results and Discussion

The chemical analysis revealed a significant difference in Pb, Zn, Cu and Ni concentrations in needles samples collected from different sites. This can be attributed to the different traffic density between the seven sites (Table 1).

Table 1. Heavy metal concentrations (ppm) in needles of *Casuarina equisetifolia.*

Sites	Zn	Pb	Cu	Ni
Site1	141.07	23.73	22.5	17.7
Site2	144	51.01	20.4	11.7
Site3	175	51.07	21.5	17.22
Site4	178	31.22	21.01	20
Site5	453	67.5	23.5	21
Site6	146	43.9	37.02	16.3
Site7	440	60.7	16.3	21.07
Control	2.33	0.54	0.21	0.60

However, comparison of concentrations of all metals showed that the zinc one had the highest concentration of all. The average highest value of Zn (453 ppm) were detected in samples collected from site 5, whilst the lowest (2.33 ppm) was measured in samples collected from the control site. It was observed that the second highest values were found in samples collected from site 7 (440 ppm). The environmental pollution of Zn greatly influences the concentrations of this metal in plants (SRINIVAS *et al*., 2009). Zn arises mainly from atmospheric deposition and could also be derived from vehicular traffic (CONTI *et al*., 2008). Zinc levels can be enhanced in automobile exhaust, may be elevated near roadways due to tire wear. On the other hand, zinc is an essential element for plants and is considered as an important factor in the biosynthesis of enzymes, auxins and some proteins. But when their concentrations reach a certain level, they become toxic to plants and reports produce various physiological and biochemical changes in plants. A critical toxic level of Zn in the leaves is about 100ppm (ALLEN *et al.*, 1974; YILMAZ & ZENNGIN, 2004). According to these values, the Zn concentrations found in our study are higher than the normal limits. Therefore, it can be supposed that all the seven sites studied were heavily polluted with Zn.

The Pb concentrations were the highest at site 5 (67.5 ppm), and the lowest at the control site (0.54 ppm), whereas the second highest value was found in site 7 (60.7 ppm). Lead pollution on a local scale is caused by emissions from motor vehicles using leaded gasoline (KOEPPE, 1981; VIARD *et al.*, 2004; YILMAZ & ZENGIN, 2004). In Algeria, the addition of lead in gasoline is 0.45g/L (SEMADI & DERUELLE, 1993). Lead is known as a deadly and cumulative poison even when consumed in small quantities and is capable of deadening nerve receptors in man (NWAEDOZIE, 1998). The relationship between lead concentrations and traffic intensity has been demonstrated in detail by many authors (GROMOV & EMELINA, 1994; LI *et al.*, 2001; VIARD *et al.*, 2004). ALLEN (1989) considered that the normal content of Pb in plants is less than 3ppm. In general, Pb concentrations in vegetation grown in industrial and urban areas have increased in recent decades owing to human activities and road traffic. According to our results, there is lead pollution in Mascara city.

The average highest value of Cu (37.02 ppm) was found in samples collected from site 6, whilst the lowest (0.21 ppm) was measured in the needles collected from the control site. Copper is an important component for many enzymes, which catalyze oxidation and reduction reactions. The main sources of Cu are home tools production, metal manipulating, road traffic and ashes (AKSOY *et al.*, 2005). KABATA-PENDIAS & PIOTROWASKA (1984) reported that the normal content of Cu in plants ranges to be 2-20 ppm, but in most cases it is in a narrower range of 4-12 ppm. According to these values, the Cu concentrations found in this study are higher than the normal limits. So we can conclude that there is copper pollution in Mascara city.

The average highest value of nickel (21.07ppm) was found in samples collected from site 7, whereas the lowest mean value was determined in the control site (0.60ppm). It was observed that the second highest values were found in samples collected from site 5 (21ppm). These results indicate that the origin of nickel in the investigated locations is related to vehicular traffic. Ni is essential element for plants in low concentrations and is absorbed easily and rapidly by them (GUNES *et al.*, 2004). According to AL-SHAYEB & SEAWARD (2001), the highest concentrations of nickel are attributed to emissions from motor-vehicle that use nickel gasoline and by abrasion and corrosion of nickel from vehicle parts. The results further revealed that the sources of nickel in Mascara city are emissions from motor vehicle running on petroleum and diesel fuel.

According to the cluster analysis (Fig 2), three distinct groups can be identified namely "cluster 1", "cluster 2" and "cluster 3" (Table 2). Cluster 2 includes the control site. This site has a good air quality (low concentrations of metals) which is explained by the absence of any sources of such contamination. Cluster 3 includes sites S1, S2, S3, S4, and S6. The mean values of Zn, Pb, Cu and Ni in this cluster are higher in comparison with data from cluster 2, but this cluster has a good air quality when is compared to cluster 1. However, all the sites of cluster 3 are characterized by low slope and low traffic density, for this reason, low concentrations of heavy metals were found. Cluster 1 includes sites S5, S7, where the highest levels of lead, zinc, copper and nickel are found. All the sites of cluster 1 are located in the central area of Mascara which is with high traffic density, frequency of cars stoppage, more abrasion of asphalt tire and brake.

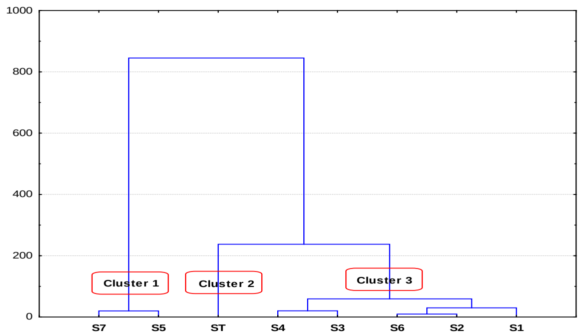

Fig.2. Diagram of cluster analysis.

In addition, these sites are characterized by important slopes. The slope requires the vehicle to develop more power, therefore emit more heavy metals (MADANY *et al.*, 1990). The braking in the slope increased the emissions of copper, from fine particles deposited on the leaf surface (MAATOUG *et al.*, 2007). AIJUAN *et al.* (2011) noted that low-speed or high-acceleration operations lead to higher emission.

Table 2. Mean of heavy metals (ppm) in the three clusters.

Clusters	Pb	Zn	Cu	Ni
Cluster 1	64.10	446.50	30.26	21.03
Cluster 2	0.54	10.33	0.21	0.6
Cluster 3	40.18	156.81	20.34	16.58

Correlation analysis showed that elemental pairs Pb/Zn (r=0.75); Pb/Cu (r=0.56); Pb/Ni (r=0.81); Zn/Cu (r=0.73); Zn/Ni (r=0.70); Ni/Cu (r=0.54) were significantly correlated with each to another. This is clear indication that the origin of metal contamination in the investigated area is related to vehicular traffic. SESHAN *et al.* (2010) noted that positively correlated metals became from the same anthropogenic source.

Conclusions

The results of this study show that the highest and the lowest concentrations of Pb, Cu, Zn and Ni were found near the road and the control site respectively. This indicates that the vehicular traffic has been major source of heavy metal contamination in urban areas. Correlation coefficients were calculated for each element-element combination. They showed positive correlation which indicated that the origin of studied metals in the investigated area is related to road traffic.

The cluster analysis divided the eight sites in three major clusters according to their characteristics, where sites with high traffic density, frequency of cars stoppage and important slope, showed the highest metal concentrations. The results of our study confirmed that *Casuarina equisetifolia* needles can be used as biomonitors of heavy metal pollution in urban areas.

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