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Concentrations of Heavy Metals in Leaves along Roadsides in Port Harcourt, Rivers State, Nigeria

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Abstract: The concentrations of Cd, Cr, Cu, Ni and Pb in leaves collected along roadsides in Port Harcourt and environs were determined using GBC Avanta flame atomic absorption spectrophotometer Version 2.02. The metal concentrations in both seasons ranged from 0.001-19.530 Cr, 0.320-2.320 Ni, 0.118-1.150 Cd, 0.001-30.230 Pb and 0.386-3.850 ppm Cu. The difference between the dry and rainy seasons concentrations were significant ($p<0.05$). The concentrations of metals from high activity areas were higher than the concentrations from medium and low activity areas. The leaves were considered polluted as the concentrations of the metals except Ni exceeded permissible limits set by Rivers State Ministry of Environment. The levels of activity, ages and height of plant leaves influenced the concentrations of metals. Leaves should be properly treated before use for cooking and herbal or medicinal purposes.

Key words: Plants, leaves, heavy metals, roadsides, Rivers state, Nigeria

INTRODUCTION

Heavy metals are present in the environment and most of them are essential for animals and plants. They are natural constituents of rocks and sediments. Heavy metals contamination of the environment is of major concern because of their toxicity and threat to human life and the environment.

The main sources of heavy metal contamination are urban industrial aerosols, created by combustion of fuels, metal ore refining, battery and power generation operations and other industrial processes. Liquid and solid wastes generated from animals, humans industrial chemicals and agricultural chemicals (Elankumaran *et al*., 2003).

The major sources of heavy metal uptake by man are food, water and air. Although, some heavy metals such as Cu, Zn and Mn are essential for the growth and well being of living organisms including man, they are toxic at higher concentrations. Other metals such as Pb, Cd and Hg are non-essential for metabolic activities and are toxic (Biney *et al*., 1994).

Presently the environment is heavily polluted by various toxic metals which create a danger for all living beings. These metals are retarding farming efficiency and destructing the health of the plants and animals. (Mudgal *et al*., 2010).

Acute lead, chromium and copper poisoning in humans causes severe dysfunction in the renal, reproductive and nervous system and are harmful to human health even at low concentrations in the environment (Wyatt *et al*., 1998).

Heavy metals like As, Cd, Co, Cu, Ni, Zn and Cr are phytotoxic either at all concentrations or above certain threshold levels. Toxic metals are biologically magnified through the food chain. The presence of heavy metals in toxic concentrations can result in the formation of superoxide radicals (O_2^-), hydrogen peroxide (H_2O_2), Hydroxyl radicals (OH^-) etc. can cause severe oxidative damage to biomolecules like lipids, proteins and nucleic acids. Cr, Cu and Zn can induce the activity of various antioxidant enzymes and also non-enzymes like ascorbate and glutathione. Certain plants absorb these toxic metals and help to clean them up from soils. These plants are termed hyper accumulators. These plants have been shown to be resistant to heavy metals and are capable of accumulating them into their roots and leaves and transporting these soil pollutants to high concentrations (Mudgal *et al*., 2010).

Cadmium (Cd) is a toxic element, its concentration is greatly increased by activities such as zinc mining, iron foundries and the use of sewage sludge as a fertilizer in agriculture. Cd may be detoxified in plants by Phytochelatins (PCs), a family of sulphur rich peptides

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which are able to bind Cd and some other heavy metals (Cobbett and Goldsbrough, 2002). The heavy metal cadmium which is present in pesticides is very toxic to biological systems. Its effect on growth of microorganisms and plants has been investigated by many researchers (Khudsar *et al*., 2001).

Helianthus annuus accumulate Pb in the leaf and stem so it could be used in the restoration of abandoned mines and factories sites contaminated with elevated Pb levels in the soil (Boonyapookana *et al*., 2005). The *Sesbania drummondii* transform lead nitrate in the nutrient solution to lead acetate and sulfate in its tissues and accumulate in roots and leaves (Sharma *et al*., 2004).

The use of plants to monitor heavy metal pollution in the terrestrial environment must be based on a cognizance of the complicated integrated effects of pollutant source and soil-plant variables. To be detectable in plants, pollutant sources must significantly increase the plant available metal concentration in soil (Cataldo and Wildung, 1978).

Effects of heavy metals on plants result in growth inhibition, structure damage, a decline of physiological and biochemical activities as well as of the function of plants (Cheng, 2003). The effects and bioavailability of heavy metals depend on many factors such as environmental conditions, pH, species of element, organic substances of the media and fertilization, plant species. But there are also studies on plant resistance mechanisms to protect plants against the toxic effects of heavy metals such as combining heavy metals by proteins and expressing of detoxifying enzyme and nucleic acid, these mechanisms are integrated to protect the plants against injury by heavy metals.

There are two aspects on the interaction of plants and heavy metals. On one hand, heavy metals show negative effects on plants. On the other hand, plants have their own resistance mechanisms against toxic effects and for detoxifying heavy metal pollution (Cheng, 2003).

Metal aerosols pollute soil and plants. Higher plants not only intercept pollutants from atmospheric deposition but also accumulate aerial metals from the soil. Aerial heavy metal deposit are taken up from the soil by plants via their root system and translocated to other regions of the plant (Mulgrew and Williams, 2000).

Particle deposition on leaf surfaces may be affected by a variety of factors including particle size and mass, wind velocity, leaf orientation, size, moisture level and surface characteristics (Bache *et al*., 1991). The deposited particles may be washed by rain into the soil, resuspended or retained on plant foliage. The degree of retention is influenced by weather conditions, nature of pollutant, plant surface characteristics and particle size (Harrison and Chirgawi, 1989).

In an investigation of Cd, Cu, Ni and Pb uptake from air and soil by *Achillea millefolium* (milfoil) and *Hordeum vulgare* (barley) in Denmark, Pilegaard and Johnsen (1984) concluded that Cu and Pb plant concentrations correlated with aerial deposition but not with soil concentrations. In contrast, Ni and Cd content in the plants correlated with deposition and soil content.

In their study of tropical plants growing in an industrial area of India, Rao and Dubey (1992) discovered that the degree of accumulation differed substantially between the five species under study. Bache *et al*. (1991) in their study of metal concentrations in grasses in relation to a municipal refuse incinerator suggested that the nature and area of the leaf surface would affect foliar deposition.

As with herbs and grasses, tree leaf surfaces may govern the extent of accumulation of particles. In Greece, Sawidis *et al*. (1995) studied a selection of tree species as biomonitors of Zn and Cu. The investigators discovered that the strongest metal accumulators possessed rougher surfaced leaves which gave rise to the effective trapping and retention of particles.

Metal content will vary depending on which part of the plant is sampled. For example in herbaceous plants, roots and leaves retain higher metal concentrations than stems and fruits (Kovacs, 1992; Csintalan and Tuba, 1992). The extent of accumulation in different plant parts will vary with species and the nature of the element. Chemical composition varies not only with the age of the plant itself but also with the age of the leaf/needle.

Positive correlations between Pb, Cu and Fe concentrations in leaf tissue and leaf surface demonstrated the significance of deposition to leaf tissue content. This supports the theory that aerial deposition to leaves is an important source of metal contamination in leaves. Further evidence was the lack of correlation between metal content in leaves and in soil. Soil samples possessed a higher metal burden than leaf samples.

Pb accumulation in leaves is a direct reflection of its deposition level. It is a non-essential plant element and deposition and accumulation on plant leaves is its primary route of uptake (Mulgrew and Williams, 2000). Therefore, analysis is not complicated by the root uptake and translocation processes apparent for other metals. Furthermore, analysis for Pb is made easier by the fact that concentrations are often unaffected by washing procedures. For example, Hernandez *et al*. (1987) discovered that the amount of Pb measured in samples of rose-bay leaves showed no difference when the samples were washed or unwashed prior to analyses.

In a study of heavy metal burden in air, soil and plants around a zinc smelter in India, Agrawal *et al*. (1988) did not observe statistically significant correlations between heavy metal content in the air, soil and plants. Local topography and microclimate of the study area also played a role in the dispersion of heavy metals. The leaves of the four plant species analysed (*Mangifera* sp., *Acacia* sp., *Triticum* sp. and *Brassica* sp.) showed great variation in heavy metal concentration depending on species, metal type and sampling site.

The objective of this study is to determine the concentrations of selected heavy metals such as copper, lead, nickel, chromium and cadmium in leaves from different parts of Port Harcourt.

MATERIALS AND METHODS

Study area: The study area, Port-Harcourt is a highly industrialized city of Nigeria, a major industrial center as it has a large number of multinational firms as well as other industrial concerns particularly businesses related to the petroleum industry. It is the chief oil-refining city in Nigeria, oil being one of Nigeria's most important commodities and the main foreign exchange earner.

Port-Harcourt lies within latitudes 4°43' and 4°54'N and longitudes 6°56' and 7°03'E, 59 feet (18 m) above sea level with a mean annual rainfall of >2000 mm and mean annual temperature of about 29°C (NMS, 1998).

Selection of sampling sites: The criteria used in selecting the stations (Table 1) include the availability of unshaded leaves and level of activity; high activity (>500,000 automobiles per day and >200 street traders including industrial activities), medium activity (<500,000 automobiles per day and <200 street traders with less industrial activities) and low activity (control), (approximately 50 automobiles day^{-1} and no street traders). On the whole five high activity stations, five medium activity stations and two control stations were selected. Figure 1 shows the map of Port Harcourt showing the sampling stations.

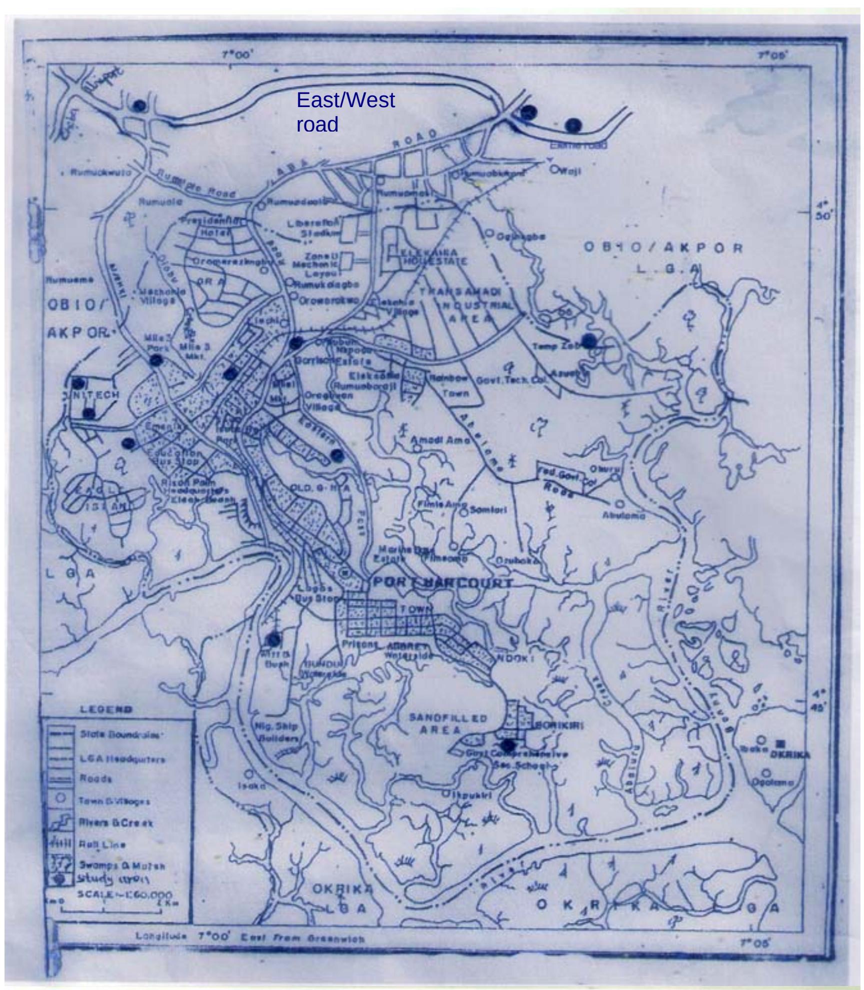

Fig. 1: Map of Port Harcourt showing study areas

Sample collection, preparation and analyses: Leaf samples from the selected stations (Table 2) were collected during the rainy season (September) and during the dry season (January) to determine the effect of seasonal variation on the concentrations of heavy metals in plants leaves. Twelve leaf samples were collected using a pen knife and carefully placed into labeled polyethylene bags and taken to the laboratory for analysis. The leaf samples were air-dried, ground to pass through a 2 mm mesh and stored at room temperature in well-labeled polythene bags. About 5 g of the sieved leaf samples were weighed into a conical flask and digested with 3 mL HCl and 1 mL HNO_3 (Sterckman *et al*., 1996). The contents were filtered through Whatman No. 42 filter paper into 50 mL volumetric flasks and made up to the mark with de-ionized water. The concentrations of Ni, Cu, Cd, Cr and Pb in the digested leaf samples were determined by GBC Avanta Ver. 2.02 atomic absorption spectrophotometer.

Table 1: Identification of study stations with geographical references and level of activity

Station No.	Station name	Station code	GPS	Level of activity
I	Aba road by Garrison junction	GAJ	N 04°48.413' E 007°00.567'	High
2	Trans-Amadi by Port Harcourt Zoo	TAZ	N 04° 48.758" E 007°02.673'	High
3	Aba road by Eleme junction	AEL	N 04°51.427' E007°04.120'	High
4	Eastwest road by Rumuokoro	ROK	N 04°52.052" E 006°59.780'	High
5	Ikwere road by Mile 3 Diobu	M3D	N 04°48.308' E 006°59.351'	High
6	Eastern By-Pass by LNG round about	EBP	N 04°47.516' E 007°00.984'	Medium
7	Banham by Lagos Street	BLS	N 04°45.761' E 007°01.544'	Medium
8	Reclammation road/ Stella Maris	RSM	N 04°45.745' E 007°00.700'	Medium
9	Lumumba Street Diobu	LBS	N 04°47.516' E 006°59.346'	Medium
10	Manilla-Pepple Street D/Line	MPD	N 04°47.990' E 006°59.902'	Medium
11	Comprehensive Sec. School Borikiri	CSB	N 04°44.535' E 007°02.101'	Low
12	RSUST Road E	UST	N 04°47.308' E 006°58.807'	Low

Table 2: Common and scientific names of leaf samples collected at the study stations

Station No	Station code	Common names	Scientific names
1	GAJ	Almond	*Terminalia catappa*
2	TAZ	Guinea grass	*Panicum maximum*
3	AEL	Paw paw	*Carica papaya*
4	ROK	Orange	*Citrus sinensis*
5	M3D	Mango	*Mangifera indica*
6	EBP	Plantain	*Musa sapientum*
7	BLS	Bitter leaf	*Vernonia amaygdalina*
8	RSM	Bitter leaf	*Vernonia amaygdalina*
9	LBS	Grape	*Citrus paradise*
10	MPD	Bitter leaf	*Vernonia amaygdalina*
11	CSB	Paw paw	*Carica papaya*
12	UST	Bitter leaf	*Vernonia amaygdalina*

RESULTS AND DISCUSSION

The results of heavy metal analysis on the leaf samples from the study area are shown in Table 1 and Fig. 2-7. The concentrations of Cr varied from 0.003 ppm at Stations 1 and 2-19.530 ppm at station 10 in the dry season and from 0.001 ppm at Stations 1 and 2-16.824 ppm at Station 10 in the in the rainy season. The

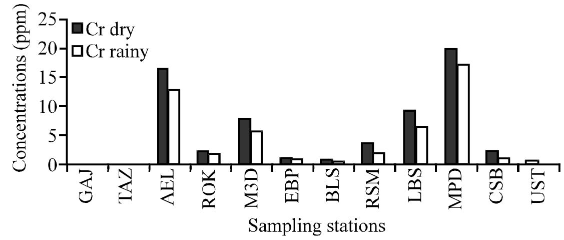

Fig. 2: Seasonal variations in concentrations of Cr with sampling stations

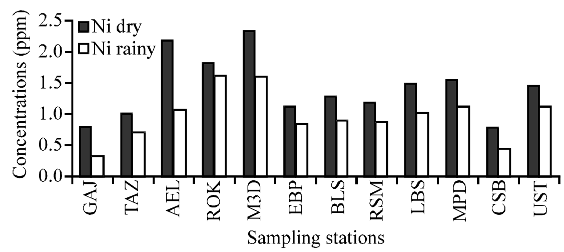

Fig. 3: Seasonal variations in concentrations of Ni with sampling stations

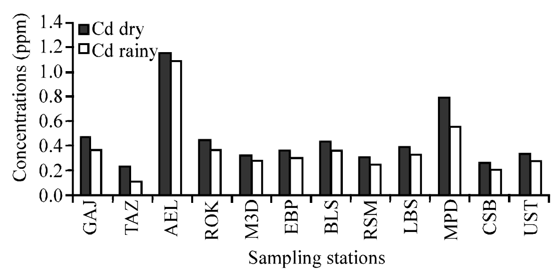

Fig. 4: Seasonal variations in concentrations of Cd with sampling stations

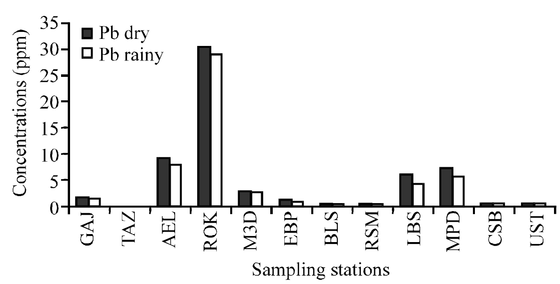

Fig. 5: Seasonal variations in concentrations of Pb with sampling stations

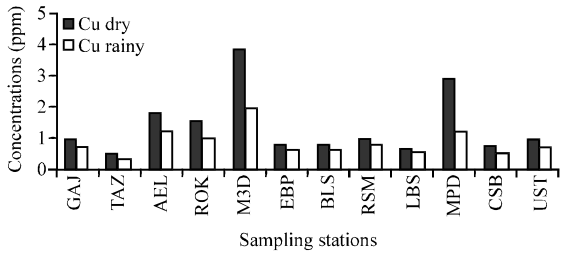

Fig. 6: Seasonal variations in concentrations of Cu with sampling stations

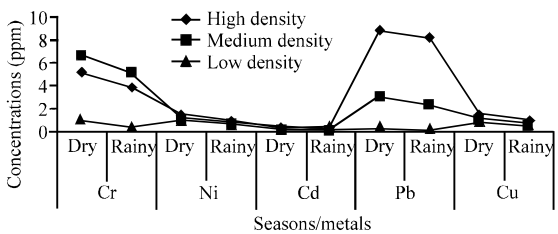

Fig. 7: Variations in mean concentrations of metals with sampling areas

highest concentration of Cr was measured in bitter leaf. The highest level of Cr exceeded permissible limit of 0.05-0.5 ppm (RSMENV, 2002) indicating pollution. The dry season concentrations of Ni ranged between 0.780 ppm at Station 11 and 2.320 ppm at Station 5 while in the rainy season the concentrations ranged between 0.320 ppm at Station 1 and 1.604 ppm at Station 5. The highest concentration of Ni in the area was measured in mango leaf and was below permissible limit of 0.5-5 ppm (RSMEnv) and therefore does not pose serious health concern.

The levels of Cd in the dry season varied from 0.240 ppm at Station 2-1.150 ppm at Station 3 while in the rainy season the levels varied from 0.118 ppm at Station 2-1.080 ppm at 3. The highest level of Cd occurred in Pawpaw leaf. The levels of Cd exceeded permissible limit of 0.01-03 ppm (RSMENV) and pose serious health concern.

In the dry season the levels of Pb varied from 0.001 ppm at Station 2-30.230 ppm at Station 4 while the rainy season concentrations of Pb varied from 0.001 ppm at Station 2-28.960 ppm at Station 4. The highest concentration of Pb was measured in orange leaves. The values of Pb obtained are within the values reported by Hernandez *et al.* (1987) who reported that Pb ranged from 13.63-74.25 ppm in rose-bay leaves (*Nerium oleander*) in Madrid Spain. The highest level of Pb is >4.5 mg kg^{-1} reported by Sawidis *et al.* (1995) and exceeded the permissible limit of 0.05-3ppm (RSMENV). The Pb levels therefore pose serious health concern in the area.

The concentrations of Cu in the dry season ranged between 0.530 ppm at Station 2 and 3.850 ppm at Station 5 while in the rainy season the levels ranged between 0.386 ppm at Station 2 and 1.975 ppm at Station 5. The highest level of Cu was measured in mango leaf. The levels of Cu were below the concentrations 5-10 mg kg^{-1} reported by Sawidis *et al.* (1995).

The mean concentrations of the metals showed highest levels at the high activity areas and least at the low activity (control) areas. However, Fig. 7 showed distinct variations in Cr and Pb concentrations but very close variations in Ni and Cd concentrations.

The highest levels of the metal concentrations were measured at different stations. For instance Cr was measured at Station 10, Ni and Cu at Station 5, Cd at Station 3 and Pb at Station 4. Also the highest metal concentrations were obtained in different plants. For instance Cr was highest in bitter leaf, Ni and Cu in mango, Cd in pawpaw and Pb in orange. These observations are attributed to the differences in ages, types and heights of the plants sampled.

The occurrence of highest level of different metals in different plant leaves is attributed to the fact that the plant leaves sampled at the different stations deferred. However, bitter leaf was sampled at medium activity stations 7, 8, 10 and 12 but the levels of metals at these stations varied according to the level of activity as well as the ages of the plants. Older leaves and leaves from higher plants had higher metal concentrations. Higher plants do not only intercept pollutants (metal aerosols) from atmospheric deposition but also accumulate aerial metals from the soil (Mulgrew and Williams, 2000).

Though Stations 1 and 2 are high activity areas the levels of Cr at Stations 1 and 2 (Fig. 2) and Pb at Station 2 (Fig. 5) were very low. With the exception of Ni in the dry season the lowest concentrations of the metals were measured at Station 2 in both seasons though Stations 1 and 2 are high activity areas. This implies that in addition to level of activity in the study areas, concentrations of the metals were influenced by the age, type and height of plant.

The concentrations of the metals followed the trend Pb>Cr>Cu>Ni>Cd at the high activity areas and Cr>Pb>Ni>Cu>Cd at the medium activity areas. However, at the low activity areas (control) the observed trend was Cr>Ni>Cu>Pb>Cd in dry season and Ni>Cu>Cr>Pb>Cd in the rainy seasons.

The highest occurring metal was Pb. Lead accumulation in leaves is a direct reflection of its deposition level (Mulgrew and Williams, 2000). The highest level of Pb (30.230 ppm) measured at Station 4, high activity area indicate that automobile emissions are a major source of the metal since the main activity in the area is vehicular. In Madrid Spain, Hernandez *et al.* (1987) found significant positive correlation between lead levels in rose-bay leaves and traffic density. However, Sawidis *et al.* (1995) in Thessaloniki reported that Pb levels were not proportional to traffic density and higher levels of Pb were associated with sites near road junctions. The highest level of Pb in *Vernonia amygdalina*, 7.3 ppm measured at station 10 is within the level (12.56 mg kg^{-1}) reportd by Abere *et al.* (2011). However, in a similar study Ideriah and Braide (2006) using Dithizone colorimetric method reported highest Pb concentration of 61.4 μg g^{-1} in *Vernonia amygdalina*. Furthermore the highest concentration of Pb (68.6 μgg^{-1}) was measured in *Panicum maxima* at Trans Amadi (Station 2, present study) while the least level (0.001 ppm) was measured in this study. This observation is attributed to the clearing of grasses and plants in the area and further affirms the influence of age on the concentrations of heavy metals in plants.

The dry season concentrations of the metals at the stations were higher than the rainy season concentrations. Statistical analysis (t-test) showed significant difference ($p<0.05$) between the two seasons with high positive correlation for Cr ($r = 0.99534$), Ni ($r = 0.87216$), Cd ($r = 0.97854$), Pb ($r = 0.99789$) and Cu ($r = 0.95547$). Analysis of Variance (ANOVA) showed no significant difference ($p>0.05$) between the sampling stations in both seasons and significant difference ($p<0.05$) between the metals in the dry season and no significant difference ($p>0.05$) in the rainy season.

With the exception of Cr the mean concentrations of the metals were highest at the high activity Stations 1-5 and lowest at the low activity (control) Stations 11 and 12. This observation is in agreement with the reports of Alfani *et al.* (1996), Albasel and Cottenie (1985), Hernandez *et al.* (1987) and Sawidis *et al.* (1995). Alfani *et al.* (1996) in their study of gradients of pollution of Cu, Pb and Fe in leaf surfaces and tissue of *Quercus ilex* (Holly oak) from Naples, Italy found that metal concentrations were significantly higher in leaves from roadside than in leaves from town squares which in turn were significantly higher than concentrations measured in urban park trees. Albasel and Cottenie (1985) reported that Cu, Zn and Pb concentrations in plants decreased with increasing distance from major high ways in Belguim. In Finland, Ylaranta (1995) found that the Pb concentration of wheat, Italian rye grass and lettuce was 1.5-3 times higher 22 m from the roads under study than in plants 200 m from the roads. Sawidis *et al.* (1995) studied the value of tree species as biomonitors of heavy metal pollution in Thessaloniki city, Greece and found that trees nearer the city centre contained higher metal levels than trees 15 km away.

CONCLUSION

This study has generated data to fill existing gap and the findings have shown that metal concentrations in leaves are influenced by the level of activity, plant species, age and height of the plant bearing the leaf. The leaves from roadside plants are polluted and require proper treatment before consumption or use for herbal or medicinal purposes.

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