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Assessment of toxic metal pollution in soil, leaves and tree barks: bio-indicators of atmospheric particulate deposition within a University community in Nigeria

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Abstract. Heavy metal contents of road–side soil, tree barks and leaves of mango (*Mangifera indica*), tick (*Tectona grandis*), almond (*Terminalia catappa*), cashew (*Anacardium occidentale*) and Gmelina (*Gmelina arborea*) collected from a University community in Iwo town, Nigeria were assessed as potential air pollution indicators. This is the first study on the heavy metal contents in selected type of sample in this town. Concentrations of Mn, Cu, Pb, Cr, and Cd in the samples from the University community were far above the background metal contents. Majority of the samples were in the range of concentrations previously reported in literature. The exception was Mn with concentration ranges of 438-980 mg kg^{-1} for soil, 460-1960 mg kg^{-1} for leaves and 1450-3840 mg kg^{-1} for tree barks. The order of abundance which probably reflects the preferential atmospheric burden of heavy metals in tree backs and leaves was majorly Mn > Cu > Pb > Cr > Cd.

Key Words: road side soil, tree barks, tree leaves, heavy metals.

Introduction. The current levels of exposure to excessive emissions of heavy metals in form of particulates and elemental deposition (Wong et al 2003) from the atmosphere particularly in urban areas are sufficient to cause health effects, which are major environmental issues in many countries (Dockery 2009; Kampa & Castanas 2008). Particulate matter in form of dusts containing heavy metals such as lead, vanadium and manganese from vehicle exhaust is inherently toxic. The toxicity includes damage to central and peripheral nervous system, blood composition, lung, liver and even death (Davydova 2005; Wijaya et al 2012). The levels of these toxic heavy metals in the atmosphere can be estimated indirectly by using biomonitors or other accumulators such as road dust (Fujiwara et al 2011), leaves and tree bark (Celik et al 2005; Sawidis et al 2011). The major reason of utilizing bark as biomonitor for pollution is to accumulate data on long term contamination. Using bark is of great advantage for the fact that its structure retains the pollutants longer and that it is widely available leaving the health of the trees unaffected. The back is exposed to heavy metal accumulation directly from the atmosphere and from stem flow. The efficient accumulation and retention of heavy metals in the bark is due to its structural porosity (Berlizov et al 2007). Leaves have also been tested as biomonitor for pollution especially on the adaxial surface but the results produced might be invalid because of the possibility of the pollutants being washed away by rain or dispersed by the wind (Al-Khashman et al 2011).

Numerous published studies have used trees for monitoring elemental deposition from the atmosphere. Such trees include *Phoenix dactylifera* (Al-Shajeb et al 1995; Aksoy & Ozturk 1996), *Pinus sylvestris* (Dmuchowski & Bytnerowicz 1995), *Pinus pinea* (Dongarra et al 2003a), *Nerium oleander* (Dongarra et al 2003b), *Pittosporum tobira* (Lorenzini et al 2006), *Acacia retinoides* and *Eucalyptus torquata* (Pyatt 2001), *Populus nigra* (Djingova et al 2001), *Tibouchina pulchra* (Moraes et al 2003), *Cedrus libani* (Onder & Dursun 2006), *Bauhinia blakeana* (Lau & Luk 2001) and several other tree species

(Baycu et al 2006; Sawidis et al 1995a,b,c, 2001). Studies of air pollution in estimating heavy metals concentrations in some part of Nigeria using bio-indicator such as mosses, linchens (Onianwa et al 1986; Odukoya et al 2000) and water leaf (Adeniyi 1996) have been reported. However, the suitability of these bio-indicators for estimating the levels of air pollutants extensively in Nigeria is limited because they are not widely spread in the country. Therefore, attention is required for the use of barks of other tree species that are commonly found in the country and whose surfaces are rough. Rough barks are noted to be better accumulators of heavy metals than smooth barks (El-Hasan et al 2002).

Atmospheric pollution in Nigeria has received little attention and there has been dearth information on the usage of bio-indicator for monitoring atmospheric pollution. Hence, this study on bio-monitoring of atmospheric pollution in Nigeria becomes essential and most of the tree species investigated in this study have rough barks and broad leaves. Heavy metals contamination in topsoil especially with Pb, Cr, and Hg in Iwo town was reported by Ipeaiyeda & Dawodu (2008). Elemental deposition from the atmosphere might have contributed to the available pools of such heavy metals in addition to the auto-exhaust emission, which was generally accepted as the major source of heavy metal pollution in the town. Furthermore, it was found that increase in population and traffic in Iwo town was traceable to the emergence of Bowen University. The aim of this work was to investigate and assess the heavy metal pollution in the atmosphere of Bowen University's community in Iwo town using barks and leaves of mango tree (*Mangifera indica*), tick tree (*Tectona grandis*), almod tree (*Terminalia catappa*), cashew tree (*Anacardium occidentale*) and Gmelina tree (*Gmelina arborea*) as bio-indicators. Heavy metals concentrations in road side soil were also assessed. The findings could be used as preliminary baseline data for future assessment and atmospheric pollution monitoring.

Material and Method

Description of study area. Bowen University is located in Iwo town, which is one of the largest towns in Southwestern Nigeria (Figure 1). It has an elevation that varies between 250 m and 300 m above sea level and it lies at latitude 7°47'N and longitude 4°33' W. It was established in 2002, and since then, there has been rapid population growth especially in the last three years. The university covers an area of around 636.4 hectares with total inhabitants of about six thousand five hundred students. The university's community activities are broadly classified into five major areas which are academic, administrative, communal and social services, staff and student housing, and playing ground areas. There is also a vast expanse of undeveloped land that is cultivated for vegetables.

Sampling areas and sample collection. Samples of roadside soil, tree bark and leaf were collected from five different locations that reflect a progressive increase in human activities and land use along the main roads within the University's community. The selected locations were as follows: Bank - Agricultural Farm Road (BAR), Hospital - Digital Centre Road (HDR), Girls Hostel Road (GHR), Boys Hostel Road (BHR) and Complex – Main Gate Road (CMR) (Figure 1). Control samples of soil, tree bark and leaf were collected from a natural reserve area in Kuta. This area is about 30 km from the University community and has negligible traffic influence.

The sampling was carried out during a dry season period in December 2012. Four soil samples from each of five locations within the University's community to make twenty samples were collected between 0-10 cm depth at about 10 m away from the road edge. The soil samples were collected with an auger and kept in polyethylene bags. One bark sample (about 500 g) was collected four times from the trees of mango, tick, almod, cashew and Gmelina. These trees are as old as the community in which the University is located. The bark samples were collected from the stem with a diameter of 80–120 cm at a height of 2 m above the ground using a stainless steel knife and kept in polyethylene bags. Leaves were also sampled randomly (about 50 g) from the lower foliage of each tree species. The selected trees at University community and control site were of the same species, namely mango, tick, almond, cashew and Gmelina trees respectively. The collected leaves and barks were not cleaned because of the purpose of using trees to estimate the metal load in order to reflect the effect of atmospheric pollution.

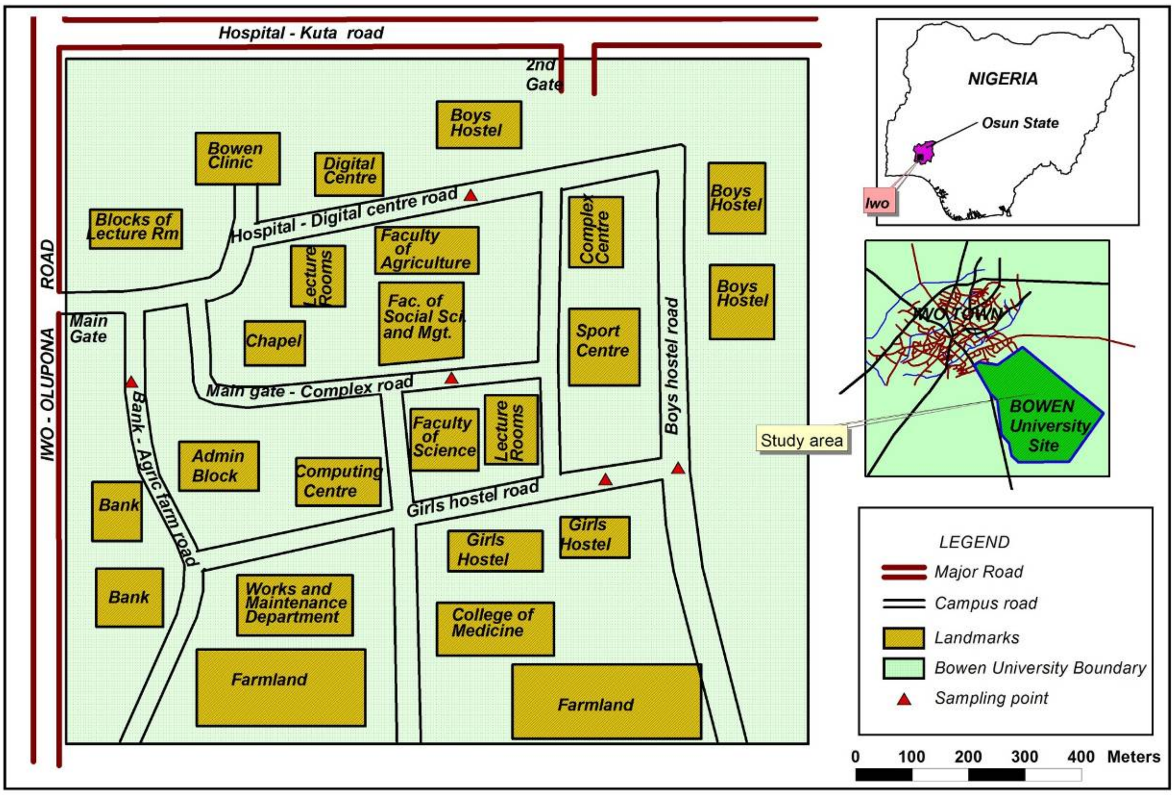

Figure 1. Schematic diagram showing sampling points along campus road within Bowen University, Iwo, Nigeria (Source: Geography Department, University of Ibadan, Ibadan).

Preparation and digestion of the sample. The collected soil samples were air dried in Chemistry laboratory in Bowen University, Iwo, sieved to 2 mm sieve and stored in polyethylene bags. The barks and leaves were dried in the oven at 105^{o}C and 40^{o}C, respectively, for about five hours to constant weight. The dried samples were pulverized to uniform size with a laboratory mill. The accurately weighed portion (1 g) of the powdered sample was ashed in a muffle furnace at about 500^{o}C (Schulz et al 1999; Odukoya et al 2000; Suzuki et al 2006; Sawidis et al 2011). A single sample was ashed in triplicate to test the reproducibility of this method. The ash was dissolved with 10 mL of 10% HNO_3 solution and left overnight. The final extract were filtered into 25 mL volumetric flask through 45 µm filters then diluted to the mark with the dilute acid. The accuracy of the procedure was estimated through a recovery test because of the lack of alternative reference materials. The recovery test was performed by spiking known amount of standard solutions of Mn, Pb, Cu, Cd and Cr to an accurately known weight of each of powdered soil, tree bark and leaves. The digests were analyzed for heavy metal concentrations using Bulk Scientific Model 205 Atomic Absorption Spectrophotometer with air-acetylene flame. The recovery ranged from 92 to 96% for Mn, 90 to 94% for Pb, 89 to 94% for Cu, 90 to 98% for Cd and 89 to 96% for Cr.

Data analysis. Statistical differences among the samples regarding their heavy metal contents were tested by one-way analysis of variance (ANOVA) and Turkey honestly significant difference (HSD) test at ($p = 0.05$).

Results and Discussion

pH and metal concentrations in soil. pH values and metal contents of soil collected from the institution premises are presented in Table 1. The studied soil samples were slightly acidic in nature with average pH of 6.5±1.5 ranging between 6.0 and 7.2. Metals are likely to be in a mobile form (Škrbić & Miljević 2002) which heightens the exposure route of metal contamination to human by inhalation or ingestion of dust from the topsoil. In order to assess the degree of anthropogenic contamination, soil from the University's community was compared with the control sample in terms of metal concentrations. Soil samples from the community displayed higher metal concentrations than the control sample. This study indicates extremely metal contamination especially for manganese (668±170 mg kg^{-1}) and lead (0.58±0.40 mg kg^{-1}). Considering manganese and lead background of 54.2±0.1 mg kg^{-1} and 0.04±0.01 mg kg^{-1} obtained respectively, manganese and lead in developed portion of the community were found to be about twelve and fifteen times higher respectively (Table 1). The elevated level of manganese is explained by anthropogenic input from vehicular emission involving the use of anti-knock agents containing manganese (Zayed et al 1999). The abundance of heavy metals in soil was found in order of Mn >> Pb > Cu > Cd > Cr (Table 1). According to Othman et al (1997) and Škrbić et al (2012), most particulate carrying traffic–related elements like Pb, Cd, Cu and Mn emitted from vehicles are deposited on roadside top soil, but some can be carried a longer distance by wind. This order of abundance, therefore, is considered as an indication of the dispersion profile of the metals in the dust possibly from soil. Street dust can be easily abstracted from topsoil (0-10 cm) and get dispersed in the atmosphere under natural conditions such as wind and rain (Charlesworth et al 2003). With the level of metal contamination in road-side soil from the University's community, the metal concentrations were still observed to be much lower than the corresponding concentrations of metals in road-side soil from other countries (Table 2).

Table 1

Soil pH and metal concentrations (µg g^{-1}) in road side top soil from Bowen University's community, Iwo town

Sample code	*pH*	*Mn*	*Pb*	*Cu*	*Cd*	*Cr*
BAR1	6.3	759	0.52	3.58	0.05	0.02
BAR2	6.4	648	0.90	2.33	0.07	0.01
BAR3	6.4	692	1.02	3.79	0.11	0.02
BARS	6.2	650	1.05	3.50	0.13	0.01
HDR1	7.2	438	0.68	2.99	0.20	0.01
HDR2	6.9	560	0.64	2.38	0.07	0.02
HDR3	6.4	480	0.77	2.08	0.24	0.01
HDR4	6.8	579	0.74	2.10	0.20	0.01
GHR1	6.5	749	0.18	3.38	0.04	0.01
GHR2	6.5	730	0.41	4.49	0.18	0.03
GHR3	6.7	642	0.18	4.63	0.11	0.03
GHR4	6.4	680	0.20	5.15	0.10	0.03
BHR1	6.2	580	0.13	4.25	0.05	0.04
BHR2	6.1	980	0.12	3.06	0.10	0.01
BHR3	6.5	681	0.17	3.29	0.06	0.02
BHR4	6.4	750	0.15	4.93	0.15	0.03
CMR1	6.7	670	0.20	4.84	0.25	0.04
CMR2	6.7	650	1.31	3.07	0.04	0.01
CMR3	6.1	750	1.13	2.99	0.02	0.02
CMR4	6.0	689	1.15	3.38	0.27	0.01
Mean±SD	6.5±1.5	668±170	0.58±0.40	3.5±1.1	0.12±0.08	0.02±0.01
Control sample	6.8±0.2	54.2±0.1	0.06±0.01	0.04±0.02	0.005±0.001	0.006±0.001

SD = Standard deviation.

Table 2

Comparison of metal concentrations (µg g^{-1}) in road-side top soil from Bowen University's community with results from other countries

Sample code	*Mn*	*Pb*	*Cu*	*Cd*	*Cr*	*Reference*
Bowen University, Iwo town	668±170	0.58±0.40	3.5±1.1	0.12±0.08	0.02±0.01	This study
Ueno street, Tokyo	-	264	-	1.40	73.9	Wijaya et al (2012)
Mido Suji, Osaka	-	229	-	1.04	35.1	Wijaya et al (2012)
Hachijo Dori, Kyoto	-	156	-	1.03	54.8	Wijaya et al (2012)
Banja Luka, Bosnia	860	74.7	32.2	2.78	4.39	Škrbic et al (2012)

Metal concentrations in tree barks. The mean concentrations of metals in some selected tree barks from the University's community and control site that is designated as reference location were shown in Table 3. Mean concentrations of Mn, Pb, and Cu were significantly ($p = 0.05$) higher in tree barks of the investigated samples in comparison to the reference tree bark. This is attributed to different anthropogenic activities between the University's community and reference site. Comparing the tree barks from the community and reference site, there was no significance difference in Cd and Cr concentrations among the tree species investigated suggesting that inter-species variation was less pronounced as to affect the adsorption capacity of the tree for atmospheric deposition. The tree barks from the University community were dominated by elevated concentration of Mn as it can be deduced from Table 2. Mn was present in highest proportion with a range of 3120–3840 mg kg^{-1} for Gmelina tree, 1750–1920 mg kg^{-1} for cashew tree, 1650–1750 mg kg^{-1} for almond tree, 1480–1620 mg kg^{-1} for tick tree and 1450–1710 mg kg^{-1} for mango tree (Table 3).

Lead is well known for its toxicity even at low concentration being a non-essential element. The lead concentrations obtained in all the trees from within the University were far low compared to the phytotoxic concentration of lead ranging from 30 to 300 mg kg^{-1} as recommended by Reeves et al (1995). Chromium is also considered as one of the most detrimental elements to the environment. The highest Cr concentration of 1.28 ± 0.75 mg kg^{-1} (Table 3) found in Gmelina tree bark is within the range of 1-5 mg kg^{-1} for which growth inhibition, decrease in chlorophyll synthesis and chlorosis were observed (Dube et al 2003). The order of heavy metals abundance in tree bark was majorly Mn > Cu > Pb > Cr > Cd for tick, almond, cashew and Gmelina trees. The only exception was that for mango tree whose heavy metal abundance followed the order Mn > Cu > Pb > Cd > Cr. The former order was not similar between the samples from the University's community and background samples. This order probably reflects the preferential atmospheric burden of heavy metals. Since the metal contents of tree back at the University community were far above the background metal contents, it could be deduced that atmospheric deposition via dust had influence on the tree back elemental profile. It is expected that fine particles of dust from soil would be accumulated and retained in the back due to its structural porosity (Berlizov et al 2007). The metals concentrations obtained in this study are compared with metal content of the bark reported elsewhere (Table 4) in order to give insight into the heavy metals ranges previously determined in tree barks of different species. The exact differences in metal contents especially for manganese could be explained from the view of plant physiology and contamination of the University's community with an excessive content of the metal. There are few high significant correlations (Table 5) between heavy metals in tree barks such as Mn and Pb ($r = 0.8958$), Mn and Cu ($r = 0.8656$), Mn and Cr ($r = 0.9854$), Pb and Cr ($r = 0.9032$), and Cu and Cr ($r = 0.8170$). This indicates that the University community is influenced by a difference source of pollution. The source might include vehicular emission for Pb and Mn, and soil dust for Cr which might form part of the investigated area.

Table 3

Mean concentrations (μg g^{-1}) (above) with ranges (below) of metals in leaves and barks of some selected trees from Bowen University's community and control site, Iwo town

	Mango tree	Tick tree	Almond tree	Cashew tree	Gmelina tree	Reference tree (control site)
Mn - leaves	1730±38	1580±25	1770±52	1850±40	1730±11	27.4±0.9
	1540-1960	1510-1650	1460-1830	1560-1930	1650-1800	28.2-30.1
Mn - bark	1660±110	1410±25	1690±25	1710±70	3250±20	24.3±0.3
	1450-1710	1480-1620	1650-1750	1750-1920	3120-3840	27.1-25.1
Pb - leaves	7.50±0.05	5.01±0.05	1.50±0.10	5.30±0.05	12.5±0.5	0.05±0.01
	7.41-8.10	5.20-6.01	1.70-2.10	5.02-5.90	11.8-14.1	0.10-0.08
Pb - bark	2.30±0.02	5.30±0.05	7.51±0.02	7.50±0.02	15.0±0.05	0.02±0.01
	2.01-2.80	4.10-6.34	7.01-8.20	6.81-8.70	14.6-15.9	0.03-0.04
Cu - leaves	3.50±0.75	2.75±0.75	4.50±0.20	3.50±0.05	2.75±0.05	0.34±0.01
	3.26-3.90	2.54-3.05	4.21-4.95	3.60-3.81	2.40-2.96	0.51-0.37
Cu - bark	4.50±0.75	2.75±0.25	2.75±0.25	4.75±0.75	6.75±0.60	0.41±0.01
	4.10-5.20	2.40-3.12	2.82-3.01	4.91-5.05	6.21-6.94	0.47-0.43
Cd - leaves	0.10±0.03	0.13±0.03	0.05±0.02	0.13±0.03	0.10±0.03	0.03±0.01
	0.09-0.16	0.10-0.17	0.04-0.07	0.09-0.17	0.09-0.13	0.05-0.03
Cd - bark	0.11±0.03	0.05±0.02	0.11±0.02	0.05±0.02	0.11±0.02	0.04±0.01
	0.08-0.19	0.04-0.07	0.16-0.18	0.04-0.07	0.10-0.16	0.05-0.04
Cr - leaves	1.10±0.25	5.50±0.25	0.45±0.03	0.50±0.20	0.51±0.25	0.05±0.01
	1.01-1.80	4.20-6.20	0.32-0.74	0.37-0.63	0.35-0.71	0.04-0.06
Cr - bark	0.80±0.01	0.45±0.10	0.45±0.01	0.50±0.01	1.28±0.75	0.03±0.01
	0.52-1.20	0.37-0.94	0.40-0.52	0.61-0.45	1.16- 13.2	0.02-0.05

Table 4

Comparison of metal concentrations (μg g^{-1}) in different road-side tree barks from Bowen University's community with results from other countries

Sample location	*Tree species*	*Mn*	*Pb*	*Cu*	*Cd*	*Cr*	*Reference*
Bowen University, Iwo town	Mango	1450-1710	2.01-2.80	4.10-5.20	0.19-0.08	1.20-0.52	This study
	Tick	1480-1620	4.10-6.34	2.40-3.12	0.07-0.04	0.94-0.37	This study
	Almond	1650-1750	7.01-8.20	2.82-3.01	0.18-0.16	0.52-0.40	This study
	Cashew	1750-1920	6.81-8.70	4.91-5.05	0.07-0.04	0.61-0.45	This study
	Gmelina	3120-3840	14.6-15.9	6.21-6.94	0.16-0.10	1.16-1.32	This study
Banja Luka, Bosnia and Heizegovina	Linden	23.7-433	14.7–125	9.88–33.5	0.96–1.03	2.98–13.8	Škrbic et al (2012)
Abuja, Nigeria	Neem tree, Gmelina	-	23–285	-	<0.1–1.0	-	Kakulu (2003)
Kiev, Ukraine	Black poplar	89–151.6	-	7.20–44.6	-	2.20–22	Berlizov et al (2007)
Czech Republic	Oak	16.6-2246	-	-	-	1.88–169.2	Bohm et al (1998)
Sheffield, UK[a]	Sycamore, oak cherry	280±360	226±153	47.3±32.5	1.40±3.62	265593	Schelle et al (2008)
Buenos Aires, Argentina	Green ash	20.6-31.3	0.71-50.1	31.9-993	-	nd–12.1	Fujiwara et al (2011)
Salzburg, Austria[a]	Platanus	-	4.193±1.363	16.6472.485	-	0.3320.102	Sawidis et al (2011)
Belgrade, Serbia[a]	Platanus	-	15.157±0.529	27.8088.482	-	0.9460.295	Sawidis et al (2011)
Thessaloniki, Greece[a]	Platanus	-	13.871±2.260	23.2814.723	-	1.2460.360	Sawidis et al (2011)

a = Mean concentration±standard deviation; nd = not detailed.

Table 5

Correlation coefficient values of all metals in leaves and tree barks from the University community

	Leaves					Tree bark				
	Mn	*Pb*	*Cu*	*Cd*	*Cr*	*Mn*	*Pb*	*Cu*	*Cd*	*Cr*
Mn	1					1	0.8958	0.8657	0.4737	0.9854
Pb	-0.0740	1					1	0.6648	0.2178	0.9032
Cu	0.5432	-0.07239	1					1	0.3021	0.8170
Cd	-0.2275	0.32161	-0.7587	1					1	0.3908
Cr	0.8883	-0.1639	-0.5154	0.4935	1					1

Metal concentrations in leaves. Table 2 equally summarizes the mean concentrations of metals in leaves. Leaves of investigated trees collected from the University's community were found to have significantly more Mn, Pb, Cu, Cd and Cr than those from the control site. This is an indication of the effect of the prevailing wind in transporting metallic contaminants which get adsorbed on the leaves. The abundance of heavy metals in leaves was majorly in the order Mn > Cu > Pb > Cr > Cd (Table 2). There were significant positive correlations (r) between the metal concentrations in tree barks and leaves ranging from 0.8834 to 0.9665 ($p = 0.05$). This suggests that the atmospheric metallic deposition on investigated tree barks and their leaves is governed by similar mechanisms such as re-suspension of soil dust by wind and sport activities. The average levels of Cu in leaves ranged from 2.75 mg kg^{-1} for Tick and Gmelina trees and 4.50 mg kg^{-1} for almond tree. The source of copper may be traceable to corrosion of metallic parts of cars and tyre wears on the street dust which is re-suspended by wind and traffic, and gets deposited on the leaves (Al–Khashman 2004; Al–Khashman & Shawabkeh 2006). Table 6 shows a comparison between the metal concentrations observed in the study with the concentrations of metals in leaves of other trees published for other locations in world. The average levels of metals reported in this study were lower with the exception of Mn with highest concentration of 1850±40 mg kg^{-1} for cashew tree and lowest concentration of 1730±11 mg kg^{-1} for Gmelina tree.

Table 6

Comparison of metal concentrations (µg g^{-1}) in different road-side tree leaves from Bowen University's community with results from other countries

Sample location	*Leaves species*	*Mn*	*Pb*	*Cu*	*Cd*	*Cr*	*Reference*
Bowen University, Iwo town	Mango	1730±38	7.50±0.05	3.50±0.75	0.10±0.03	1.10±0.25	This study
	Tick	1580±25	5.01±0.05	2.75±0.75	0.13±0.03	5.50±0.25	This study
	Almond	1770±52	1.50±0.10	4.50±0.20	0.05±0.02	0.45±0.03	This study
	Cashew	1850±40	5.30±0.05	3.50±0.05	0.13±0.03	0.50±0.20	This study
	Gmelina	1730±11	12.5±0.5	2.75±0.05	0.10±0.03	0.51±0.25	This study
Thessaloniki, Greece	Platanus	-	10.440±3.736	21.772±7.242	-	0.621±0.153	Sawidis et al (2011)
Salzburg, Austria	Platanus	-	3.703±0.735	13.998±2.404	-	0.388±0.114	Sawidis et al (2011)
Belgrade, Serbia	Platanus	-	13.748±2.569	25.197±9.228	-	0.472±0.,136	Sawidis et al (2011)
Ma'an city, Jordan	Date palm	-	179.1±5.8	41.2±1.4	-	4.35±2.00	Al-Khashman et al (2011)
Grapes Hill, Norwich	Birch	222	29	-	-		Maher et al (2008)

Conclusions. This study demonstrated the suitability of the barks and leaves of Mango, Tick, Almond, Cashew and Gimelina as inexpensive bio-indicators of heavy metal contamination. The level of heavy metals contamination reported in this study was low compared to levels reported in developed countries. The only exception was Mn which was attributed to vehicular involving the use of anti-knock agent. Further work is proposed to assess the airborne contamination in the entire Iwo town using similar materials used in this study. In view of this, more intensive sampling and studies will be required to measure any increase in elemental contents in the town.

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