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STUDY OF ATMOSPHERIC POLLUTION LEVELS BY TRACE ELEMENTS ANALYSIS OF TREE BARK AND LEAVES

A.A. Olajire* and E.T. Ayodele

Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

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ABSTRACT. The concentrations of Pb, Cu, Zn, Ni, Fe, and Mn in leaf and bark samples of 7 tree species at 22 sampling locations with different pollution levels, in Ogbomoso, Nigeria, were investigated. The metal concentrations (mean ± RSD in μg g^{-1}) in leaf and bark samples, respectively, were: Pb, 203±70, 282±120; Cu, 19.5±4.2, 12.7±2.6; Zn, 42.7±12.9, 42.8±13.1; Ni, 30.0±11.1, 20.0±9.9; Fe, 869±348, 504±118; and Mn, 108±18, 73.7±13.8. The high-pollution automobile parking lots showed higher levels of these elements ($p < 0.05$). The correlation coefficient between element pairs of high and low-pollution automobile parking lots was carried out to determine the extent of relationship between the elements investigated.

KEY WORDS: Atmospheric pollution, Trace elements analysis, Tree bark, Tree leaves

INTRODUCTION

The increasing input of heavy metals into the biosphere from anthropogenic and natural sources requires constant global monitoring of these pollutants. In the last few decades, due to rapid industrial and technological growth, the emissions of these metals from various human activities have increased. Consequently, the translocation of these toxic metals from the environment to living systems, and their accumulation are the concern of most environmental protection agencies.

Plants are sensitive to environmental conditions, and their elemental composition actively responds to changes in the condition of the environment [1-3]. The uptake of trace elements by trees depends on the reserves of the nutrient in the soil and its availability [4]. The soil pH, soil organic matter content, and plant genotype have a marked effect on nutrient availability [5]. The mechanism of uptake of trace elements by plants is based on root uptake of metals and foliar adsorption, including deposition of particulate matter on the plant leaves. Kloke *et al.* [5] reported that Cd, Tl and Zn have the highest soil-to-plant transfer coefficients, in part because of their relatively poor sorption in the soil, while elements such as Cu, Co, Cr, and Pb have low transfer coefficients, and are stably bound to the soil structure. The intensity and extent of the uptake therefore influence the actual content of an element in the plant. Three different uptake patterns may be differentiated as a function of the plant species under consideration, the element species, and the specific site condition [6, 7]. In certain cases, there is a linear function between the measured content of a substance in the environment (*e.g.*, of a heavy metal) and the measured content within the organism which is to serve as the biomonitor. In this case, the specific element content of the plant reflects the concentration relations of the pollutant in the environment. The chemical plant composition thus has an indicative character [8]. This linear relationship has been observed for a number of plants and various elements, both experimentally and in the field, and is being increasingly applied in ore prospecting or the use of lower plants for environmental monitoring (biomonitoring) [8]. However, Markert *et al.* [9] reported a logarithmic correlation between the biomonitor and the environment.

*Corresponding author. E-mail: olajire@esscon.skannet.com

Less frequently than element accumulation, rejection may occur; *i.e.*, reduced uptake of individual elements, as has already been determined for numerous plant species [10]. The reduction in the concentration of an element in the organism may result from a complete or partial exclusion. According to Ernst and Joosse Van Damme [11], bacteria, algae, and higher plants have heavy metal-resistant populations which are capable of considerably reducing the uptake of heavy metals by excreting mucilaginous substances or by altering the cell walls.

In an ecosystem, the paths and persistence of the elements may be specifically influenced by organismic activities, *e.g.*, by a selective element uptake and concentration. Elements occurring together may therefore influence their transport or accumulation within the organism positively and/or negatively [12-15]. Many plants are in position to take up large quantities of certain elements from the environment. For example, Ericaceae are distinguished by a high content of manganese, irrespective of the content in the soil; and birch trees are distinguished by high zinc content [10]. Irgolic and Martell [16] found that a number of chemical elements, especially metallic ions, exercise a catalytic function in the cell metabolism as a metal complex compound, and are termed enzymatic elements. Elements such as lead, cadmium, arsenic, and mercury have played an important role for years at the ecotoxicological level [17].

The usefulness of tree bark and leaves in detecting atmospheric metals was reported by various investigators for various species of trees. Barnes *et al.* [18] analyzed wood samples from different tree rings for Pb by atomic absorption spectrometry, and found that the Pb concentration in tree bark at several sites was particularly sensitive to the traffic flow at that site. Some authors [19-21] used trace metal levels in various species of Nigerian tree bark as an indicator of atmospheric pollution. The pollution was reportedly due to vehicle exhaust. Tanka and Ichikuni [22] also used the bark samples of Japanese Cedar trees to monitor the heavy metals in airborne particles. Zafar and Qadir [23-25] studied the leaves of various species in urban parks in Pakistan and used them to detect atmospheric metals. The significant pollution was reported to be due to vehicle exhaust. However, this aspect of atmospheric pollution with heavy metals has not been investigated in this part of Nigeria. Thus, the aim of the present study was to investigate the atmospheric pollution levels of heavy metals in Ogbomoso Town, the second largest city in Nigeria and a tourist center, by analysis of tree bark and leaves in automobile parking lots where vehicular emissions are frequent and pollution levels important.

EXPERIMENTAL

Sampling

The sampling area is shown in Figure 1. The area shows no industrial activity in the vicinity of the sampling locations. Leaves and bark of different degrees of roughness of different tree species were sampled from different locations in Ogbomoso, representing parking lots of different automobile density. The sampling points are designated B (for bark samples) and L (for leaf samples) with subscripts 1-7, 15-17, and 20-22, representing parking lots of high automobile density and subscripts 9-14, 18 and 19, representing parking lots of low automobile density. A suitable place (B_8 and L_8) at the University campus (LAUTECH Farm), remote from the parking lots, served as an unpolluted reference point.

Trees of about the same age, situated at the center of activities in the parking lots were selected. Thin chips of bark and leaves were carefully stripped and cut from the trunk with a stainless steel pen knife at an average height of about 2 m above the ground [18] for the tree bark, and at topmost height for the tree leaves. The leaf and bark samples were kept in paper envelopes and then placed in polyethylene bags. The samples were dried in the oven at 110-120 ^{o}C for about 3 h to constant weight and then pulverized to uniform size.

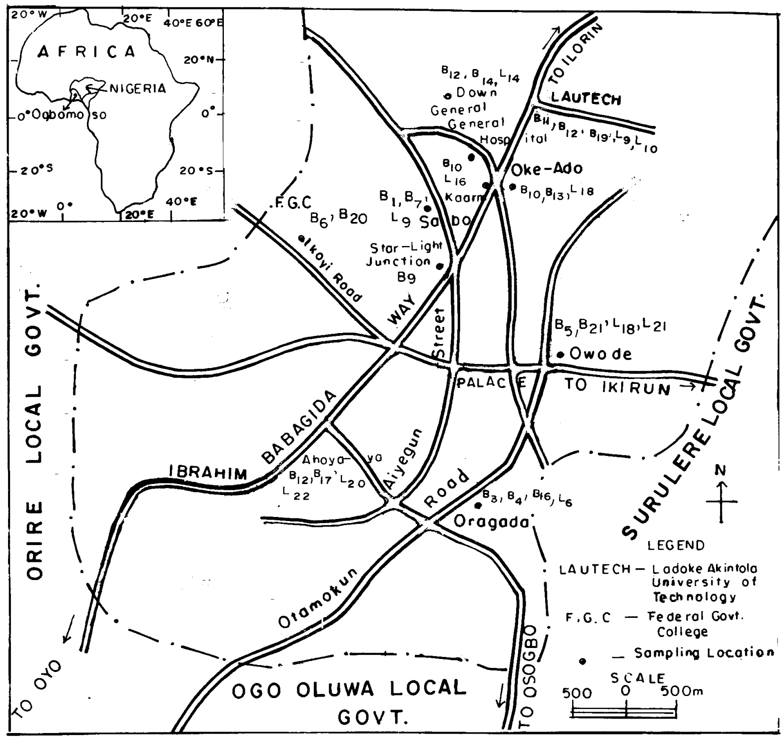

Figure 1. Map of Ogbomoso showing sampling locations.

A pulverized sample (1 g) was accurately weighed into properly cleaned vitrosil crucibles and ashed at a temperature between 450-500 ^{o}C. The ash was dissolved in 5 mL of 11.6 M HCl (1 M = 1 mol dm^{-3}), filtered, and then made up to mark in a 100 mL volumetric flask with doubly-distilled water.

A reagent blank was prepared by mixing 5 mL of 11.6 M HCl with doubly-distilled water in a 100 mL volumetric flask. Standard solutions used for preparing calibration curves were prepared by stepwise dilution of the stock certified standard solutions of heavy metals.

To validate the method of ashing, the bark of *Terminalia catapa* from a high auto density parking lots was digested with a mixture of hot concentrated nitric (800 mL) and sulphuric (200 mL) acids. The result obtained was compared with the value obtained from the ashing of the bark of *Terminalia catapa* from a high auto density parking lots (Table 1). The values for the student's 't' calculated from these data ($p < 0.05$) showed no difference between the two methods of digestion.

Atomic absorption analysis

Pb, Cu, Zn, Ni, Fe, and Mn concentrations were measured with a Chem Tech Analytical Alpha 4 atomic absorption spectrometer. The instrument was operated in accordance with the instrument's manual. Results were corrected for reagent blanks and non-atomic absorption. The reproducibility of the method of ashing the bark and leaf samples was checked by carrying out a duplicate analysis. Duplicate results did not differ by more than 10% of the mean.

RESULTS AND DISCUSSION

Table 2 gives the results of the chemical analysis for the categories of high- and low-automobile density parking lots for bark from *Terminalia catapa.* High concentrations of elements were observed in samples taken from high-automobile density parking lots. This is an indication of an enhanced heavy metal level in the atmosphere surrounding these automobile parking lots. Furthermore, concentrations of metals are low in parking lots of low-automobile density.

Table 1. Statistical[*] evaluation of two different analytical methods of digestion for heavy metal analysis of bark of Nigerian *Terminalia catapa* from high auto density parking lots.

Analytical method	Pb	Cu	Zn	Ni	Fe	Mn
Ashing method (6 samples)						
Mean (μg g^{-1})	483	37.5	50.3	30.5	496	74.6
R.S.D. (%)	8.65	31.7	20.1	14.9	27.2	19.7
Wet oxidation (6 samples)						
Mean (μg g^{-1})	502	49.8	37.8	45.2	511	82.4
R.S.D. (%)	15.8	37.2	29.6	33.2	39.9	33.6
σ	69.4	17.0	11.7	12.1	189.4	24.3
t	-0.47	-1.25	1.85	2.11	-0.14	-0.56

[*]Critical value of 't' for 10 degree of freedom is 2.23 at 95% confidence level. R.S.D. is relative standard deviation.

Table 2. Concentration[a] of heavy metals in bark[b] of *Terminalia catapa* at high-auto density and low-auto density parking lots.

Sample number	Bark feature	Tree location	Concentration, μg g^{-1} sample, dry weight					
			Pb	Cu	Zn	Ni	Fe	Mn
B_7	High- auto density park	Sabo Garage	514 ± 27	49.6± 2.5	50.7± 3.6	33.4± 2.7	604 ± 32	87.4± 5.1
B_{16}		Oragada	487 ± 30	37.4±1.9	49.2± 2.8	30.7± 2.1	587 ± 36	70.5± 4.5
B_{22}		Cow-shed (Kaara)	564 ± 29	48.7± 2.7	60.4± 3.2	39.2± 2.0	659 ± 40	66.8± 3.7
B_{17}		Ahoyaya	476 ± 31	29.8± 1.8	45.3± 2.4	28.5± 1.8	499 ± 37	52.6± 3.6
B_{20}		Ikoyi Road	485 ± 23	34.5± 2.1	40.6± 2.1	29.8± 2.4	417 ± 28	59.2± 4.4
B_{21}		Owode	448 ± 22	27.4±1.6	48.1± 2.5	26.9± 1.5	326 ± 20	75.1± 3.9
B_{11}	Low- auto density park	General Hospital	297 ± 18	16.8±1.0	27.4± 3.1	18.4± 1.3	321 ± 26	40.7± 2.5
B_{14}		Down Gen. Hospital	342 ± 20	23.4±1.5	23.8± 1.3	14.6± 1.5	298 ± 18	49.3± 2.8
B_{12}		OkeAdo Sabo	364 ± 19	14.6±0.9	18.7± 1.2	13.7± 1.0	249 ± 15	44.6± 3.1
B_{10}		Oke Ado Sabo	269 ± 15	15.8± 1.2	25.3± 2.1	15.9± 1.6	257 ± 21	57.5± 2.5
[c](L_8)		LAUTECH Farm	175 ± 10	9.2± 0.6	10.2± 1.1	6.38± 0.5	209 ± 17	32.4± 1.9

[a] Means of duplicate sampling and analysis. [b]All back features are the same. [c] Unpolluted reference point.

Table 3 shows the mean concentration of elements in the two categories of bark samples. The significant difference between the two means of the elements analysed was demonstrated by the student t-test. The value for the student's 't' calculated from these data ($p < 0.05$) showed the difference between samples taken from high pollution automobile parking lots and low-pollution automobile parking lots.

Correlation analysis was carried out to determine the extent of the relationship between the elements investigated (Table 4). The correlation matrix shows that Pb correlates with Ni, Fe and Cu, with r between 0.77 and 0.99. There is also significant correlation ($p < 0.05$) between Ni and Cu with r = 0.89 and between Fe and Ni with r = 0.83 in samples taken from high-automobile density parking lots. There is low correlation ($p < 0.05$) between other metals pair in samples of both high- and low-automobile density parking lots.

Table 3. Statistical assessment of heavy metal contents of bark of Nigerian *Terminalia catapa* from two areas (parking lots) of different automobile density.

Area	Pb	Cu	Zn	Ni	Fe	Mn
High-auto density parking lots (6 samples)						
Means (μg g^{-1})	496	37. 9	49.1	31.4	515	68.6
R.S.D (%)	7. 98	24. 8	13. 4	14. 0	24. 5	17.8
Low-auto density parking lots (4 samples)						
Means (μg g^{-1})	318	17.7	23. 8	15. 6	281	48.0
R.S.D (%)	13. 5	22.1	15. 6	13.1	12.1	15.1
*T – values	6. 01	3. 64	6. 23	6.01	3.24	2.72

*Critical value of 't' for 8 degree of freedom is 2.31 at 95% confidence level. R.S.D. is relative standard deviation.

Table 4. Correlation coefficient between element pairs of high-auto density and low-auto density parking lots.

Coefficient of correlation (r*)		
Elements pairs	High-auto density parking lots	Low-auto density parking lots
Pb-Zn	0.77	-0.80
Pb-Ni	0.99	-0.70
Pb-Cu	0.89	0.21
Zn-Cu	0.68	0.22
Pb-Fe	0.85	-0.16
Zn-Fe	0.69	-0.72
Ni-Mn	0.20	-0.28
Ni-Cu	0.89	-0.12
Fe-Ni	0.83	0.71

*Critical values of 'r' for 4 and 2 degrees of freedom are 0.81 and 0.95, respectively, at 95% confidence level.

In automobile parking lots of similar vehicular density, the heavy metal accumulations on bark and leaf samples were compared (Tables 5 and 6). Lead and zinc were found to accumulate more on tree bark than tree leaves. For example, for *Azadirachta indica* taken at Oragada automobile parking lots, the concentrations of Pb and Zn in tree bark (B_{16}) were 321 μg g^{-1} and 42.5 μg g^{-1}, respectively, and the concentrations of Pb and Zn in tree leaves (L_6) of the the same species were 238 μg g^{-1} and 27.9 μg g^{-1}, respectively. This observation can be related to the nature of the tree bark compared with the smooth surface of the leaves. The high bioaccumulation of Zn in tree bark could also be a result of its high transfer coefficient [5], which is a reflection of its relatively poor sorption in the soil. Lead with a low transfer coefficient, must have been accumulated by the foliar absorption of atmospheric deposits on plant leaves. The bioaccumulation of other metals analyzed varied between the tree bark and leaves. Similarly, the total loads of heavy metals in the tree bark and leaves were compared. The tree leaves accumulated a greater load of heavy metals than the tree bark. For example, for samples taken at Cow-shed (Kaara) automobile parking lots, the total loads of heavy metals in *Cassia siamea Lam.* tree bark (B_{22}) and leaves (L_{16}) were 1.23 g kg^{-1} and 1.26 g kg^{-1}, respectively. The higher total load of heavy metals in tree leaves can be attributed to the greater exposure of the foliage to the environment. This study provides greater awareness to the people of Ogbomoso and its environment about the atmospheric pollution levels in most automobile parking lots.

Table 5. Concentration[a] of heavy metals in tree bark at different city parking lots for other Nigerian tree species.

Concentration, µg g^{-1} samples, dry weight								
Tree species	Bark feature	Tree location	Pb	Cu	Zn	Ni	Fe	Mn
Azadrachia indica	Rough, thick and hard	Sabo Garage	476±25	15.4± 0.9	67.4 ±4.7	29.9±1.8	695± 35	85.7±6.3
Azadirachta inidca	“	Oragada	321±21	10.3±0.7	42.5±2.1	19.9±0.8	500±32	84.5±4.9
Azadirachta inidca	“	Ikoyi Raod	252±15	14.6±1.3	30.4±2.5	24.9±2.0	541±36	62.6±3.5
Mangifera indica L.	“	Ahoyaya	238±12	8.57±0.5	29.4 ±2.5	5.00±0.5	425±28	76.3±4.2
Mangifera indica L.	“	General Hospital	266±16	11.1±0.4	39.5± 3.2	32.3±2.4	496±31	59.1±3.0
Ficus religiosa L.	Fairly smooth, rough and thick	Owode (Agbowo)	318± 17	13.7±0.8	45.8±2.2	10.0±1.0	267±23	95.1±5.3
Ficus religiossa L.	“	Oragada	310±22	11.1±0.6	51.6±3.6	17.4±1.3	493±30	82.3±4.0
Anacardium Occidentale L.	Rough, thick and hard	General Hospital	210±19	12.2±0.5	25.6±2.3	7.50±0.4	466±25	50.6±3.5
Cassia Siamea lam.	“	Cow-shed (Kaara)	400±23	17.4±0.5	56.8±3.8	30.6±2.1	654±37	73.7±3.9
Acasia senegal	“ “	Down General Hospital	25.8±2.9	12.8±0.4	39.5±2.9	22.4±1.4	502±28	66.8±2.7
[b]*Ficus reliogiosa* (*B_8*)		LAUTECH Farm	157±11	5.94 ±0.5	19.8 ±1.8	2.84±0.2	260±15	46.7±2.5
Mean			282±120	12.7±2.6	42.8±13.1	20.0±9.9	504±118	73.7±13.8
Range			257	8.83	41.8	27.3	428	44.5
R.S.D. (%)			26.0	20.7	30.6	49.4	23.4	18.7

[a]Means of duplicate sampling and analysis. [b]Unpolluted reference point.

Table 6. Concentration[a] of heavy metals in tree leaf at different city parking lots for Nigerian tree species.

Concentration , µg g^{-1} samples, dry weight							
Tree species	Tree location	Pb	Cu	Zn	Ni	Fe	Mn
Azadrachia indica	Oragada	238 ± 12	25.7 ± 1.4	27.9 ± 1.6	37.3 ± 1.9	907 ± 46	90.0± 5.2
Anacardium occidentale L.	General Hospital	198 ± 8	24.0 ± 1.7	37.4 ± 2.5	29.9 ± 1.5	1360± 75	137 ± 8
Ficus religiosa L.	Sabo Garage	182 ± 10	25.7 ± 2.1	73.5 ± 3.7	24.9 ± 2.1	1507± 84	123 ± 10
Ficus religiossa L.	Down General Hospital	194 ± 7	13.7 ± 1.6	38.9 ± 1.9	32.3 ± 2.5	509 ± 28	103 ± 7
Ficus religiosa L.	Owode (Agbowo)	309 ± 14	20.6 ± 1.1	35.7 ± 3.2	44.8 ± 3.0	871 ± 37	128 ± 11
Ficus religiossa L.	Ahoyaya	199 ± 10	19.7 ± 2.3	31.3 ± 2.8	39.8 ± 2.8	1018± 94	124 ± 12
Mangifera indica L.	Ahoyaya	119 ± 6	15.4 ± 1.8	50.6 ± 4.1	17.5 ± 1.2	448 ± 32	86.5± 5.2
Mangifera indica L.	General Hospital	105 ± 8	16.3 ± 2.0	44.7 ± 4.0	12.4± 2.0	407 ± 29	84.0± 3.7
Cassia Siamea Lam.	Cow-shed (Kaara)	167 ± 6	18.9 ± 1.2	37.9 ± 3.6	37.3 ± 3.4	907 ± 55	96.8± 5.9
Terminalia catapa	Owode (Agbowo)	336 ± 15	17.4 ± 2.2	55.3 ± 4.2	39.3 ± 3.8	749 ± 47	113 ± 12
Acasia senegal	Oke- Ado Sabo	186 ± 10	17.1 ± 1.9	36.8 ± 3.4	14.9 ± 2.1	878 ± 54	102 ± 9
[b]*Ficus reliogiosa* (*L_8*)	LAUTECH Farm	74.9 ± 3.5	10.7 ± 1.5	22.8 ± 2.1	5.90 ± 0.8	248 ± 15	75.4± 4.8
Mean		203 ± 70	19.5 ± 4.2	42.7±12.9	30.0±11.1	869± 348	108 ± 18
Range		231	12.0	45.6	32.4	1100	53.0
R.S.D (%)		34.5	21.1	30.2	37.0	40.0	16.8

[a] Means of duplicate sampling and analysis. [b] Unpolluted reference point.

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