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Selected Heavy Metals as Indices of Atmospheric Pollution in African Locust Bean (*Parkia biglobosa*) Tree Barks

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Abstract: Metallurgical industries are pollution "hot spots" for emission of dust, particulates of heavy metals and gaseous contaminants at levels that can be injurious to man and environment. The atmospheric levels of selected heavy metals around Ajaokuta Steel Company Nigeria were assessed using barks of *Parkia biglobosa* trees. The tree barks were randomly collected during wet and dry seasons, sorted and digested according to standard methods. Heavy metals were analysed using flame atomic absorption spectrophotometer (Unicam 969, UK). The mean concentrations (mg/kg) of metals in *P. biglobosa* tree barks were 33.23±5.03, 12.98±1.24, 3.65±0.69, 1.65±0.36, 1.20±1.16, 0.55±0.10 and 0.33±0.16 for Zn, Mn, Pb, Cu, Ni, Cr and Cd respectively. The concentration distribution sequence in barks are in the order Zn > Mn > Pb > Cu > Ni > Cr > Cd. Zn with the highest level ranged between 26.39±5.24 and 40.93±4.64 mg kg^{-1} relative to other metals. There was significant difference ($p<0.005$) between metals' concentration in tree barks during the dry and the wet seasons, with Zn and Mn showing about 5-15% variation, while corresponding values for Cd, Cr and Pb were not significantly different.

Keywords: Heavy Metals, Tree Barks, Atmospheric Levels, Pollution, Concentration

Introduction

Airborne heavy metal particulates, constitutes air pollutants that may be deposited directly on aerial part of the plants, soil and water surfaces (Senesi *et al*., 1999). Once in the different biological or environment matrices, these substances are partitioned or redistributed through a complex and inter-related pathways (Ryding, 1994). The non-degradable character of metals results in their persistence, tendency to accumulate in the environment and in tissues of biological species, with attendant consequences and potential toxicities. Vick (1983) and UNEP (2000) reported that, metallurgical emissions can cause severe local environmental damage and as well contribute to more distant or global phenomena such as acid rain and climate change. Vegetation within local community of metallurgical operations can be contaminated by heavy metals. The consumption of such contaminated plants, or its products as food (primary producers) may be major sources of exposure of human and other biotic functions, to heavy metals (EEC, 1980; Goyer, 1993; Abadin *et al*., 1997). Hence the release and recirculation of heavy metals associated with mineral ores, during extraction and other metallurgical operations is undesirable.

Metallurgy industries may be regional pollution "hot spots", for the emission of trace metals, oxides of sulphur, oxides nitrogen and polycyclic aromatic hydrocarbons. This is because industrial operations involving the separation of metals from gangues such as iron from iron ore, through heating and smelting produces very large amount of particulate metals and other air pollutants (OECD, 1990). Ferrous and non-ferrous smelters for instance, emit large quantity of arsenic, lead, cadmium and other heavy metals into the environment, except where highly efficient pollution control equipment are used (Borrego, 1998; Pacyna and Pacyna, 2001; Vaisman and Lacerda, 2003). Nriagu (1989) reported that, the smelting of copper and other non-ferrous metals, release an estimated six million tons of

sulphur dioxide (SO_2) into the atmosphere each year, which sums up to about 8% of total worldwide emissions.

The baseline assessment and characterization of air quality within and around metallurgical industries, as well as other hotspots and sources is an imperative. This is in order to provide a benchmark for periodic time bound air quality monitoring and metallurgical environment Air Quality Inventory (AQI). Air quality assessment has been largely restricted to passive measurements and evaluations, including particulate monitoring ($PM_{1.0}$, $PM_{2.5}$, PM_5 and PM_{10}), with less attention on levels of air borne contaminants reaching both biotic and abiotic components within near and farther environments from source points. Unlike active samplers which provides information about time-trend air quality over a period, passive air sampling (chemical sensing) approach does not account for the dynamics of air quality changes, since it is only able to produce instantaneous information about air quality. Active sampling on the other hand, has the advantage of real time measurement of air quality parameters, particulate metals and dust fluxes; and particulate metals/dust deposition and soiling.

The ability of plants to attenuate and hold contaminants from air have been exploited for use as air purifiers (www.trueactivist.com). Since they are exposed to direct deposition of airborne metals and other pollutants, they can be used active samplers and atmospheric pollution biomarkers. The use of vegetation as active sampler in bio-monitoring of heavy metals, has the advantage of high temporal and spa tial resolution due to the availability of plants, especially deciduous plants which are long living and can facilitate repetition over time, as well as its low sampling cost (Ballach and Wittig, 2001; Breuste and Qureshi, 2011). Markert (1995; Aksoy *et al*., 2000) concluded that plants can be effectively used as bio-monitors of environmental pollution especially in urban areas.

In this study, the levels of Cadmium (Cd), Manganese (Mn), Chromium (Cr), Nickel (Ni), Copper (Cu), Zinc (Zn) and Lead (Pb) were investigated in barks of *Parkia biglobosa* (African Locust bean) trees used as indicator of the air quality status around a non-functional metallurgical industry in North Central Nigeria. Information concerning the atmospheric levels of heavy metals and particulate flux deposition around the Steel Plant is scarce and scanty. Results from this study may serve as part of preliminary bio-assessment of atmospheric baseline for future air quality and metal-flux bio-deposition monitoring survey and air quality inventory collation.

Materials and Methods

Study Area

The study area covers vicinities of Ajaokuta Steel Company up to the banks of River Niger. Ajaokuta is located along the bank of River Niger within the Lokoja-Okene Area delimited by latitudes 7° and 8° N and longitudes 6° and 7° E (Fig. 1) which covers Kogi and part of Edo States. Sampling was centred around the Ajaokuta Steel Company Complex located on N 7° 30,669", E 6° 41,550" and altitude range 74-187 m of the River Niger alluvium at Ajaokuta, North Central Nigeria (Fig. 1).

Vegetation

Vegetation around Ajaokuta Steel Company is essentially of the Guinea Savannah type, although denser forest fringes some of the rivers and the steeper slopes formed by outcrops of cretaceous rocks where they immediately overlie the basement. Patches of high forest also occur on the sediments in the south of the area particularly in the valleys and on the steeper slopes, but these are not extensive except in the forest reserve in the southeast (Hockey *et al*., 1986). However, vegetation within the immediate environment of Ajaokuta Steel Company is of the secondary re-growth type. There are scattered shrubs and deciduous trees within the region.

Samples Collection

The use of *P. biglobosa* as active sampler is strategic due to their nutritional importance (food) and medicinal uses. It was not possible to carry out systematic sampling due to the irregular distribution pattern of *P. biglobosa* and the fairly thick vegetation of the study area. Thus random sampling was adopted within 2.5×2.5 km grids, set up along each of the cardinal direction (northward, eastward, westward and southward).

Barks were scale off the stems of *P. biglobosa* trees into aluminium foil sheets using a stainless steel knife, wrapped properly and transferred into well labelled paper bags. These were kept in dry coolers containing ice parks for onward transmission to the laboratory. Each of the *P. biglobosa* tree sampled was tagged with labels for proper identification.

A total of 384 tree barks samples were collected between December 2003 and November 2005 covering the dry and wet seasons each year. This consists of a total of 384 tree barks from 6 sampling stations within each of the 4 grids along the geographical cardinals, at a sampling frequency of 4 expeditions per season, spanning two climatic season each year, for a period of 2 years. A total of 64 control samples were also collected at a serene locations; northward, eastward, westward and southward directions, during the sampling campaigns.

Analysis

The tree bark samples of *P. biglobosa* were air-dried under ambient laboratory conditions for seventy two to ninety six hours as described by Wang *et al*. (1997) and crushed to fine particle sizes using porcelain mortar and

blended with stainless steel cutters (National blender MX-491 N model). About 2 g each of the fine tree barks were weighed (Sauter Re: 1614 digital balance) into 100 cm^3 kjeldahl flasks. 5 cm^3 Analar grade concentrated nitric acid (British Drug House: BDH) was added to each beaker and heated at 80°C (Wang *et al*., 1997). The digested solutions were filtered and made up to 100 cm^3 mark. Procedural blank was aspirated along with the analytical samples for background correction. The digested sample solutions were quantified for Cd, Cr, Mn, Ni, Cu, Zn and Pb, using Flame Atomic Absorption Spectrometer (FAAS) (Unicam 969, UK) over a 2 mm burner.

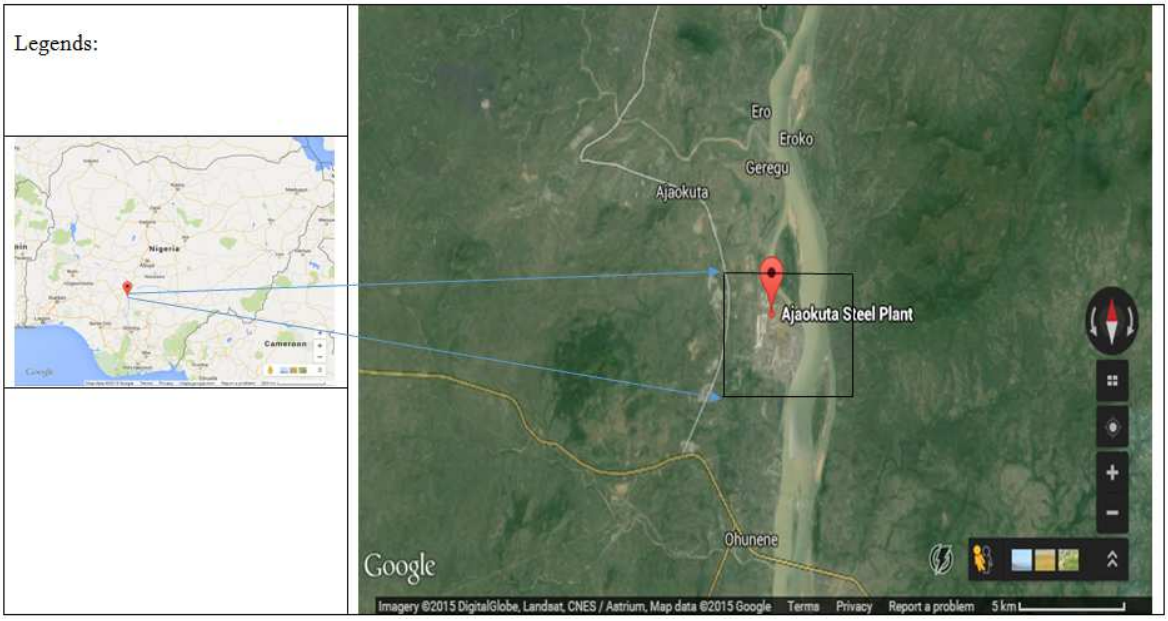

Fig. 1. Location map of the sampling area at Ajaokuta in Kogi State, North Central Nigeria

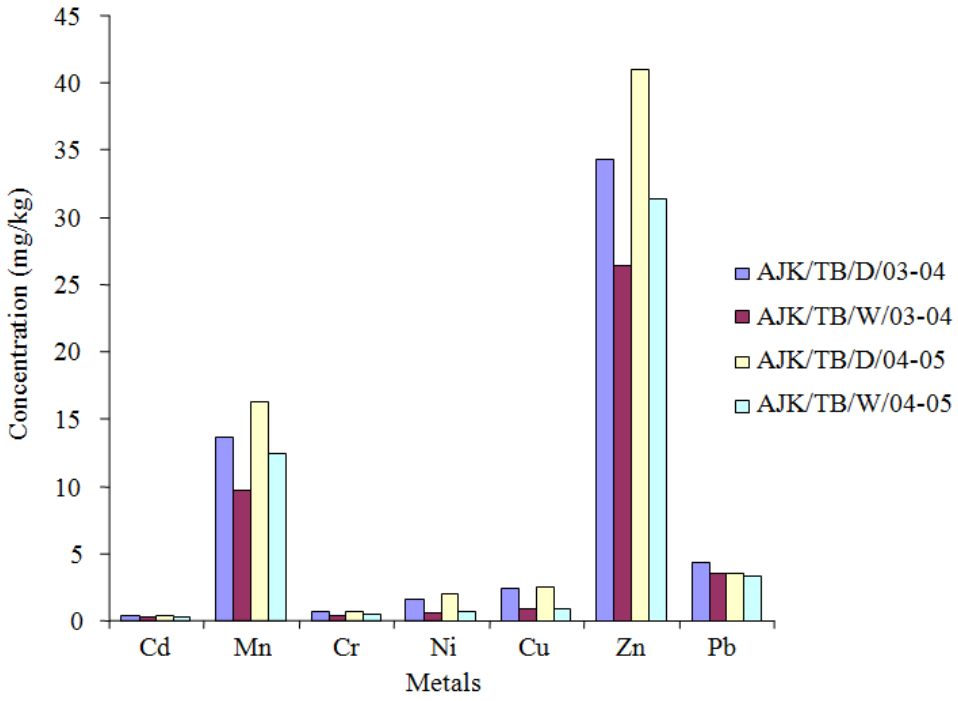

Fig. 2. Seasonal variations in levels (mg/kg) of heavy metals in tree bark of parkia biglobosa around Ajaokuta Steel Company at Ajaokuta during 2003-2005

Recovery Studies

Ten tree bark samples were randomly selected, subjected to recovery studies. The selected samples were spiked with standard solution of Cd, Cr, Mn, Ni, Cu, Zn and Pb in triplicates, at low, medium and high spike concentrations in order to verify the efficiency of digestion procedure. The analytes were then recovered from the spiked samples using the same extraction procedure applied on the un-spiked samples and analyzed. The percentage increase in analyte concentration i.e. percentage amount of standard analyte that were recovered was then determined.

Data Analysis

The raw data were subjected to descriptive statistics and the study results presented as Mean and standard deviation (Mean ± SD) of triplicate subsamples for each tree bark samples within each sampling station grid. Content relationship between individual metals in the bark samples were compared using Pearson Correlation Coefficient. Multi Analysis of Variance (ANOVA) was used to evaluate the differences between the concentrations of the heavy metals detected in tree barks of *P. biglobosa* plants within the sampling station grids Northwards, Eastwards, Southwards and Westwards ($p \leq 0.05$, $p \geq 0.05$).

Results and Discussion

Recovery Studies

The result of recovery studies showed that the coefficient of variation of the replicate analysis on spiked the tree bark samples lies between 5.79 and 18.60%, with recoveries of 88.95-104.72%. The recoveries of each of the metals tested were within the acceptable recovery limits of 100±20% (Table 1).

Concentrations of Heavy Metals in Tree Bark of Parkia biglobosa

The concentration levels of the heavy metals (mg/kg) in the analyzed tree barks of *P. biglobosa* are presented in Table 2.

Table 1. Results of recovery studies of pulverized tree barks for validation of digestion procedure

	Cd mg/kg	Mn mg/kg	Cr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Pb mg/kg
Number of replicates	3	3	3	3	3	3	3
Concentration of analyte in unspiked sample (U)	0.03-0.47	8.72-19.45	0.24-0.96	0.36-3.84	0.59 -3.65	18.79-50.07	1.65-5.74
Mean concentration (N = 10)	0.32	12.98	0.55	1.20	1.65	33.23	3.65
Standard Deviation	0.05	1.24	0.10	0.29	0.36	5.03	0.69
Coefficient of Variation %	15.63	9.55	18.18	24.17	21.82	15.14	18.90
Concentration of analyte in spiked sample (S)	0.67-1.72	16.91-57.35	1.18-2.26	2.74-9.08	1.52-9.23	35.09-78.69	4.60-20.47
Mean concentration (N = 10)	0.69	38.11	1.46	4.57	6.25	54.93	14.08
Standard Deviation	0.04	7.28	0.09	0.85	1.05	7.46	1.69
Coefficient of Variation	5.79	19.63	6.16	18.60	16.80	13.58	12.00
% Recovery	92.00	94.13	98.25	96.80	89.25	104.72	88.95

Table 2. Ranges and mean concentrations (mg/kg) of heavy metals in barks of *Parkia biglobosa* (locust bean) tree around Ajaokuta Steel Company at Ajaokuta during 2003-2005

Sample identity	Cd mg/kg	Mn mg/kg	Cr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Pb mg/kg
AJK/TB/D/03-04							
Concentration range	0.03-0.45	12.63-15.03	0.49-0.73	1.16-2.05	1.67-3.35	27.92-43.07	3.40-5.21
Mean ± Standard Deviation (N = 96)	0.35±0.05	13.63±0.68	0.64±0.07	1.61±0.27	2.37±0.54	34.25±3.94	4.31±0.56
AJK/TB/D/04-05							
Concentration range	0.32-0.47	13.62-19.45	0.54-0.87	0.86-3.84	1.59-3.68	33.54-49.49	2.03-4.96
Mean ± Standard Deviation (N = 96)	0.39±0.04	16.23±1.37	0.69±0.09	2.01±0.67	2.56±0.64	40.93±4.64	3.46±0.79
AJK/TB/W/03-04							
Concentration range	0.16-0.33	8.72-11.05	0.27-0.51	0.36-0.66	0.65-0.95	18.79-41.73	2.85-4.23
Mean ± Standard Deviation (N = 96)	0.26±0.05	9.66±0.81	0.39±0.06	0.54±0.08	0.80±0.09	26.39±5.24	3.52±0.47
AJK/TB/W/04-05							
Concentration range	0.21-0.39	9.24-16.43	0.24-0.96	0.38-0.81	0.59-1.12	22.50-50.07	1.65-5.74
Mean ± Standard Deviation (N = 96)	0.31±0.04	12.39±2.09	0.48±0.17	0.62±0.14	0.88±0.16	31.37±6.28	3.29±0.95

Codes: AJK = Ajaokuta; TB = tree bark of *Parkia biglobosa* (locust bean); D = dry season; W = wet season; 03-04 = study year 2003-2004; 04-05 = study year 2004-2005

The mean heavy metal concentrations (mg/kg) in the tree barks of *P. biglobosa* collected from the different sampling stations were variable. The biannual mean concentrations (mg/kg) of heavy metals detected in tree barks of *P. biglobosa* during the study period 2003-2005 were Zn, 33.23±5.03, Mn, 12.98±1.24, Pb, 3.65±0.69, Cu, 1.65±0.36, Ni, 1.20±1.16, Cr, 0.55±0.10 and Cd, 0.33±0.16. The concentration distribution sequence in barks are in the order Zn > Mn > Pb > Cu > Ni > Cr > Cd. The concentration of zinc was moderate, although the highest in respect of the metals determined, ranging between 26.39±5.24-40.93±4.64 mg kg^{-1}, (compared with FAO/WHO: Zn; 10-150 mg kg^{-1}), followed by manganese 9.67±0.81-16.23±1.38 mg kg^{-1}. Zinc and Manganese showed about 5-15% variation in concentrations during dry and wet seasons, while the other heavy metals determined did not show any seasonal variation i.e., their concentrations were fairly consistent. Thus, significant difference ($p<0.05$) exist between metal concentration levels detected during the dry and the wet seasons, with higher tree barks metal levels in dry season than in wet season, except for Cd, Cr and Pb (Fig. 2).

According Berlizov *et al*. (2007) "the efficient accumulation and retention of heavy metals in tree barks is a function of its structural and morphological porosity". Analysis of Variance (ANOVA) showed that there were significant differences ($p<0.05$) between the mean concentrations of the content of the metals Zn, Mn and Pb in the tree barks at the different locations, while location variability were not significant ($p>0.05$) for the other metals, Cd, Ni, Cu and Cr. Cluster analysis showed that there were similarities between the levels of investigated heavy metals detected in *P. biglobosa* tree barks in the all the sampling station grids, Northward, Eastward, Southward and Westward. However, the levels observed in in barks of *P. biglobosa* in the Southward grid were slightly higher. The reason for the slight differences is not very clear, however the levels observed in the Southward wind may not be unconnected to the prevailing wind direction. A recent study reported by Petrova *et al*. (2014) suggests that elemental concentration in plants may be sampling site dependent; hence the extent of pollution may show location variability.

The detected heavy metal concentrations in tree barks of *P. biglobosa* around Ajaokuta Steel Company falls within the guidelines for normal concentration of heavy metals in plants with Cd, 0.05-2.0 mg kg^{-1}, Cr, 0.1-0.5 mg kg^{-1}, Ni, 0.1-5.0 mg kg^{-1}, Zn, 10-150 mg kg^{-1} and Pb, 0.5-10 mg kg^{-1} as reported by Tiejan (1975); Kabata-Pendias and Pendias (2000) and Boularbah *et al*. (2006) and are therefore not considered toxic. The values detected may be a function of individual plant responses and exposure time. Though the health of trees are best considered in the pathological sense (Innes, 1993), it is apparent that they do not appear to be at levels harmful to both plants and humans. However phyto-toxicity levels of heavy metals may determine thresholds for toxicity guidelines, expressed as Toxicity Equivalent Factor (TEF) and benchmark concentrations of heavy metals in plants. Toxicity guidelines depend on the form in which metals are present, i.e., either in bounded or bioavailable form (Ravi *et al*., 2003).

Surface wetting of aerial parts of plants (leaves and barks) may result in washing off of particulate metals (Boularbah *et al*., 2006). The washing off of contaminants from surfaces of plants, e.g., leaves and tree barks as result of thunder storms, may lower metal concentrations (Bingol *et al*., 2008). Weather condition (climate effect) such as this could also provide impetus for leaching or drainage of metals on one hand, while the detected metal levels may perhaps be characteristic of *P. biglobosa* or an adaptive trend levels within the ecological locality and geographical location. Sawidis *et al*. (2011) reported that pollutants deposited on leaves, especially on the adaxial surface can be washed away by rain water or can be dispersed by wind.

Cells in many plant barks are dehydrated and may be disconnected from plant osmo-diffusivity mass movement and fluid flow of the cortical region, leading to cell flaccidity during the dry season. This result in the concentration of heavy metals entrapped within the cell units of the barks of tree trunks. The protoplasmic fluids therefore sequester heavy metals and other mineral substances, resulting in cell localization of minerals and metals. This probably explains the high residual concentrations of heavy metals in the barks of *P. biglobosa* during dry seasons of study. However, aerial absorption of water by flaccid tree bark cells and leaves, as well as root uptake of water during wet season, result into cell dissolution of heavy metals and other minerals in protoplasmic fluid. In such cells, increase in water volume may exert pressure on cell membrane, facilitating inter-cellular material transfer which leads to remobilization of minerals. Material transfer processes through cell wall, will result in depletion of concentration levels of heavy metals, consequently low bark concentration during wet seasons. This probably forms the basis for the depuration and elimination of toxic substances in plants metabolic processes.

The concentrations of metals detected in tree barks of *P. biglobosa* were moderate and below phytotoxic levels (Kabata-Pendias and Pendias, 2000; Boularbah *et al*., 2006) and the Food and Agriculture Organization Joint Expert Committee on Food Additives (JCFA) recommended concentration levels for heavy and trace metals in food substances (FAO/WHO, 1999).

Environmental Air Quality Inventory (AQI)

The availability or development of a complete emission and air quality inventory is an important step

in an air quality management process (US EPA, 1998). This is because, aside from the natural emission sources of release of heavy metals and other air contaminants into the atmosphere, the extraneous levels of these substances may arise from combustion processes (Filby and Shah, 1975; MES, 2001). Currently, comprehensive Air Quality Inventory (AQI) for Ajaokuta Steel Company and its catchment areas is not available. According to US EPA (1998) the availability of air quality and emission inventory may provide basis for the determination of significant air pollutants; establishing their emission and atmospheric concentration trends over time; targeting regulatory actions and estimate air quality status. Few scattered data may however exist from some independence investigation, although the acquisition may not be systematic, holistic and comprehensive. Such data may further be limited by the dynamics of weather conditions and the inability to identify and characterize emission sources, as well as predict emission quality and rate, especially where hand held equipment which only gives instant picture of air quality are used.

The estimation of the levels of various regulated pollutants and the short and long term air contaminant flux settling rate on bio-receptors and time bound changes, can better be evaluated using deciduous plants. This is because the acquisition of Air Quality Inventory (AQI), requires continuous monitoring in order to measure actual atmospheric pollutants flux concentrations and content; and extrapolating the results from the short to long term pollutants levels in deciduous plants bio-receptors, by averaging over a given time span. US EPA (1998) noted that "whenever possible, the development of local emission factors is highly desirable".

Conclusion and Recommendation

The use of deciduous tree *P. biglobosa* as bio-indicator for the assessment of atmospheric pollution provided the opportunity to assess time bound variations in heavy metal levels using the tree barks collected from same plants. Result from the sampling expedition revealed variability in air particulate metals fluxes bio-deposited and settled on the rough bark of the trees. The concentrations of metals detected in tree barks of *P. biglobosa* were however below phytotoxic levels. This implies that particulate metals in air around Ajaokuta Steel Company are low, signifying low metals atmospheric content (a nearly pristine atmosphere). The data obtained in this study could serve as baseline levels for particulate metals in air that reaches plants, because air quality assessment was not conducted before sitting and construction of the Steel Company at Ajaokuta.

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Author's Contributions

All the authors made valuable contributions; in the facilitation of the development of analytical method, sampling, analysis and in scripting and editing of the study report.

Ethics

The author's wishes to declare that the data reported here in this study, is a part result of a section of a holistic study on the environmental status of a metallurgical industry within the North Central region of Nigeria and has not been reported previously in any other scientific journal.

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