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Assessment of Atmospheric Profile of Some Heavy Metals in Barks of *Parkia biglobosa* (African locust bean) Trees

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Natural resource exploitation involving the mining of iron-ore from earth's deposits result in the release of aerodynamic size particulate metals, dusts and other atmospheric pollutants. The atmospherics baseline levels some iron-ore associated heavy metals were assessed around Itakpe iron-ore deposit, North Central Nigeria, using tree barks of African locust bean (Parkiabiglobosa) as indicator. Tree barks of *P. biglobosa* were randomly scaled off dried and digested using standard procedures. The digests were quantified for Cd, Mn, Cr, Ni, Cu, Zn and Pb in flame of Unicam 969 atomic absorption spectrophotomer. The concentration of Zn, 20.387-52.07 mg/kg was the highest in respect of other metals determined, followed by Mn, 8.74-24.18 mg/kg and then Pb, 2.95-8.66 mg/kg. Cu levels ranged 0.68-3.14 mg/kg, Ni, 0.34-3.12 mg/kg and Cr, 0.34-0.91 mg/kg. Cd concentration was the least; 0.16-0.48 mg/kg in barks of *P. biglobosa* trees. The overall mean concentrations (mg/kg) were: Zn, 34.21 ± 4.09; Mn, 13.59 ± 2.04; Pb, 25 ± 0.75; Cu, 1.34 ± 0.34; Ni, 1.18 ± 1.05; Cr, 0.55 ± 0.09; and Cd, 0.33 ± 0.06, with availability sequence is in the order Zn > Mn > Pb > Cu > Ni > Cr > Cd. The detected heavy metals levels in the barks of *P. biglobosa* trees were variable, and may be a function of vegetation proximity/orientation to source points, plant distribution/population density, level of exposure and atmospheric stability, which is dependent on prevailing climatic factors. The evaluated *P. biglobosa* barks did not contain the heavy metals at concentrations capable of impacting negatively on the plant. Thus, the tree barks concentration of the evaluated metals were within natural concentration levels, and are therefore regarded as not polluted. This implies that atmospheric levels of the aerodynamic particulates heavy metals were low and not hazardous. The detected levels could serve as baseline concentration for monitoring against potential atmospheric deposit build up of heavy metals when mining becomes fully operational.

Key Words: Atmospheric, Aerodynamic size, Particulate, Heavy metals, Tree barks, Baseline levels.

INTRODUCTION

Activities arising from human exploitation of natural resources have greatly impacted on the environment. At the root of the impacts were the growing changes in technological knowledge and applications which end up with stress of contaminants on the environment. Environmental problems such as pollution of air[1,2], water and soil have become important[3,4] as a result of their harmful health effects. Forest and wildlife populations are confronted with a bewildering array of pollutants that are released into the environment[5]. Although air burden of contaminants may be eased within immediate environment, long range trans-boundary transport of contaminant can constitute problems; hence air burden of both short and long-range contaminants should be kept as low as possible.

The main air quality issue in mining industry is from the working of open pits, crushing and grinding operations which lead to the generation of dust and particulates[6]. Dusts and particulates emissions consisting of heavy metals, fugitive emissions, asbestos, cyanide and other air borne chemicals/toxic materials from mining, ore beneficiation processes and tailing dams can be significant and especially more intense within confined spaces and living areas close to mine sites/beneficiation plants[6,7]. Particle fall-out (mine dust) around mine sites can contaminate soils and water and damage vegetation[6,8]. Consequently, both terrestrial and aquatic environments receive atmospheric deposition of air borne metal pollutants from mining industries. Preliminary data of some industrial discharges showed elevated concentrations of heavy elements 5-20 times background levels and strong evidence for post depositional diffusion/mobility[9-11].

Plants are important member of terrestrial ecosystem representing a major pathway for material biogeochemical cycle. It occupies strategic position in ecosystem's energy distribution structure being primary producers and could be a major source of exposure to different heterotrophs since food intake is one major route of exposure of higher heterotrophs and humans to most chemical substances[12,13]. Contamination resulting from heavy metals can lead to poor plant growth, as a result of their cytotoxic effects. Gene mutations may also be induced in plant protoplasm by chemical mutagenesis, and this can be permanent, thereby constituting a threat to food security and/or subsequent loss of habitat. Thus, residue of bioactive substances and their metabolites transported in air must be monitored because when bioactive metal contaminants present in plants are ingested by a component in the ecosystem, there is every likely hood of spread up the heterotrophic levels[13,14].

The use of plants as environmental bio-indicators in ecological studies is scientifically accepted[15-17]. Lower plants such as mosses and lichens have been used as bio-indicators of heavy metals in soil environment because of their high capacity for accumulation[18,19]. The past few decades saw the use of higher plants as bio-indicators for atmospheric monitoring of heavy metals[15,16,20], which *hitherto* are largely monitored by passive sampling. The evaluation of atmospheric levels of heavy metals in the environment using barks of trees as indicator provides active information on exposure and the probable amount trapped by plants *via* aerial deposition and adsorption on plant surfaces. Sawidis *et al.*[17] highlighted on various evergreen trees used as bio-monitors for air and soil pollution in urban environments and noted that plants bears the advantage of high spatial and temporal resolution due to availability and low sampling cost, coupled with wide distribution[21] and long live which can facilitate repetition of investigation and monitoring time trend distribution of particulates heavy metals.

In this study, an extensive baseline concentration assessment of some selected heavy metals in barks of *Parkia biglobosa* (locust bean) tree was carried out around Itakpe iron ore deposit in North Central Nigeria. The result obtained may be used to define the baseline levels of the metals in plants because of their likely phytotoxicity, potential health risk associated with inhalation in air and injestion through local use of *P. biglobosa* barks in herbal therapy.

EXPERIMENTAL

Study area: Itakpe is located off the Lokoja-Okene transit route near Osara in North Central Nigeria. The study perimeter covers vegetation around footages areas of Itakpe iron ore deposit and the industrial area *i.e.* iron ores beneficiation plant embedded within Lokoja-Okene area, delimited by latitudes 7º and 8º N and longitudes 6º and 7º E. Plant distribution assessment showed dominance of shrubs along with scattered deciduous trees around the Itakpe hill ranges. Soil cover structure is moderate as grasses are mostly restricted to the low type over the inter-twinned basement and sedimentary formation rocks. Hockey *et al.*[22] reported that fringes along rivers and in steep slopes of cretaceous rocks outcrops overlying the basement consist of dense forest, especially in the southern valleys made up of patches of high forest on sediments terrain, although this is not extensive except around the southeast forest reserve.

Samples collection: Sampling was centred around the industrial area of the Nigerian Iron Ore Mining Project located on N 07º 37, 420", E 006º 18, 284" and altitude ranging from 241-325 metres of Itakpe iron ore mining field, North Central Nigeria, as shown in Fig. 1. The topographic inequalities of the land form and irregular vegetation distribution structure constrained systematic sampling, thus random sampling was adopted. The collection of samples spanned 24 months between 2003-2005 (dry and wet seasons), during which a total of 160 samples of tree bark of *P. biglobosa* (locust bean tree) were collected and processed.

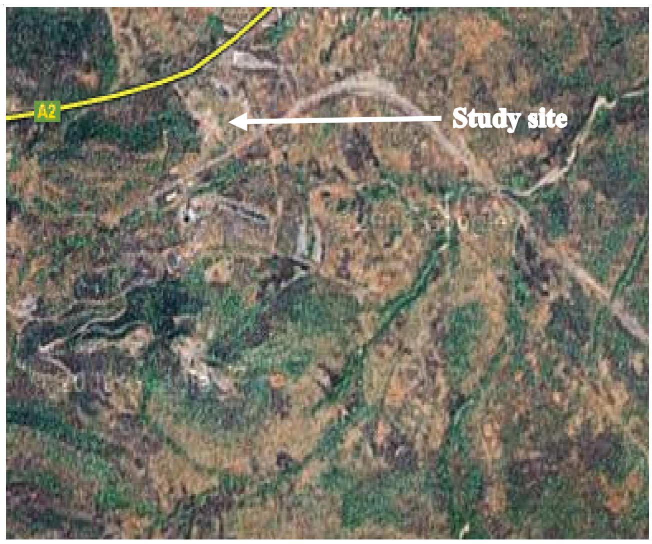

Fig. 1. Location map of the sampling area at Itakpe in Kogi State, North Central Nigeria

Sample digestion and analysis: The collected tree bark samples of *P. biglobosa* were air-dried in laboratory, crushed and blended to fine sizes using porcelain mortar[23] and blender (National MX-491 N model) with stainless steel cutters. 1 g each of tree barks samples was weighed (Sauter Re: 1614 digital balance) into 100 cm^3 kjeldahl flasks. 5 mL concentrated Analar grade nitric acid (British Drug House: BDH) was added to each and heated at 80 ºC for 3 h[23]. The resulting digest solutions were filtered into 100 mL volumetric flask (Technico BS 1792 B in 20 ºC) and made up to mark with distilled water. Procedural blank was prepared and aspirated in order to correct for background absorption. The digested sample solutions were quantified for Cd, Cr, Mn, Ni, Cu, Zn and Pb in flame atomic absorption spectrometer (FAAS) (Unicam 969).

RESULTS AND DISCUSSION

Replicate analysis conducted on spiked tree bark samples showed good recoveries. The coefficient of variation of the spiked replicates lies between 1.40 % and 18.25 %, with recoveries of 88.95-104.72 %. The recoveries of each of the metals tested were within the acceptable recovery limits of 100 ± 20 %. The result of the determination of heavy metals concentrations in barks of *P. biglobosa* (locust bean) trees during dry seasons 2003/2004 and 2004/2005 and wet seasons during 2003/2004 and 2004/2005 are presented in Table- 1.

The mean concentrations (mg/kg) of heavy metals (with range in parenthesis), in the barks of *P. biglobosa* tree during

TABLE-1
RANGES AND MEAN CONCENTRATIONS (mg/kg) OF HEAVY METALS IN BARKS OF *P. biglobosa* TREES AROUND THE IRON ORE DEPOSIT

Sample identity	Cd (mg/kg)	Mn (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
ITK/TB/D/03-04							
Concentration range	0.27-0.45	8.74-10.40	0.35- 0.54	0.68-1.34	0.78-2.14	24.88-35.06	3.69-5.34
Mean (SD)	0.37(0.06)	9.50 (0.56)	0.43 (0.06)	1.08 (0.23)	1.38 (0.47)	30.96 (2.75)	4.49 (0.54)
ITK/TB/D/04-05							
Concentration range	0.31-0.48	10.28-24.18	0.59-0.85	1.60-3.12	0.95-3.14	39.64-52.07	3.55-6.25
Mean (SD)	0.39 (0.05)	17.97 (4.03)	0.75 (0.07)	2.30 (0.49)	2.05 (0.56)	45.89 (4.19)	22 (0.78)
ITK/TB/W/03-04							
Concentration range	0.16-0.40	8.97-12.21	0.35-0.54	0.34-1.05	0.68-1.15	20.87-31.24	2.95-4.45
Mean (SD)	0.27 (0.07)	10.92 (1.03)	0.45 (0.06)	0.58 (0.16)	0.92 (0.15)	26.00 (3.42)	3.95 (0.37)
ITK/TB/W/04-05							
Concentration range	0.22- 0.42	11.43-19.48	0.34- 0.91	0.48-1.21	0.74-1.27	25.14-45.95	3.08-8.66
Mean (SD)	0.31 (0.06)	15.98 (2.55)	0.58 (0.17)	0.75 (0.17)	1.01 (0.16)	33.99 (5.99)	5.54 (1.32)

Codes: ITK = Itakpe; TB = tree bark of *P. biglobosa* (locust bean); D = dry season; W = wet season; 03-04 = study year 2003–2004; 04-05 = study year 2004-2005

dry season 2003/2004 were as follows: Pb, 4.49 ± 0.54 (3.69-5.34); Cu, 1.38 ± 0.47 (0.78-2.14); Ni, 1.08 ± 0.23 (0.68-1.34); Zn, 30.96 ± 2.75 (24.88-35.06); Cr, 0.43 ± 0.06 (0.35-0.54); Mn, 9.50 ± 0.56 (8.74-10.40); and Cd, 0.37 ± 0.06 (0.27-0.45) and during dry season 2004/2005: Pb, 22 ± 0.78 (3.55-6.25); Cu, 2.05 ± 0.56 (0.95-3.14); Ni, 2.30 ± 0.49 (1.60-3.12); Zn, 45.89 ± 4.19 (39.64-52.07); Cr, 0.75 ± 0.07 (0.59-0.85); Mn, 17.97 ± 4.03 (10.28-24.18); and Cd, 0.39 ± 0.05 (0.31-0.48).

Also, the mean concentration levels (mg/kg) of heavy metals in barks samples during wet season 2003/2004 were: Pb, 3.95 ± 0.37 (2.95-4.45); Cu, 0.92 ± 0.15 (0.68-1.15); Ni, 0.58 ± 0.16 (0.34-1.05); Zn, 26.00 ± 3.42 (20.87-31.24); Cr, 0.45 ± 0.06 (0.35-0.54); Mn, 10.92 ± 1.03 (8.97-12.21); and Cd, 0.27 ± 0.07 (0.16-0.40), while result for wet season 2004/2005 were: Pb, 5.54 ± 1.32 (3.08-8.66); Cu, 1.01 ± 0.16 (0.74-1.27); Ni, 0.75 ± 0.17 (0.48-1.21); Zn, 33.99 ± 5.99 (25.14-45.95); Cr, 0000.58 ± 0.17 (0.34-0.91); Mn, 15.98 ± 2.55 (11.43-19.48); and Cd, 0.31 ± 0.06 (0.22-0.42). Bark concentrations of Zn and Mn generally showed the highest concentration variability.

The concentration of Zn (20.387-52.07 mg/kg) was the highest in respect of other metals determined, followed by Mn, 8.74-24.18 mg/kg and then Pb, 2.95-8.66 mg/kg. Copper levels ranged 0.68-3.14 mg/kg, Ni, 0.34-3.12 mg/kg and Cr, 0.34-0.91 mg/kg. Cd concentration was the least; 0.16-0.48 mg/kg in barks of *P. biglobosa* trees (Table-1). The overall mean concentrations (mg/kg) were: Zn, 34.21 ± 4.09; Mn, 13.59 ± 2.04; Pb, 25 ± 0.75; Cu, 1.34 ± 0.34; Ni, 1.18 ± 1.05; Cr, 0.55 ± 0.09; and Cd, 0.33 ± 0.06, with availability sequence in the order Zn > Mn > Pb > Cu > Ni > Cr > Cd. The detected heavy metals levels in barks of *P. biglobosa* trees were variable and probably a function of the following factors: atmospheric stability which relies on prevailing climatic factors, plant distribution and population density within an habitat, proximity, orientation/exposure to anthropogenic source points, plant ages and response.

The observed result in this study is consistent with findings of Aksoy *et al.*[16] who reported Cd, 0.61 ± 0.08 mg/kg; Zn, 36.00 ± 2.75 mg/kg; with higher concentration for Pb, 27.04 ± 3.01 mg/kg and Cu, 10.48 ± 1.14 mg/kg in barks of Robinia pseudo-acacia trees collected in a suburban environment in Turkey. Bark tissues of street tree Sophora japonica was reported to accumulate Pb, 11.0-199.0 mg/kg and Ni, 15.0-169 mg/kg[20], which are several folds higher than found in this study. Sardans and Penuelas[24] also reported low levels for Mn, 0.016 - 0.07 mg/kg in plant samples collected from different areas in Spain than observed in this study. Kakulu[8] reported high concentration levels of Cu, 12.0 ± 4.0 µg/g; Pb, 133.0 ± 32.0 µg/g; Zn, 61.0 ± 10.0 µg/g; and Ni, 13.0 ± 3.0 µg/g above natural concentrations in tree bark samples from commercial high traffic areas in different districts of Abuja, Nigeria than levels found in this study, for which automobile emissions was indicted and with low levels Cd, 0.3 ± 0.2 µg/g comparable with study report.

However, the detected levels of heavy metals in barks of *P. biglobosa* trees were below the probable plants phytotoxic concentrations, Cd, 5-700 mg/kg; Cr, 1-10 mg/kg; Ni, 10-100 mg/kg; Zn, >100 mg/kg; Cu, 20-100 mg/kg and Pb, 30-300 mg/kg reported by Kabata-Pendias and Pendias[18] and Boularbah *et al.*[25]. Therefore, the levels of heavy metals observed in barks of *P. biglobosa* trees around the iron ore deposit do not occur at concentrations injurious to both plants and consequently humans. This suggests that the levels of metals were within normal concentrations range for healthy plant growth.

The levels of heavy metals in barks and other plant surfaces are exacerbated by aerodynamic deposition. Some metals such as primary, secondary and essential micro/macro-nutrients are important to health and proper metabolism in living organisms such as in plants and animals, while some others are clearly toxic. Heavy metals present in trans-located alongside mineral nutrients may be accounted for by the relative amount found resident within different plant organs depending on their ecophysiological peculiarity and metabolic activities[26,27]. For metals such as Pb, Cr, Cu and Fe, bark concentrations may be predictive of atmospheric deposition, because these metals tend to accumulate in the root and are scarcely trans-located into above ground organs[18,27]. Thus the amount of bio-available heavy metals trans-located to above ground plant organs is determined their concentration in the rooting zone[28-30] and plant selective preference for heavy metals. Lindberg[1] and Nriagu[31] reported that residual quantities of heavy metals in the barks of deciduous trees are largely a function of contamination from atmospheric sources. Linberg[1] also noted that surface absorption by leaves and barks contributes to the total metal loads in plants. Apparently the detected heavy metal levels were not totally from aerial deposit, but additive with contribution from immobilized natural concentrations and from normal plant uptake.

Aerial adsorption of particulate metals by tree barks accounts for their aerodynamic depositional levels which in turns measures atmospheric quality for particulates metals. It was observed that bark levels of metals vary with season in that surface wetting result in the washing off of particulate metals loosely adhered to plant surfaces leading to concentration reduction. This probably accounts for the slightly higher concentration levels of heavy metals observed in barks of *P. biglobosa* tree during dry season except for Pb, Cr and Mn, while Cd levels was only slightly affected by changes in seasonal climate (Fig. 2). This observation is consistent with the findings of Boularbah *et al.*[25].

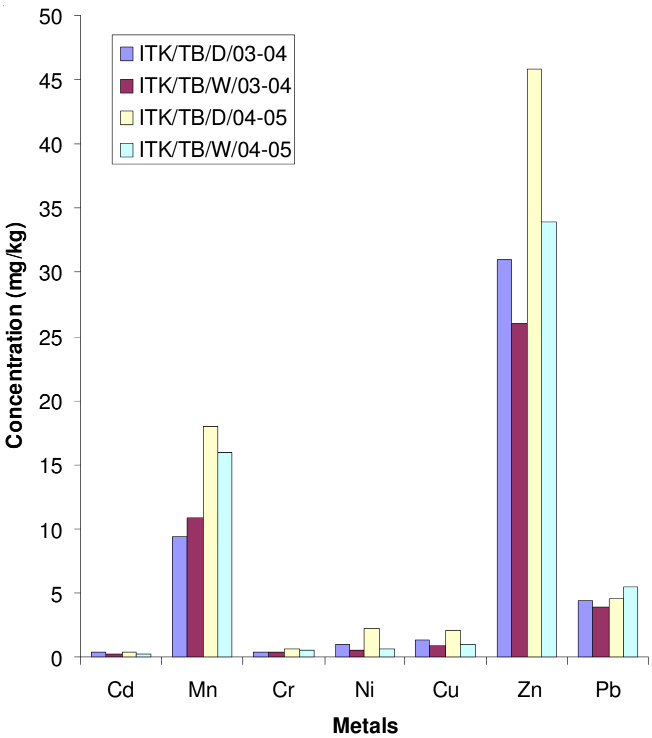

Fig. 2. Concentration levels (mg/kg) variations of heavy metals in bark of *P. biglobosa* (locust bean) tree during different climatic seasons; Code: ITK = Itakpe; TB = tree bark of *P. biglobosa*; D = dry season; W = wet season; 03-04 = year 2003-04; 04-05 = year 2004-05

The atmospheric stability of the study area largely controls flux density of metals particulates in air within the different atmospheric boundary layers and is not known to be stable due to differential turbulence caused by the sun's heating effect on the area unequal topographic sequenced earth's surface, similar to the observation of Fernando *et al.*[32]. Atmospheric stability also influences long distance trans-boundary transport of particulates metals. Consequently the levels of metal particulates in the atmosphere and the depth of the mixing layers will depends on rates of emission from sources and the prevailing weather conditions. Parlange and Brutsaert[33] suggested that during windy and/or cloudy conditions, the atmosphere is normally neutral. Thus predicting air quality and flux concentration of metals using passive method can be misleading as a result of atmospheric instability. Aside from weather conditions, variation in barks concentration levels of heavy metals in plants is also function of biogeochemical and hydro-geochemical processes and balances[34-36] and this largely controls metal levels and availability in the environment as well[37,38].

However owing to the fact that mining operations at the iron ore deposit is abysmally low, erratic and demand base, the observed levels in the barks can be taken as the natural aerial flux density of the measured metals defining the natural atmospheric quality of particulate metals around Itakpe iron ore deposit in North Central Nigeria.

Conclusion

The concentration levels of heavy metals in barks of *P. biglobosa* were found to fall below or within the levels detected elsewhere in the world. The detected levels can be taken as baseline concentrations against which environmental build up heavy metals in plants can be monitored. Active monitoring setup should be in operational, residential and vegetated areas to ensure human and environmental health and safety. This should take into cognizance distances and prevailing direction of air current. There is also need to identify the most sensitive short and long range receptors of atmospheric deposition of particulate metals and other releases from mine locations.

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