

Bio-Indication of Potentially Toxic Metals Utilizing Barks of Different Species of Tree Plants in Urban Centre of Kazaure, Jigawa State

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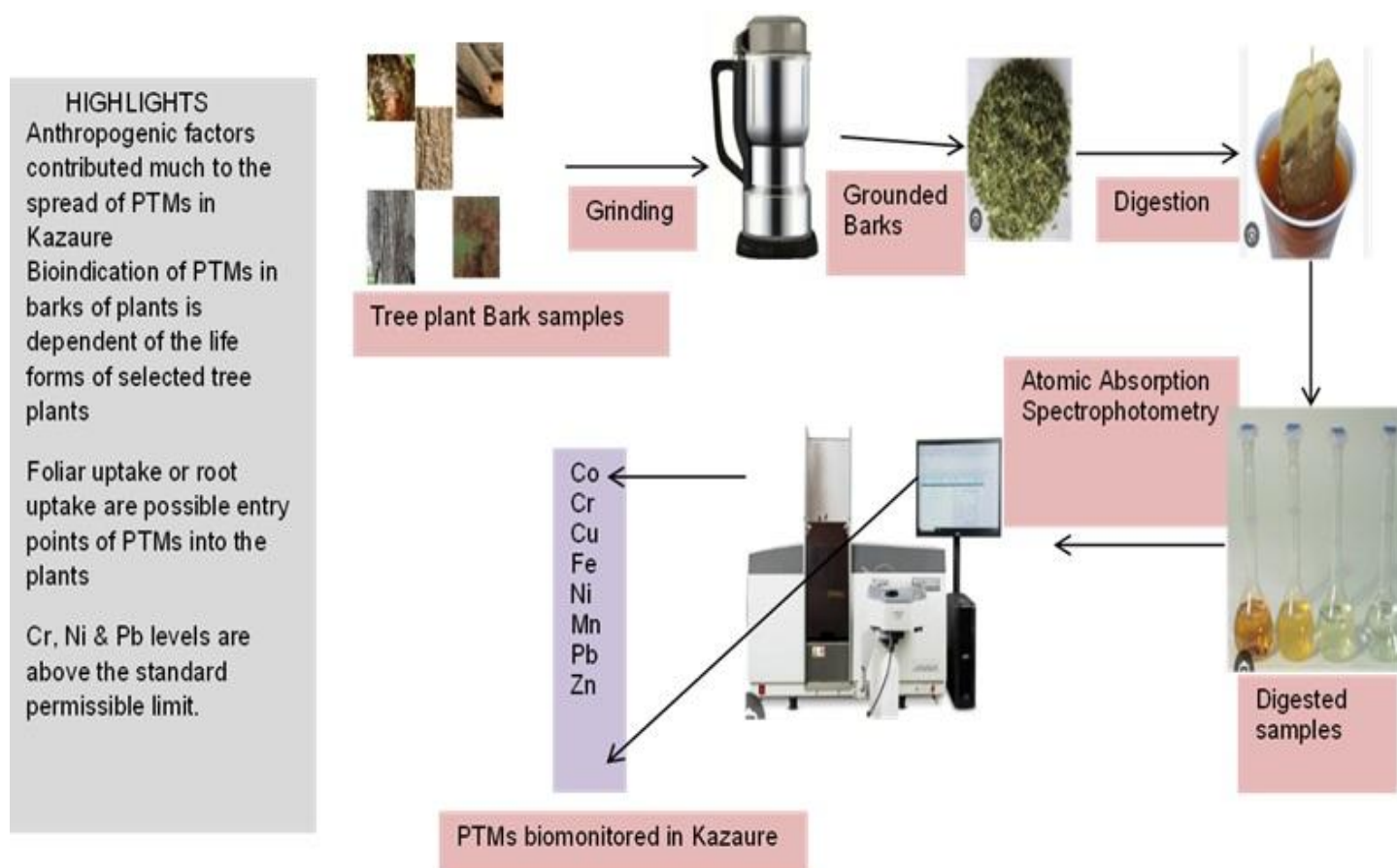
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GRAPHICAL ABSTRACT



ABSTRACT

The food chain of area like Kazaure is bound to be unarguably affected by the entry of large sums of potentially toxic metals, PTMs into the green environment courtesy the activities of the construction companies and vehicular emissions that took over the atmospheric environment of the studied area. These man-made factors uphold upper hand over the natural factors that include topography of the chosen area of study. Selected portion of Kazaure was therefore chosen for the investigation of the PTMs fallouts using the barks of common tree plant species (*Cassia acutifolia*, *Casuarina equisetifolia*, *Dalbergia nigra*, *Mangifera indica* and *Terminalia catappa*) in the region as bioindicators. The findings unveiled the availability of all the assayed PTMs and the good potential of bioindicating status of all the barks of tree plants so considered. The following trends were revealed by this study; *C. acutifolia* (Fe > Co > Pb > Zn > Ni > Mn > Cu > Cr); *C. equisetifolia* (Fe > Mn > Co > Zn > Cr > Ni > Pb > Cu); *D. nigra* (Fe > Cr > Mn > Pb > Zn > Co > Ni > Cu); *M. indica* (Fe > Cr > Co > Mn > Pb > Zn > Ni > Cu); *T. catappa* (Fe > Co > Mn > Pb > Cr > Zn > Cu > Ni). All the PTMs were significantly bioaccumulated with the exception of Pb in *C. equisetifolia* and *M. indica* as statistically deduced by two-way ANOVA. None of the plant species are hyperaccumulator but are good bioindicators and could serve as phytoremediators if the chance arises. There are no significant differences in the levels of PTMs among the topographic positions of the plant species. Land use practices, however, differed significantly indicating anthropogenic interference as a predominant determinant of PTMs enrichment of soil-plant systems. Metal tolerant dominant plants in Kazaure LGA could be classified as metallophytes. Indigenous species, accumulators and excluders, showed prospects for phytoremediation and rehabilitation of metal contaminated areas, respectively. Concentrations of Cr, Ni and Pb in assayed tree plant barks exceeded the international permissible limits, which highlighted the necessity to estimate human health risks for PTMs in disturbed regions.

Keywords: Potentially toxic metals; Bioindicators; Kazaure; Topography; Anthropogenic factors

INTRODUCTION

Urban centers are harbinger of heavy metals emission, the causative elements of environmental pollution as a result different anthropogenic undertakings which had a direct or indirect negative effect on the environment. Among the heavy metals, (HMs) that constitute this environmental malady are Cd, As, Hg, Pb, Pt and Cr (Er Caliskan et al., 2021). Some of these HMs are also called potentially toxic metals (PTMs) and their presence in the soil is affected by the topography of the land (Gaspar et al., 2020). These prominent PTMs equally constitute atmospheric air pollutants which are responsible for significant dangers in the environment and human health. Some of these PTMs successfully bind to elements like sulfur, nitrogen, and other functional groups present in biomolecules in human system and thus, interfere with their metabolic functions. Such consequential impacts are apparent in DNA mutations, cell cycle malfunctions, neurological problems, liver and kidney damage, impairment of endocrine systems, cardiovascular dysfunction. In many ecosystems, high and/or low levels of heavy metals can also degrade air and water quality, causing degradation of biodiversity, biotic and abiotic components inclusive. Due to the negative effects of these pollutants on human health and the environment, it has become necessary to indicate and control them (Er Caliskan et al., 2021). Although HMs are naturally existing in the ecosystem, their levels are supposedly hike by man-made activities. More so, these PTMs possess long biochemical half-lives and are not biodegradable culminating in their lengthy stay in the food chain. This waiting moment afford PTMs the much needed avenue to dislodge the natural setting in human beings on consumption of food stuffs such as plants, fish and animals (Sevik et al., 2020). Aside this, PTMs may also find their ways into the human system via respiration and for plants through photosynthesis. Based on this premise, the determination of PTMs concentrations is of great importance in terms of unveiling the risk areas and the risk levels (Cetin 2017; Cetin et al. 2017; Saleh 2018; Turkyilmaz et al. 2018; Cetin et al. 2018). Okparaocha et al., (2019) mentioned that tree plants growing along the busy highways act as sink and efficiently decrease the heavy metal concentrations in the atmosphere. This trait qualifies tree plants parts as active bio-indicators and bio-monitors of heavy metal pollution in the environment. It is crystal clear that several studies have reported the use of plants as bio-indicators for heavy metals in the environment using tree plants as environmental pollution markers.

Bio indication is the measure of urban environmental degradation with the aid of living components of the ecological system. This biological approach is gradually being used as a cost-effective alternative method to

instrumental methods for studying local air pollution in the terrestrial environment (Moreira et al. 2018). The tree plant bark are unarguably effective substrate for collection of airborne contaminants and offers the advantage of being available throughout the year, easily accessible and serves as a passive bio-indicator of environmental pollution (Parzych et al. 2017). Generally, PTMs often accumulate in the bark of tree plants through wet and dry deposition processes (Tovar-Sanchez et al. 2019), whereas root uptake of these metals by tree plant bark is limited. The tree plants that thrive on metal-rich soil are often referred to metallophytes (Baker et al., 2010). Metal-rich soils or edaphic environment with abundant metals are said to be metalliferous (Siebert et al., 2018). The various plant species from metalliferous ecosystem around the globe are reported to hyperaccumulate PTMs like Co (*Persicaria punctata*, van der Ent et al., 2020), Cu (*Geniosporum tenuiflorum*, Rajakaruna and Baker, 2004), Mn (*Macadamia neurophylla*, van der Ent et al., 2013), Ni (*Alyssum murale*, Drozdova et al., 2021; *Senecio conrathii*, Siebert et al., 2018) and Zn (*Arabidopsis halleri*, Pollard et al., 2014). Hyperaccumulators, excluders and accumulators, are uncompromised valuables for green technologies whose application in rehabilitation (i.e., reclaiming PTMs disturbed vegetation), restoration (i.e., re-establishment of the original vegetation in PTMs degraded ecosystems), phytoremediation (i.e., to decontaminate PTMs polluted environments using plants) and phytomining (i.e., economically viable recovery of elements through the deployment of plants termed hyperaccumulators) (Ali et al., 2013; O'Dell, 2014; Paul et al., 2018; van der Ent et al., 2015, 2021). Elevated levels of PTMs in the urban environment have already been reported by a large number of researchers. Tree plants do possess the capability to uptake PTMs via the leaves and bark thus accumulating pollutants directly from the atmosphere though they never got any ornamental function in urban areas (Yousaf et al., 2020).

Cassia acutifolia, *Casuarina equisetifolia*, *Dalbergia nigra*, *Mangifera indica* and *Terminalia catappa* are tree plants common in Kazaure metropolitan area. Due to their prominence in the study area the sampling of the bark of these tree plants was considered for the study. The primary objective of this study is to assess the bark of these tree plants as bio-indicator of PTMs (Cu, Pb, Mn, Ni, Fe, Cr, Co and Zn) that constitute atmospheric heavy metal pollution in urban centre of Kazaure, Jigawa State of Nigeria and the impact on the immediate environment.

MATERIALS AND METHODS

Reagents and Instrument

Chemicals such as lead chloride (99%), chromium (III) trioxonitrate (V) (60.5%), cobalt chloride (98%), manganese tetraoxosulphate (VI) (97%) and zinc trioxonitrate (V) ($\geq 99\%$) employed in the production of standard solutions of lead (Pb), chromium (Cr), cobalt (Co), manganese (Mn) and zinc (Zn) were all obtained from Sigma-Aldrich (St. Louis, USA). Copper (II) tetraoxosulphate (VI), nickel chloride and iron (III) trioxonitrate (V) nonahydrate used for the preparation of standard solutions of copper (Cu), nickel (Ni) and iron (Fe) were purchased from Fluka (Durban, South Africa). Trioxonitrate (V) acid (95-97%) bought from Friendemann Schmidt (Parkwood, Australia) was used for digesting the samples. The drying of the leaves and bark samples was conducted in an oven (Asturias, Spain). The grinding of the leaves and barks samples were accomplished with the aid of pestle and mortar (Oregon, USA). Desiccator (Enigma Business Park, UK) is employed to provide temporary air-tight storage for the prepared samples prior to digestion. Furnace (Waltham, USA) aided the ashing of the samples. Elemental determination was performed using atomic absorption spectrophotometer, AAS (model Perkin Elmer 3110) (Massachusetts, USA). Other chemicals are of qualitative analytical grade. Deionized water was used to prepare the aqueous solutions.

Study Area

The location where the present study was stationed is the premises of Hussaini Adamu Federal Polytechnic, (HAFED POLY) Kazaure. To be precise, the study site is the botanical garden housed in the department of Science Laboratory Technology, School of Science and Technology (Fig. 1). This garden has a vast array of tree plants. The study area is characterized with varying degrees of human impact as a function of anthropogenic activities, such as vehicular emissions, pollution from street frying of potatoes, beans cake and yam, roasting of fish, chicken, maize and meat and farming activities. The natural impact is also evident like blowing of winds on the tree plants and climatic conditions. The coordinates of the study area is (12038'04.8" N, 8025'17.2" E).

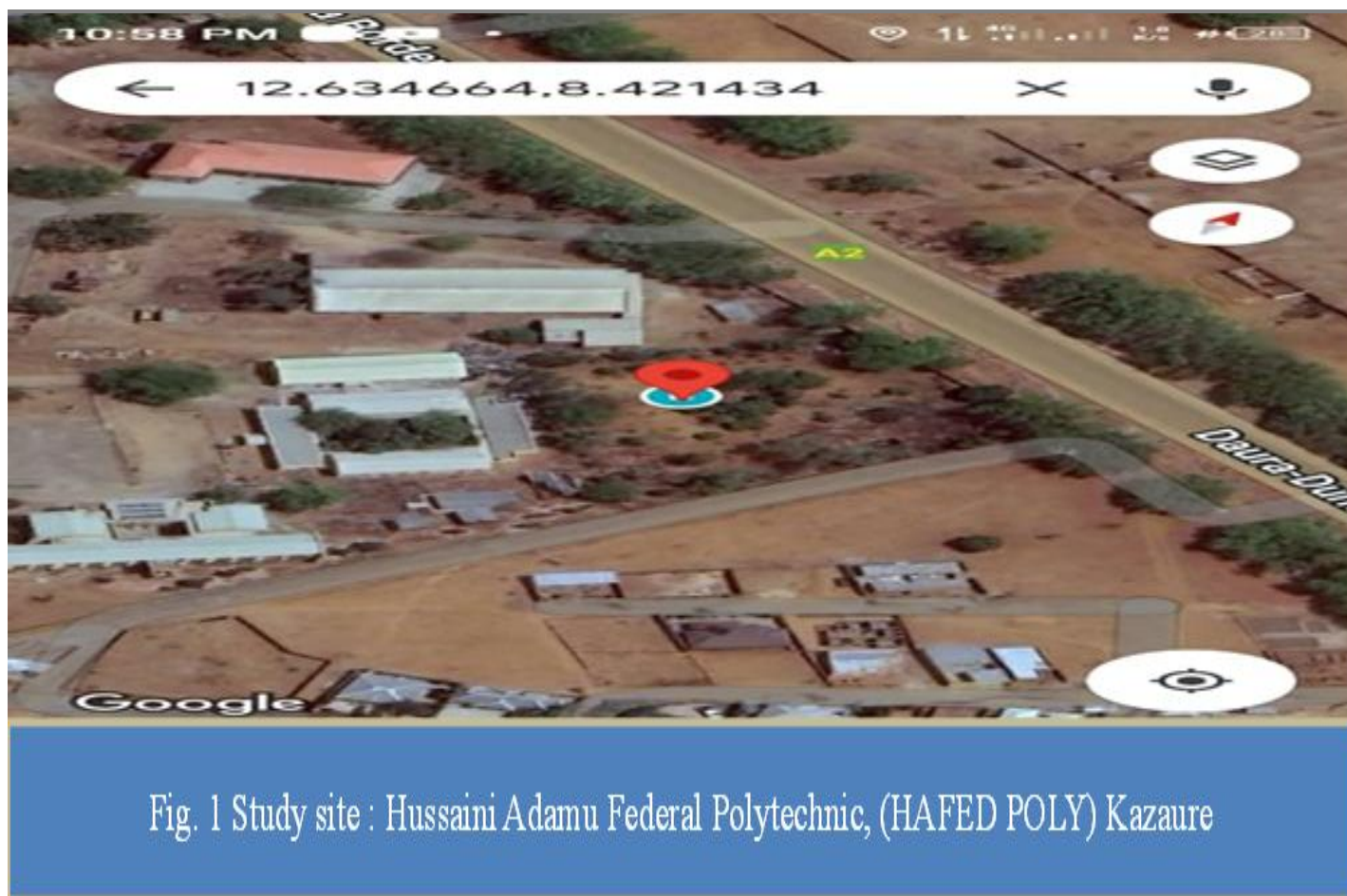


Fig. 1 Study site : Hussaini Adamu Federal Polytechnic, (HAFED POLY) Kazaure

Sample Collection and Treatment

Samples of barks were obtained during the months of July, August and September 2023 from different locations in the premises of HAFED polytechnic (Botanical Garden), Kazaure. Ten samples of each tree plant barks were gathered for analysis. Samples of barks from each tree plant were collected at varying distances from one another with the aid of stainless-steel knife at breast height and above to a maximum height of 2 metres from the ground (Fowotade and Jimoh, 2013). These sampled portions of various plants' barks were placed in plastic bags, labeled and transported to the biological laboratory of the department of Science Laboratory Technology, HussainiAdamu Federal Polytechnic, Kazaure where they were authenticated by a botanist, Rabi Rabi Abubakar. The samples were then sorted and dregs discarded. The sorted samples were air dried in the open, grounded into powder and sieved to obtain fine powder of what particle size ($d > 250\mu\text{m}$). Each powdered samples (23g) were weighed into 100cm^3 beaker of known weight and oven dried at a temperature of 105°C until a constant weight was reached. Each sample (20g) was stored in an air tight container. Sample solution was prepared by digesting 10g of each sample which has been ashed at 550°C using 10cm^3 of 6M nitric acid. The mixture was filtered into 50cm^3 volumetric flasks and de-ionized water was added up to the mark (Fowotade and Jimoh, 2013). The solutions were analyzed for Mn, Zn, Pb, Cr, Co, Ni, Cu and Fe, using atomic absorption spectrophotometer at 2000°C (Model Perkin Elmer 3110). A procedural blank and a set of standards for each element were determined each time a series of samples were run. Average readings of the samples were corrected with the blank reading and a calibration curve was constructed for each standard solution. The concentrations of each element under investigation in parts per million (PPM) were determined from the curve of its standard by interpolation.

Statistical Procedure

The statistical tools used include the mean, variance and standard deviation. The analysis of variance, ANOVA was employed to measure the significance of the levels of HMs so obtained in the present study. The spearman's rank is also used to correlate the concentrations of HMs so determined. The obtained data were evaluated with the help of the SPSS package, and Tukey post hoc test using IBM SPSS Statistics V23 software.

RESULTS AND DISCUSSION

The eight selected heavy metals, HMs (Co, Cr, Cu, Fe, Ni, Mn, Pb, Zn) are successfully determined in all the bark samples of the tree plants considered in this study. The levels of PTMs reported in this study will be used as a yardstick for the bio-indicator potential of the tree barks. The outcomes are presented as figures (1 – 5), showing the levels or concentration of HMs on the vertical axis and the names of selected HMs in each tree barks on the horizontal axis. Our findings confirmed that all tree plants barks are non-excluders of the selected PTMs.

Cassia acutifolia barks exercised a prolific tendency towards accumulation of PTMs. The bark samples of this tree plant sometimes referred to as Alexandrian senna, concentrated metals as follows Co (12.01±0.15 mg/Kg), Cr (0.75 ±0.02 mg/Kg), Cu (4.04±0.14 mg/Kg), Fe (104.98±0.17 mg/Kg), Ni (7.97±0.35 mg/Kg), Mn (6.03 ±0.25 mg/Kg), Pb (10.33 ±0.45 mg/Kg), Zn (9.55 ±0.28 mg/Kg). These results are summarized in Fig.2.

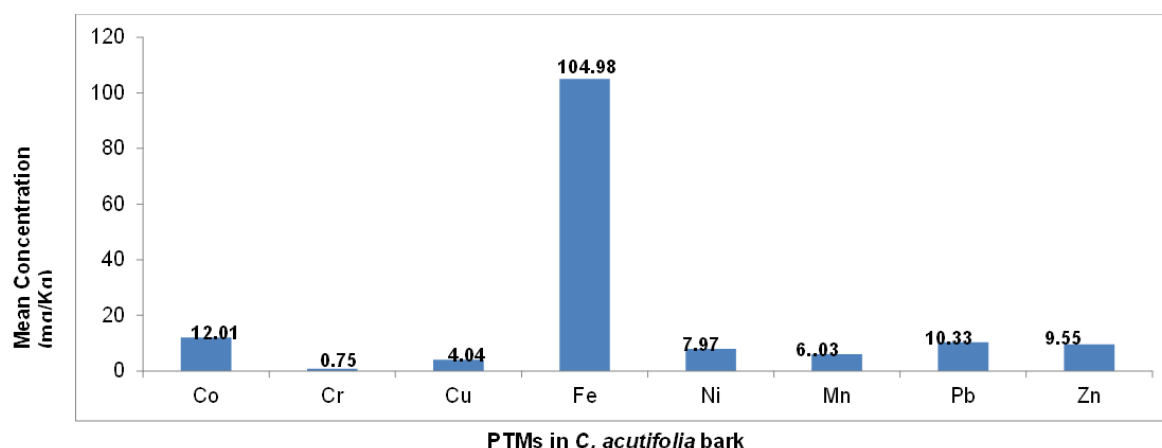


Fig. 2: Mean concentration of PTMs in *C. acutifolia* bark

The metal with the highest concentration is Fe (104.98 mg/Kg) while the metal with lowest concentration is Cr (0.75 mg/Kg). Other metals that also gain prominence on the tree bark of *C. acutifolia* are Co (12.01 mg/Kg), Pb (10.33 mg/Kg) and Zn (9.55 mg/Kg). Mn (6.03 mg/Kg) and Ni (7.97 mg/Kg) may be said to be averagely concentrated, while Cu (4.04 mg/Kg) is below average. The bark of *C. acutifolia* is a good bio-indicator of Fe. The decreasing order of bioaccumulation of PTMs in barks of is *C. acutifolia* as follows Fe > Co > Pb > Zn > Ni > Mn > Cu > Cr.

The barks of *Casaurina equisetifolia* also display excellent accumulation of the PTMs in the studied area. The following amounts of PTMs were determined from the bark samples of the tree plant. Co (13.97±0.25 mg/Kg), Cr (7.54 ±0.16 mg/Kg), Cu (0.35±0.02 mg/Kg), Fe (124.98±0.26 mg/Kg), Ni (5.03±0.35 mg/Kg), Mn (24.07 ±0.40 mg/Kg), Pb (3.08 ±0.29 mg/Kg), Zn (12.93 ±0.31 mg/Kg). These results are summarized in Fig.3.

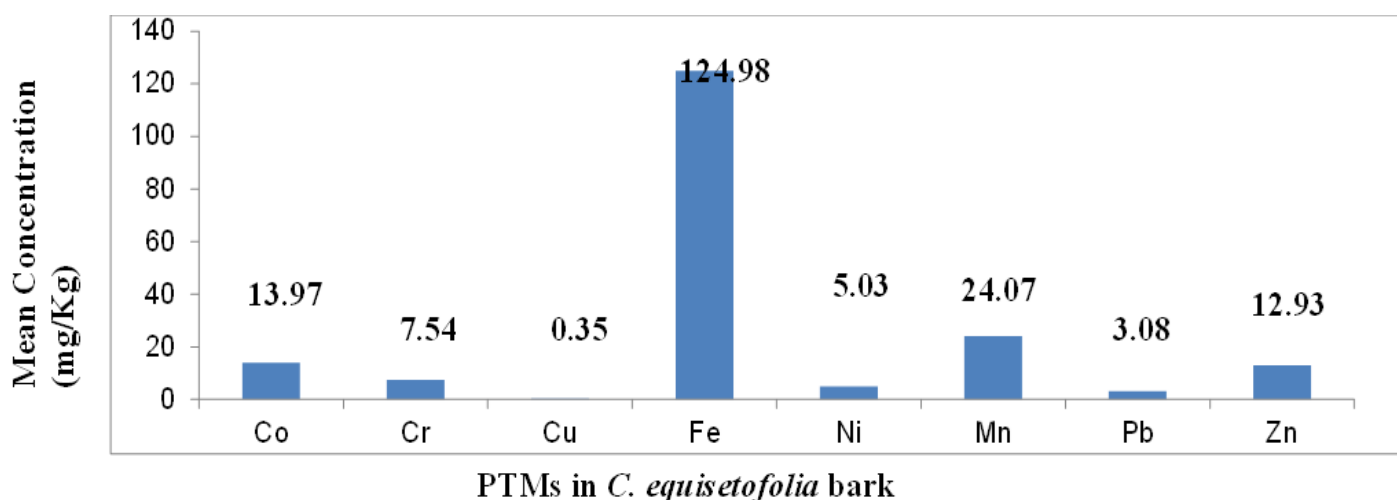


Fig. 3: Mean concentration of PTMs in *C. equisetifolia* bark

As observed in *C. acutifolia*, Fe is the most accumulated PTM in the bark of *C. equisetifolia* with mean concentration of 124.98 mg/Kg. The least concentrated PTM is copper with mean level of 0.35 mg/Kg. The bark of the *C. equisetifolia* bio-accumulated Co at almost twice the level of the mean concentration of Cr. The amount of Mn so determined is approximately 5-folds more than the level of nickel, while the level of Zn is clearly 4-folds higher than that of lead. The decreasing order of bioaccumulation of PTMs in barks of *C. equisetifolia* as follows $Fe > Mn > Co > Zn > Cr > Ni > Pb > Cu$.

The bark samples of *Dalbergia nigra* equally accumulated all the mentioned PTMs in the urban centre of Kazaure. Our findings presented the following outcomes: Co (2.03 ± 0.45 mg/Kg), Cr (8.53 ± 0.15 mg/Kg), Cu (0.65 ± 0.03 mg/Kg), Fe (62.55 ± 0.23 mg/Kg), Ni (1.98 ± 0.27 mg/Kg), Mn (8.07 ± 0.31 mg/Kg), Pb (4.10 ± 0.36 mg/Kg), Zn (3.45 ± 0.17 mg/Kg). These results are summarized in Fig.4.

The PTMs with the highest mean concentration as revealed by the bark analysis of *D. nigra* is iron (62.55 mg/Kg) while copper (0.65 mg/Kg) assumed the lowest concentration. Exact trend is observed in the barks of *C. equisetifolia*. Chromium level almost quadrupled cobalt and nickel level in the bark of this tree plant. The level of Mn is twice the level of lead and zinc on approximation. The decreasing order of bioaccumulation of PTMs in barks of *D. nigra* as follows $Fe > Cr > Mn > Pb > Zn > Co > Ni > Cu$.

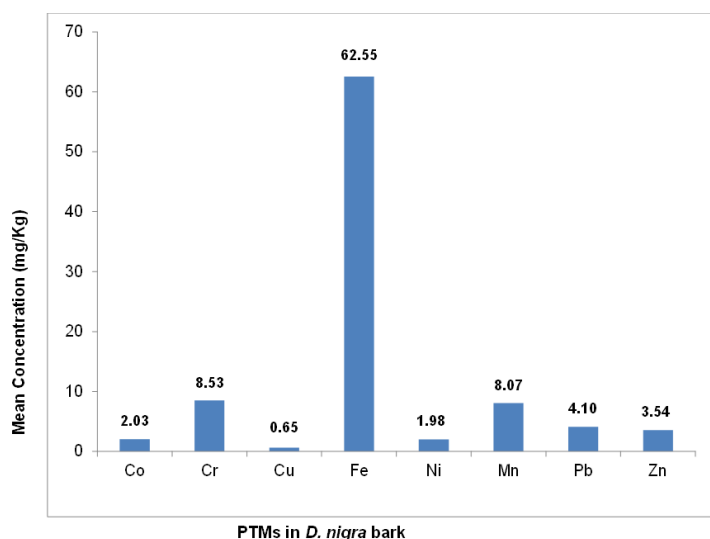


Fig. 4: Mean concentration of PTMs in *D. nigra* bark

The barks of *Mangifera indica* exhibited promising bio-indicator potential towards all the considered PTMs in the metropolitan area of Kazaure. The followings are the results of the determinations of the PTMs observed from the barks of *M. indica*, Co (9.53 ± 0.15 mg/Kg), Cr (12.03 ± 0.16 mg/Kg), Cu (0.76 ± 0.03 mg/Kg), Fe (157.52 ± 0.17 mg/Kg), Ni (1.03 ± 0.24 mg/Kg), Mn (4.03 ± 0.25 mg/Kg), Pb (3.00 ± 0.19 mg/Kg), Zn (1.73 ± 0.14 mg/Kg). These results are summarized in Fig.5.

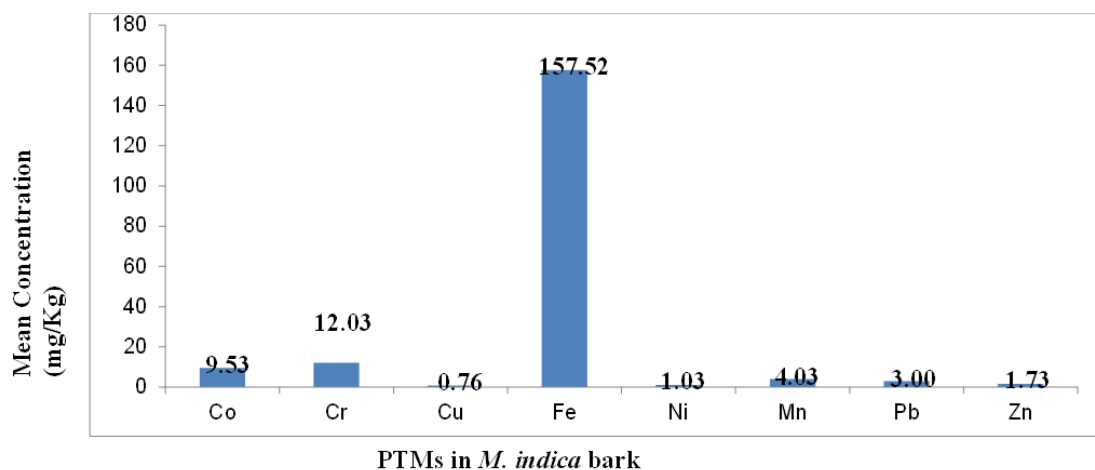


Fig. 5: Mean concentration of PTMs in *M. indica* bark

As previously observed in the other tree plant barks, the mean concentration of Fe (157.52 mg/Kg) is the most senior in the case of the bark samples of *M. indica* as well while that of Cu (0.76 mg/Kg) is the most junior among the assayed PTMs. This trend is also observed in *D. nigra* and *C. equisetifolia*. The concentrations of Co and Cr tripled the duo of Pb and Mn respectively. The concentration of Cr is also 6-folds higher than the concentration of Zn and approximately twelve times more than the concentration of Ni. The decreasing order of bioaccumulation of PTMs in barks of *M. indica* as follows $Fe > Cr > Co > Mn > Pb > Zn > Ni > Cu$.

The samples of the bark of *Terminalia catappa* show cased an outstanding potential towards the bioaccumulation of the selected PTMs in the urban centre of Kazaure. The report of the present study revealed the following levels of the metals, Co (21.03 ± 0.24 mg/Kg), Cr (4.03 ± 0.15 mg/Kg), Cu (1.97 ± 0.14 mg/Kg), Fe (142.10 ± 0.36 mg/Kg), Ni (1.40 ± 0.46 mg/Kg), Mn (10.53 ± 0.25 mg/Kg), Pb (5.03 ± 0.35 mg/Kg), Zn (3.76 ± 0.09 mg/Kg). These results are summarized in Fig.6.

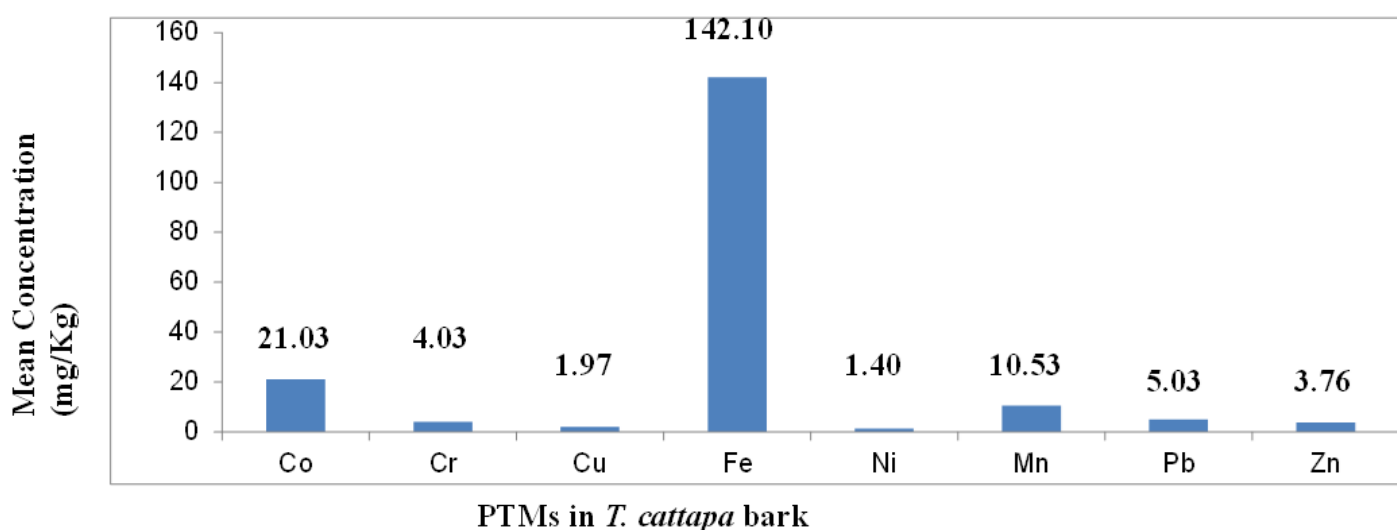


Fig. 6: Mean concentration of PTMs in *T. catappa* bark

The PTM with the peak mean level is Fe (142.10 mg/Kg) replicating the same observations in the previous tree plant barks of *C. acutifolia*, *C. equisetifolia*, *D. nigra* and *M. indica*. Unlike the outcome of the PTMs determinations in *C. equisetifolia*, *D. nigra* and *M. indica* nickel has the bottom mean level of 1.40 mg/Kg. Furthermore, the level of Co is approximately 5-folds and 10-folds higher than Cr and Cu respectively. The level of Mn however doubles that of Pb in the same plant and almost two and half times the level of zinc. The decreasing order of bioaccumulation of PTMs in barks of *T. catappa* as follows $Fe > Co > Mn > Pb > Cr > Zn > Cu > Ni$.

Based on the trends of the PTMs as related above, the *M. indica* and *D. nigra* exhibited the same positional trend for the seven PTMs namely Fe, Cr, Mn, Pb, Zn, Ni and Cu. *C. acutifolia* and *T. catappa* displayed similar trend for Fe, Co and Cu. The topography of the studied area plays no significant impact in the bio-indication of PTMs by the tree barks. This is due to the fact that all the plant species are located in a close perimeter to one another in the botanical garden. PTMs availability in soils portends a distinction between the upper slopes and other slope positions due to the parent material mineralogy (Gaspar et al., 2020) as the former harbors higher amount of metals than the later (Qiao et al., 2019). Despite the richness in metals the upper or topmost slope is prone to natural attack such as water and wind attack eroding its reservoir of PTMs easily thus resulting to devastating loss of surface metals (Tamfuh et al., 2017). All the tree plant species are bounded by the same topographical and climatic exposure as well as similar anthropogenic effects. So, the only variation at bio-indicating PTMs is tree plant bark specific. Distinctive metal spread pattern are often seen in valleys due to higher presence of metals trapped in soils rich in clay content as binder (Alloway, 2013). In other words, valleys experienced larger deposition of eroded metals from highlands, waterways and other agents of erosion (Du Plessis et al., 2020). The urban centre of Kazaure is an example of such valley. The determinant factor for bio-indication could be root uptake and foliar uptake by the various plant trees considered in the present study. This statement is corroborated by Sevik et al., (2020) when the team posited that uptake and retaining capability of tree plants is a function of

their physiological and physical traits. The trio of Pb, Fe and Co had been established by researchers to spread through routine vehicular trafficking (Mossi 2018; Shahid et al. 2017; Turkyilmaz et al. 2019).

Employing the benchmark of 9.00 mg/Kg as bioindication limit for tree barks in the present study, the following results are unveiled, 80% of the tree plant barks concentrated Co (Cassia acutifolia, Casuarina equisetifolia, Mangifera indica, Terminalia catappa) above the mark, Cr had 20% (Mangifera indica) , Cu is 0% (none), Fe 100% (all the plants), Ni 0% (none), Mn 40% (Casuarina equisetifolia, Terminalia catappa), Pb 20% (Cassia acutifolia) and Zn 40% (Cassia acutifolia, Casuarina equisetifolia) in the studied area. This implies that almost of the tree barks are good bio-indicator of cobalt and iron. The plants displayed below average mark bio-indication towards Mn and Zn despite the fact that both metals are plants available. Elemental constitution of tree plant barks are functions of numerous agents like transport of crown-intercepted pollutants by stem flow, wet and dry aerial deposition of particulate matter (Adebiyi and Ore, 2021) and root uptake of mineral elements (Gaspar et al., 2020). Copper is the least concentrated PTMs, though it is also one of the essential elements in plants. Naturally, Cu occurs in rocks, water and air. In the anthropogenic sense, Cu is a component of pesticides and fungicides, manufacturing of electrical utensils, used in construction like roofing and plumbing and industrial machinery (Dogan et al., 2014) and automobile parts. The lowly reported values for copper in the urban centre of Kazaure, might be due to the low industrialization of the area. This also give rise to reduced urbanization thus witnessing drastically low vehicular movement that may be a major contributor of particulates containing the metal and other potentially toxic counterparts. The found variation in the level of Pb in this study is corroborated by the findings of Yousaf et al, (2020). The found concentrations of other PTMs are in agreement of the work of Dogan and Co. (Dogan et al., 2014).

Table 1: Total Concentration of PTMs found in tree plant barks

Tree barks	Cassia acutifolia	Casuarina equisetifolia	Dalbergia nigra	Mangifera indica	Terminalia catappa
Total PTMs (mg/Kg)	155.66	191.95	91.45	189.63	189.85

Focusing the found outcomes in Table 1, four of the assayed tree plants may be said to be metallophytes. These are plant species that are tolerant to metal-rich edaphic ecosystems (Baker et al., 2010). Original effort needed to be exerted on such plants because they are potential accumulators, hyperaccumulators or excluders of metals in both essential and non-essential category from the soil (Siebert et al., 2018). Setting the concentration mark for metallophytes at 100.00 mg/Kg, the results of our findings may be right to mention that Cassia acutifolia, Casuarina equisetifolia, Mangifera indica and Terminalia catappa are metallophytes judging from the total metallic load being well above the given bench mark. As stated by the researchers, metallophytes are very excellent at phytoremediation of the any environment suffering from PTMs disturbance. The urban centre of Kazaure is one of such, though relatively under-developed, it can boast of a railway construction company owned by Chinese, which is currently enjoying its array of activities in the area of our present undertakings. Additionally, the Daura-Kazaure-Kano highway is another major contributor of many of the analyzed PTMs aside the Chinese construction firm in the present study, due to automobile trafficking along the road.

Potentially toxic metals loads in Urban Cities of the World

A brief summary of the comparison of PTMs loads in Kazaure (this study), Toronto (Yousaf et al., 2020), Amman City (El-Hasan et al. 2002), Buenos Aires (Fujiwara et al. 2011), and Pretoria (Olowoyo et al. 2010) is shown in Table 2 & 3. The load of Pb in Kazaure (5.11 mg/Kg) is 5 times lower than in Toronto (26.5 mg/Kg) and is 59 times lower than in Amman City (302 mg/Kg), 15 times less than in Pretoria (78.3 mg/Kg), and approximately 10 times lower than in Buenos Aires (50.1 mg/Kg). The higher loads of Pb recorded in these cities over Kazaure town suggests the level of vehicular trafficking obtainable via leaded gasoline. Higher level of Pb is linked with neurological disorders in children and cardiovascular effects in adults resulting in major health effects associated with the higher levels of Pb (EPA-USA 2017). The load of Mn in

Kazaure (6.30 mg/Kg) is lower than those of Toronto (55.3 mg/Kg), Amman City (29.5 mg/Kg) and Buenos Aires (31.3 mg/Kg). Copper load in Kazaure (7.23 mg/Kg) is also lower than 26.4 mg/Kg reported in Toronto,

65.3 mg/Kg in Pretoria, and 69.7 mg/Kg in Buenos Aires. However, with exception of higher Ni loads in Toronto (6.55 mg/Kg) and Pretoria (18.5 mg/Kg), the value obtained in this study (3.48 mg/Kg) is higher than those reported in Amman City (2.32 mg/Kg) and Buenos Aires (2.84 mg/Kg). Zinc loads in Toronto (95.20 mg/Kg), Buenos Aires (127 mg/Kg), Pretoria (125 mg/Kg) and Amman City (48.8) were comparably higher than in Kazaure (6.30 mg/Kg). The load of Cr in Ramadi City (6.0 mg/Kg) is almost the same as that reported in Kazaure (Table 3). The load of Co in the present study (11.7 mg/Kg) is higher than the value mentioned by Al-Heety et al., (2021) in Ramadi city (2.0 mg/Kg). . Aside the use of leaded gasoline, other source of Pb may be via brake wear and loss of Pb wheel weights. Mn loads in Kazaure could be attributable to emission of ethyl cyclopentadienyl manganese tricarbonyl, MMT (antiknock additive in unleaded gasoline) due to high traffic density sometimes experienced along Kazaure-Kano highway. The main sources of Cu, Ni, and Zn could be traffic emissions from exhaust, tires, and brake wear (Yousaf et al., 2020).

Table 2: PTMs loads in Selected Cities around the globe

City	Period	PTMs load (mg/Kg)					Reference
		Cu	Mn	Ni	Pb	Zn	
Kazaure, Nigeria	2023	7.2	10.5	3.5	5.1	6.3	This study
Toronto, Canada	2011	26.4	55.3	6.55	26.5	95.2	Yousaf et al., (2020)
Amman City, Jordan	2001	15.1	29.5	2.32	302	48.8	El-Hasan et al. (2002)
Buenos Aires, Argentina	2006	69.7	31.3	2.84	50.1	127	Fujiwara et al. (2011)
Pretoria, South Africa	2007	65.3	302	18.5	78.3	125	Olowoyo et al. (2010)

Table 3: PTMs loads in Kazaure and Ramadi city

City	Period	PTMs load (mg/Kg)		Reference
		Cr	Co	
Kazaure, Nigeria	2023	6.6	11.7	This Study
Ramadi City, Iraq	2020	6.0	2.0	Al-Heety et al., 2021

Statistical Analysis

Two-way ANOVA was employed in the statistical procedure for the present study. As evident in Table 4, almost all the potentially toxic metals are significantly accumulated by the barks of the selected tree plant species in Kazaure. The only PTM that does not display significance bioaccumulation is Pb in the barks of *Casuarina equisetifolia* and *Mangifera indica*.

Table 4: Analysis of variance between metal concentrations in the barks of tree plant species

Sample	Co	Cr	Cu	Fe	Ni	Mn	Pb	Zn
Cassia acutifolia	12.01± 0.15 ^a	0.75± 0.02 ^e	4.04± 0.14 ^a	104.98± 0.17 ^c	7.97± 0.35 ^a	6.03 ± 0.25 ^d	10.33± 0.45 ^a	9.55 ± 0.28 ^b
Casuarina equisetifolia	3.97± 0.25 ^c	7.54± 0.16 ^c	.35± 0.02 ^e	24.98± 0.26 ^e	5.03± 0.10 ^b	24.07± 0.40 ^a	3.08± 0.29 ^d	12.93± 0.31 ^a
Dalbergia nigra	2.03± 0.45 ^d	8.53± 0.15 ^b	.65± 0.03 ^d	62.55± 0.23 ^d	1.98± 0.27 ^c	8.07± 0.31 ^c	4.10± 0.36 ^c	3.54± 0.17 ^d

Mangifera indica	9.53± 0.15 ^b	12.03± 0.16 ^a	.76± 0.03 ^c	157.52 ±0.17 ^a	1.03 ± 0.24 ^e	4.03± 0.25 ^e	3.00 ± 0.19 ^d	1.73± 0.14 ^e
Terminalia catappa	1.03± 0.24 ^e	4.03± 0.15 ^d	1.97 ±0.14 ^b	142.1± 0.36 ^b	1.40± 0.46 ^d	10.53± 0.25 ^b	5.03 ± 0.35 ^b	3.76± 0.09 ^c

Notes: presented values were shown as mean and standard deviation; significant differences between means were identified by two-way ANOVA, and Tukey's posthoc test the different letters within the same column indicate significant differences between heavy metal concentrations in different locations at 0.05 level ($P < 0.05$).

CONCLUSION

The present study unraveled the bio-indicating potentials of barks of selected tree plants in Kazaure LGA towards potentially toxic metals, PTMs in the chosen area. All the PTMs were successfully determined and significantly bio-accumulated by the barks samples of the selected tree plants. Aside the effect of topography which also doubles as natural effect that appears to be the same for all the tree plant species, anthropogenic effects played a giant role in the release of PTMs in the studied area. The incursions of the Chinese railway construction company, the encroaching dualization of Daura-Kazaure-Danbatta-Kano highways by BUA group of company and the vehicular trafficking on this road has undoubtedly enhanced the release of large levels of PTMs in Kazaure and its neighborhood as depicted by the results of our findings. *Cassia acutifolia*, *Casuarina equisetifolia*, *Mangifera indica* and *Terminalia catappa* are metallophytes judging from the total metallic load being well above the given bench mark. The quadruple plants could as well function effectively in phytoremediation process at any given opportunity. Thus, future research findings on metallophytes of the region should be prioritized to identify the best-performing organ of tree plant species suitable for green technologies. Prompt conduction of human health risk assessments for PTMs in Kazaure and its environs is pertinently inevitable at this juncture to ensure the safe use of locally harvested plant materials. Globally, continuous monitoring of the spatial distribution of toxic metals in soils is urgent, specifically in fast developing region like Kazaure, as rapidly changing land use patterns could lead to further alterations in metal-soil-plant dynamics at the landscape level, which ultimately influence the food chain.

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