

Bio-Monitoring of Atmospheric Heavy Metals (Co, Cr, Cu, Fe, Ni, Mn, Pb, Zn) Using Leaves of Five Different Tree Plants in Kazaure Metropolis

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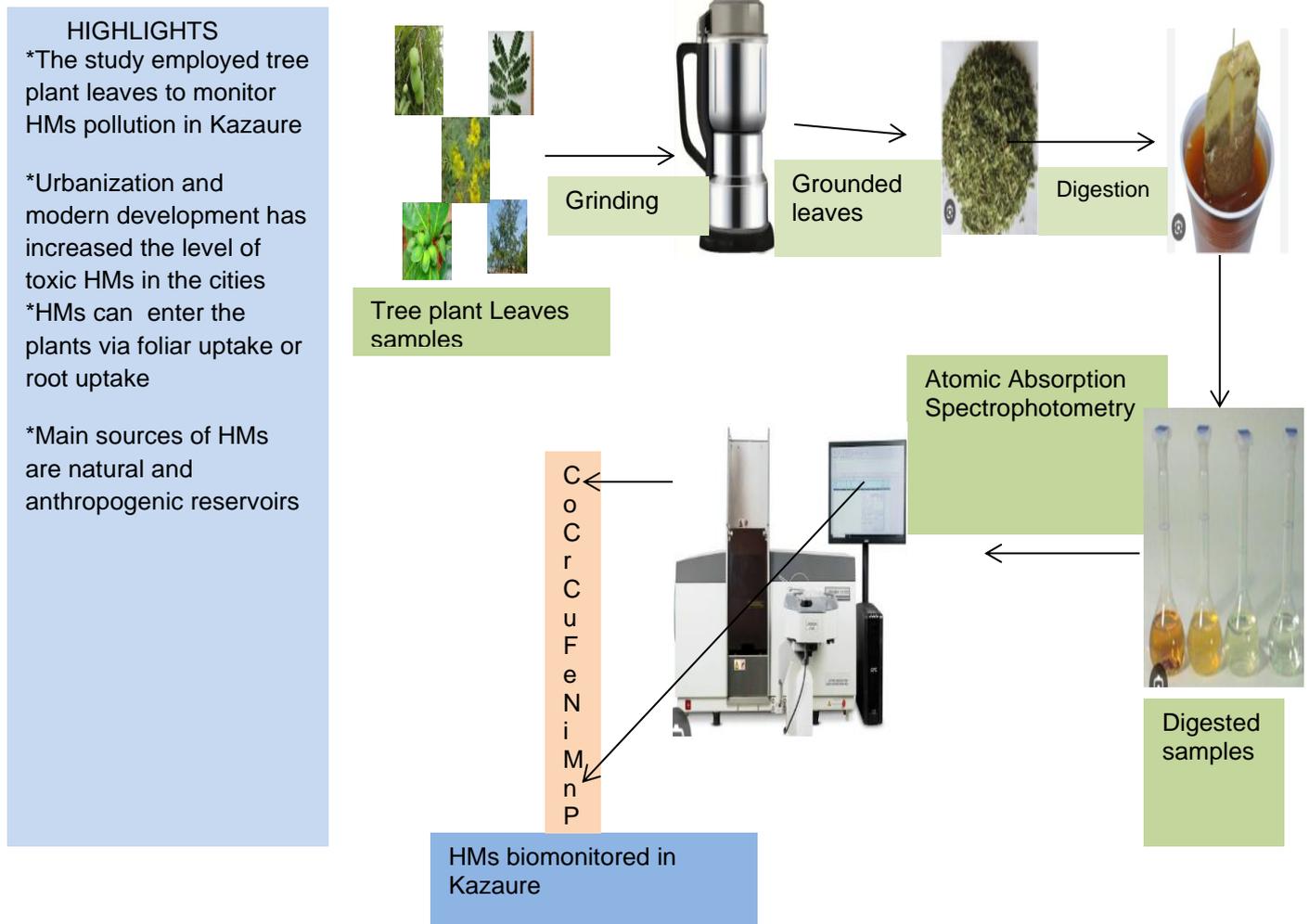
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GRAPHICAL ABSTRACT



ABSTRACT

Tree plants species are essential biotic components of ecosystems. These plants are often grown in urban areas to serve a number of purposes such as beautification, wind break, shades etc. the urban centres no doubt are greeted with numerous anthropogenic activities which introduce lots of contaminants in the name of heavy metals, HMs into the clean environment. Leaves of five tree plant species (*Cassia acutifolia*, *Casuarina equisetifolia*, *Dalbergia nigra* *Mangifera indica* and *Terminalia catappa*) were used to monitor the levels of HMs in Kazaure Local Government Area, LGA. Concentrations of Co, Cr, Cu, Fe, Ni, Mn, Pb, Zn were determined by Atomic Absorption Spectrophotometer, AAS. The leaves samples bioaccumulated all the assayed metals in the environs of Kazaure. The results revealed the following range; Leave of *C. acutifolia* (0.40 – 92.52 mg/Kg), *C. equisetifolia* (0.50 – 199.92 mg/Kg), *D. nigra* (0.80 – 100.02 mg/Kg) *M. indica* (0.60 – 75.03 mg/Kg) and *T. catappa* (0.73 – 185.02 mg/Kg). The leaves of *C. equisetifolia* and *T. catappa* accumulated the highest level of total metals. Though none of the studied plant species is a hyperaccumulator, they are good biomonitor of toxic metals in the locality of Kazaure. Concentration of Ni is only above the permissible limit in *C. equisetifolia* and *T. catappa*. The level of Pb is above the permissible limit in all the plant species suggesting the contamination of the studied area. Cr level is also higher in *C. equisetifolia* and *D. nigra*. The levels of other HMs reported in this study are lower than the permissible limit. The findings here-in may be utilized for future surveillance as preliminary reference values for amount of HMs in metropolitan settings.

Keywords: Biomonitoring, Heavy metals, Tree plants, Kazaure, Hyperaccumulator, Phytoremediation

INTRODUCTION

Metropolitan areas are often faced with environmental pollution as a result of rapid and uncoordinated urbanization and industrial developments across many cities. Elevated levels of heavy metals, HMs in metropolitan areas emanated from industrial plants effluents and chain of automobiles exhaust thus impacting on the air, water, soil, plants and animals in the ecosystem. Heavy metals such as Pb, Cd, Cr, Mn, Ni, Cu, Zn and as constitute the main environmental pollution in the metropolis owing to their toxic impacts and accumulation throughout the food chain, leading to severe problems in the environment and health (Youssef, 2020). Incessantly, rapid urbanization and industrialization have led to increase in the pollution of the metropolitan area from landfill leachates, industrial effluents, vehicular emissions, fossil fuels, erosion of fertilizer from agricultural farm run-off, herbicides and pesticides, sewage and municipal wastes. All these contributed to the accumulation of pollutants in the surrounding ecosystems (Adesuyi et al., 2018). The chemical nature, concentration and stability of atmospheric pollutants are part of the parameters that determine the severity of environmental pollution as related by previous studies. The above permissible limit of heavy metals due to their hyperaccumulation is precipitated on the many developmental activities of man, thus signaling environmental mayhem. Despite the shared properties of metals, heavy metals are somewhat difficult to define. Hence heavy metals can be expressed in terms of toxicity and weight. Metals weighing above 5 g/cm³ are termed “heavy”. For instance lead (Pb), zinc (Zn), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), copper (Cu) silver (Ag), iron (Fe), and the platinum group (Hlail, 2019)

Tree plants in particular are essential biotic components of ecosystems. They have improved the quality of metropolitan environment by acting as shades, beautification, fruit bearers, wind break and soil binders (Hlail, 2019). Plants especially tree plants possess the ability to uptake and accumulate heavy metals from their immediate surroundings through their deep root system, broad stem and elongated leaf surfaces. Based on the foregoing, lots of tree plant species are capable of absorbing and accumulating levels of possible toxic metals in the atmosphere. Unlike tree or shrub components such as buds, flowers and needles, bark and leaf have proved to be a better bio-monitor of heavy metals due to the ability of the latter to accumulate more air pollutants and their durability in drastic weather situations. The capability of foliage accumulation via dry or wet deposition is a function of the spatial distribution of the trees, the duration of exposure and climate, species type (leaf area, surface texture), the habitus of the plants (evergreen or deciduous) and the exchange of gas (rate between leaf and atmosphere, multiple stress responses) (Youssef, 2020). The ability of tree plants to accumulate metals is dependent on the humic substances or other chelating substances, temperature and salinity.

An efficiently good bio-monitor will not only exhibit the presence of the pollutant but also provide additional information about the quantity and intensity of the exposure. Metal uptake by

vegetation can be element specific, plant species specific and plant tissue specific (Adesuyi et al., 2018). Fast-growing, metal accumulating tree plants have been considered as tangible replacement for herbaceous hyperaccumulators, in the development of workable phytoextraction model. Unarguably, uninterrupted phytoextraction process could be achieved on a perennial basis employing readily manageable tree plants that could accumulate large levels of heavy metal pollutants in their aerial tissues, while, producing high biomass (Olayiwola et al., 2021). Buttressing this assertion, *Salvinia minima* was discovered to have the capacity to remove lead from aqueous solutions, whilst *Cladophora* sp. is able to hyperaccumulate arsenic (Adesuyi et al., 2018). Tree plants are reported to be filters of air pollutants generated from the various anthropogenic activities, domestic undertakings and industrial factory players. Tree plants also act as excellent bio-indicators of air quality. Undoubtedly, some of these heavy metals have an unknown metabolic function, such as Cd, Pb, As and Hg, while others are classified as essential elements used as micronutrients necessary for plant growth and development, such as Zn, Cu, Mn, Ni, and Co. The leaves of tree plants are therefore perfect indicators of atmospheric air pollution. Previous studies maintained that chlorophyll and protein components of the leaves of plant species are lower in trees growing in polluted areas compared to their counterparts in pollution free regions. The slow disappearance of chlorophyll is a confirmation of the yellowing of leaves (Salih and Aziz, 2018).

Considering the near to zero scientific information about the bioaccumulation of heavy metals in arid tree plant species in Kazaure metropolis, hence, the objectives of this present study are to identify the causal elements in environmental pollution, to investigate the concentration of heavy metals in dominant tree plants species present in kazaure metropolitan area; and to assess the opportunity of using these aforementioned plant species as indicators of the arid ecosystems pollution level with heavy metals and also their feasibility for phytoremediation.

MATERIALS AND METHODS

Reagents and Equipment

The reagents such as chromium (III) trioxonitrate (V) (60.5%), cobalt chloride (98%), lead chloride (99%), manganese tetraoxosulphate (VI) (97%) and zinc trioxonitrate (V) ($\geq 99\%$) employed in the production of standard solutions of 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 samples was conducted in an electric oven (Asturias, Spain). The grinding of the leaves 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 Areas

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, HAFED polytechnic, Kazaure (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).

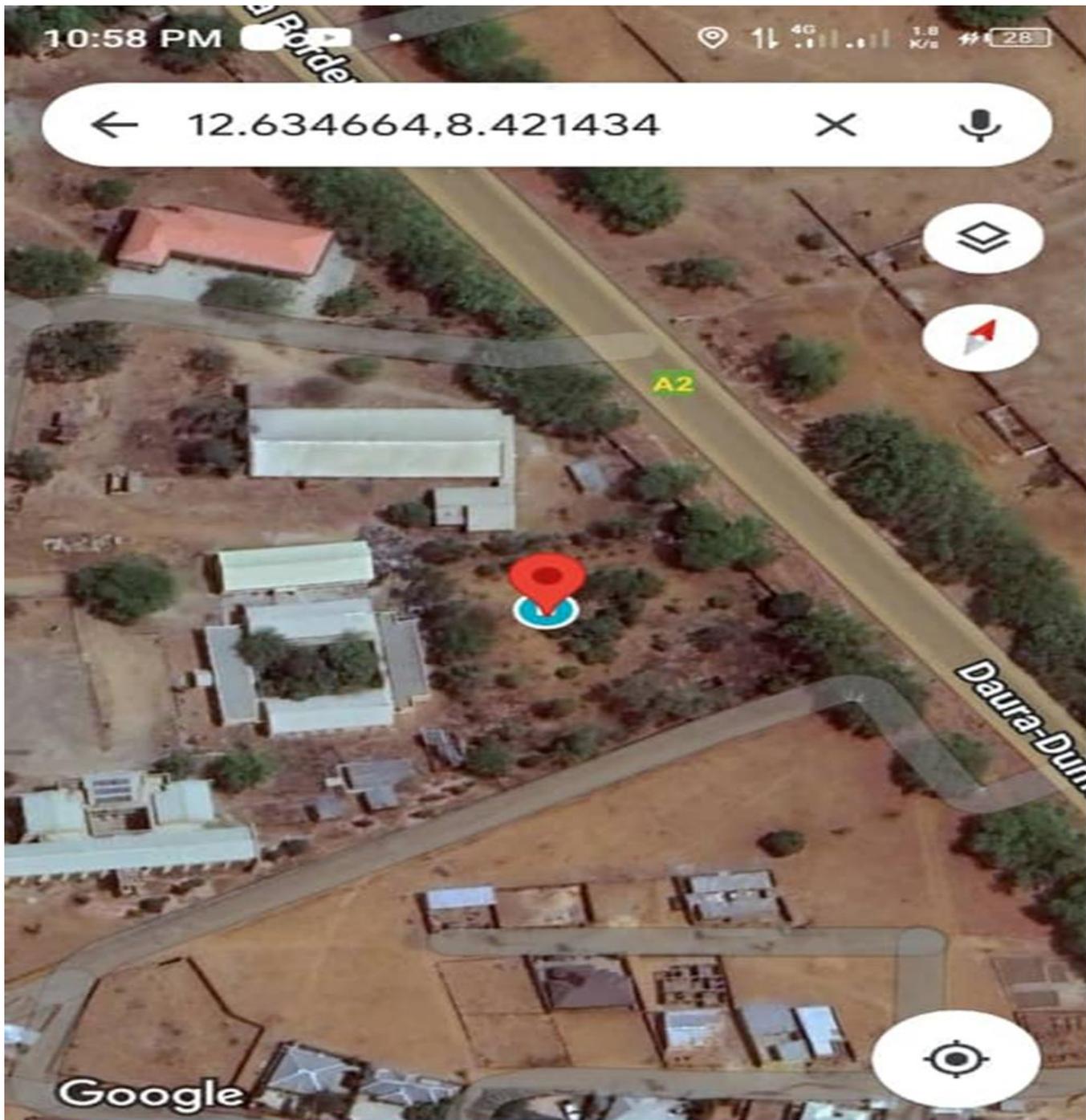


Fig. 1 Study site : Hussaini Adamu Federal Polytechnic, (HAFED POLY) Kazaure

Sample Collection and Treatment

Samples of leaves were obtained during the months of July, August and September 2023 from different locations in the premises of HAFED polytechnic, Kazaure. Ten samples of each tree plant leaves were gathered for analysis. Samples of leaves from each tree plant were collected at varying distances from one another by hand clipping 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 were placed in plastic bags, labeled and transported to the biological laboratory of the department of Science Laboratory Technology, Hussaini Adamu 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, ground into powder and sieved to obtain fine powder of what particle size ($d > 250\mu\text{m}$). Each powdered samples (23g) were weighed into 100cm³ beaker of known weight and oven dried at a temperature of 105⁰C 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 550⁰C using 10cm³ of 6M nitric acid. The mixture was filtered into 50cm³ 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 2000⁰C (Model Perkin Elmer 3110). A procedural blank and a set of standard 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 proposed HMs in the likes of cobalt (Co), Chromium (Cr), copper (Cu), iron (Fe), manganese, (Mn), nickel (Ni), lead (Pb) and zinc (Zn) are all detected. Triplicate reading and value recording was carried for each heavy metal determination via AAS. The mean and standard deviation of the values were evaluated and thus tabulated as shown in Table 1. The evaluated values of mean and standard deviation are approximated to two places of decimal for easy interpretation and discussion. This is also done for the sake of uniformity in data reporting. The heavy metals are tabulated against the named tree plants as the case may be. The heavy metals are arranged horizontally in an almost alphabetical order. The same order is applicable to the vertically placed tree plants (Table 1). The mean and standard deviation of the instrumentally measured values of the heavy metal types that constitutes environmental burden in Kazaure Local Government Area of Jigawa State is hereby presented in Table 1.

Table 1: Concentration of heavy metals (Co, Cr, Cu, Fe, Ni, Mn, Pb, Zn) in tree plants in Kazaure

Tree plants	HMs Concentration in the leaves of Tree plants, mg/Kg, Dry Matter							
	Co	Cr	Cu	Fe	Ni	Mn	Pb	Zn
Cassia acutifolia	12.01± 0.18	0.95± 0.02	0.50 ±0.01	92.52± 0.17	0.40 ± 0.02	44.05± 0.21	3.03± 0.16	1.75 ± 0.03
Casuarina equisetifolia	5.03± 0.16	8.56± 0.22	0.50 ±0.02	199.92± 0.39	2.02 ± 0.17	46.02± 0.17	3.03 ± 0.16	12.54± 0.20
Dalbergia nigra	20.00± 0.18	3.06± 0.12	1.06± 0.31	100.02± 0.17	0.80 ± 0.03	25.03± 0.16	3.03± 0.18	13.01± 0.18
Mangifera indica	12.02± 0.17	0.60± 0.03	3.05± 0.11	75.03± 0.16	0.90 ± 0.03	4.03± 0.16	1.02± 0.17	75.02± 0.16
Terminalia catappa	2.52± 0.21	0.73± 0.17	2.00± 0.12	185.02± 0.14	5.06 ± 0.14	16.80± 0.06	4.04± 0.17	12.54± 0.18

Means of three replicates ± standard error (n = 3)

As unveiled in Table 1, based on specific tree leaves analysis, Cassia acutifolia leaves accumulated 92.52 mg/Kg Fe as the highest and 0.40 mg/Kg Ni has the least HMs. The bio-monitoring potential of this plant in respect of

Cu (0.50 mg/Kg) and Ni (0.40 mg/Kg) is almost the same. These results also suggest that leaves of *C. acutifolia* are good bio-monitor of iron (92.52 mg/Kg), manganese (44.05 mg/Kg) and cobalt (12.01 mg/Kg). Considering *Casuarina equisetifolia* the range of bio-accumulated HMs level is 199.92 mg/Kg – 0.5 mg/Kg. The leaves sample of *C. equisetifolia* displayed great bio-monitoring potential in respect of Fe (199.92 mg/Kg), Mn (46.02 mg/Kg) and Zn (12.54 mg/Kg). The bio-accumulation range of HMs in *Dalbergia nigra* is 100.02 mg/Kg – 0.80 mg/Kg. The bio-monitoring tendency of the leaves of *D. nigra* to access the levels of Fe (100.02 mg/Kg), Mn (25.03 mg/Kg), Co (20.00 mg/Kg) and Zn (13.01 mg/Kg) is high in Kazaure and its environs going by the outcomes of this study. In the case of *Mangifera indica* the range of HMs is 75.03 mg/Kg – 0.6 mg/Kg. The levels of Fe and Zn approximate to the same value. The results suggest that leaves of *M. indica* are capable of bio-monitoring Fe (75.03 mg/Kg), Zn (75.02 mg/Kg) and Co (12.02 mg/Kg). The range of HMs divulged by the leaves of *Terminalia catappa* is 185.02 mg/Kg – 0.73 mg/Kg. The leaves of *T. catappa* revealed excellent bio-monitoring potential towards Fe (185.02 mg/Kg) and good monitoring prowess towards Mn (16.80 mg/Kg) and Zn (12.54 mg/Kg). The mean total HMs level in the leaves of the five tree plants used for the present study is as follows; *C. acutifolia* (19.40 mg/Kg) *C. equisetifolia*, (34.70 mg/Kg) *D. nigra* (20.75 mg/Kg) *M. indica* (21.46 mg/Kg) and *T. catappa* (28.59 mg/Kg) (Fig. 2). The results advocated that *C. equisetifolia* is a prominent bio-monitor of HMs in the environment of Kazaure LGA over other tree plant leaves. Tree plants in the urban centers are potential reductants of environmental pollution as they accumulate HMs via their tissues (Al-Heety, et al., 2021). Going by the outcomes of this study, most of the plant’s species are hyperaccumulators. This quality corroborates their phytoremediation potential in the biomonitoring of HMs based environmental pollution. Leaves of tree plants with above the normal level of bioavailable HMs may be said to exhibit hyperaccumulation. The excess amount of which may be introduced from the environment.

However, HMs level in leaves (tissue) of tree plants may be attributed to a number of variables such as age of plant, species of plant, plant organ or tissue, type of soil, soil organic content, pH of soil, edaphic (geological) metal concentration and cation exchange capacity (Al-Heety, et al., 2021).

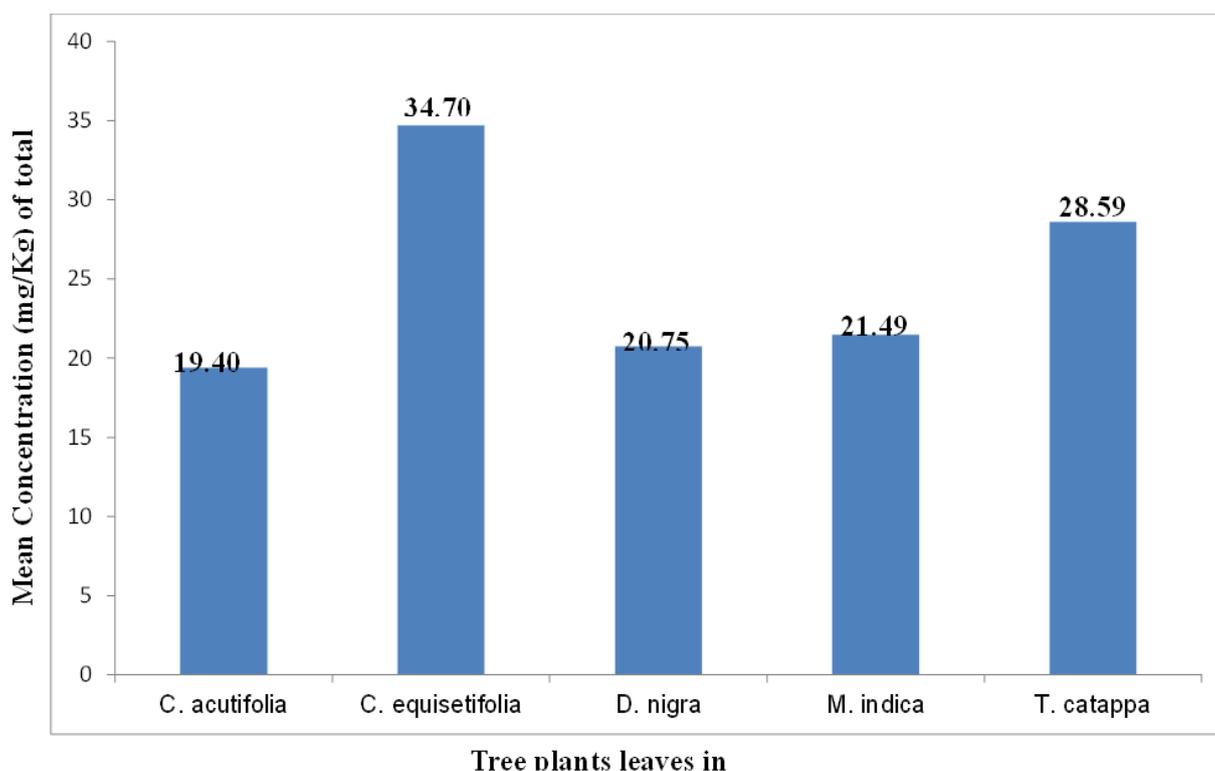


Fig. 2: Mean concentration of total HMs in leaves of tree plants in Kazaure

On the metal bias analysis, the individual heavy metal is discussed with respect to the accumulation potential of leaves of the five tree plants under study.

Cobalt is one of the essential heavy metals required in trace quantity for plant development (Akanbi et al., 2024). Excess level of Co often resulted in metabolic processes disruption (Smilagić et al., 2021). Animal or human

that feeds on such plant will be at risk, thus constituting environmental pollution (Salih and Aziz, 2018). As manifested in Table 1, the highest (20.00 mg/Kg) and lowest (2.52 mg/Kg) concentration of Co in the leaves samples were found in *D. nigra* and *T. catappa* respectively. Salih and Aziz (2018) in their study of five plants species (*Olea europaea* L., *Eucalyptus amygdalina*, *Nerium oleander* L., *Dodonaea viscosa*, and *Phragmites australis*) in the city of Erbil, Iraq observed cobalt concentration range of 2.24 – 4.30 mg/Kg. These values are far smaller than those reported in the present study. Also Al-Heety, et al., (2021) reported lower Co concentration range of 1.71 to 2.24 in their study using six plant species to determine HMs in Ramadi city Baghdad, Iraq. Cobalt is one of the essential HMs necessary for plant growth and development usually in trace amounts (Salih and Aziz, 2018, Akanbi et al., 2024). The levels of Co metal in *C. acutifolia*, *M. indica* and *D. nigra* are superior to the toxic level 10 mg/kg in plants. The FAO/WHO (2007) permissible limit for Co is 0.05 mg/Kg for plants. The concentrations of cobalt in all the analyzed plant leaves are well above the FAO/WHO permitted level. The high levels of Co among the plants suggest that all the plants are hyperaccumulators of Co. The excess concentration might have arisen from the activities in ecosystem of Kazaure. Such activities include numerous power generators (Al-Heety, et al., 2021) and heavy traffic in the studied area (Akanbi et al., 2024). This equally implies that the leaves of the plants studied are excellent biomonitors of Co in the environment of Kazaure. Additionally, the levels of Co in *C. acutifolia* (12.01 mg/Kg), *M. indica* (12.02 mg/Kg) are slightly above the toxic concentration of 10.00 mg/Kg mentioned by Salih and Aziz (2018). Co concentration in *D. nigra* (20.00 mg/Kg) is the highest among the tree plants studied. The level of Co in *C. equisetifolia* (5.03 mg/Kg) almost doubles that of *T. catappa* though both values are below the toxic level.

Chromium is one out of many toxic HMs affecting the biotic components of the ecosystem. People that possess allergy to Cr are prone to asthma attack. Nasal discharge, nasal bleeding and itching are evident. Air borne Cr if inhaled leads to perforations of the upper respiratory tract (Aricak et al., 2019). Chromium displayed the most towering level in *C. equisetifolia* (8.56 mg/ Kg) and a stubby level in *M. indica* (0.60 mg/Kg). In the study of Qadir et al., (2021), the concentration range of Cr among *Azadirachta indica*, *Cassia fistula* and *Pithecellobium dulce* leaves is 1.08 – 4.83 mg/Kg across three seasons in suburban regions of Delhi India. Qadir and co thus reported a lower level of Cr compared to the findings of the present work. The permissible limit set by FAO/WHO (2007) for Cr is 2.30 mg/Kg. the Cr level in *C. equisetifolia* almost quadruples the standard limit and it is also the highest concentration recorded for the metal among all the studied plants. The amount of Cr in *D. nigra* is approximately a unit more than the standard limit. Conversely, the Cr level in the trio of *C. acutifolia*, *M. indica* and *T. catappa* approximates unity (Table 1) and below the standard limit. Cr is one of the important mineral elements present in tree plants (Smailagić et al., 2021). These results suggest that *C. acutifolia*, *M. indica* and *T. catappa* are deficient in Cr. They may be said to be poor bio-accumulators of Cr. The elevated level of Cr recorded in the duo of *C. equisetifolia* and *D. nigra* is toxic. Such toxicity may be unveiled in non-carcinogenic human health hazards (Smailagić et al., 2021) when these plants are consumed. The excess concentration of Cr may be introduced to the plant via its interaction with the environment. These outcomes purport that the duo *C. equisetifolia* and *D. nigra* are good bio-accumulators of Cr. Additionally, *C. equisetifolia* is an excellent bio-accumulator of Cr and may be adjudged the most prominent bio-monitor of Cr in the studied area.

Copper is useful in correcting nutritional deficiencies in plants at low concentration. Higher concentration gives rise to physiological malfunctions in developing plants (Salih and Aziz, 2018). The level of copper is elevated in the leaves sample of *M. indica* (3.05 mg/ Kg) while the level of the same metal is least in *C. acutifolia* and *C. equisetifolia* (0.50 mg/ Kg). Both plants flaunted the same bio-monitoring potential towards Cu. The concentration range of Cu (26.39 – 64.02 mg/ Kg) determined by Salih and Aziz (2018) is senior to the values reported in our findings, likewise the outcomes of Qadir et al., (2021) on Cu (12.94 – 26.60 mg/ Kg) content in tree plants grown in Delhi India. The concentration range of 1.00 – 20.00 mg/ Kg describes the genuine amount of Cu in plants (Salih and Aziz, 2018). The levels of Cu in the leaves samples of all tree plant species unveiled in the present study are below this limit. The results of this study concord with the findings of Rahman et al., (2022). The results of the present work advocate that there is zero contamination of the plant organ from the environment of Kazaure. Despite, the fact that particulate can gain entry into the tree plants through the stomata of the leaves (Jamhar et al., 2022), the stomata of the studied plant leaves seems to defy this assertion. The outcomes also typify zero interaction between the plants and the environment. The low level of Cu observed in this work is due to the inhibitory effect of large amount of Zn present in the leaves of all the studied plants (Fig. 3). This reason often corroborates the opposite trend for the level of Cu and Zn in tree plants (Smailagić et al.,

2021). Furthermore, the leaves of all the plants are deficient in Cu as indicated by the results of this study. Thus, all the tree plants are poor bio-accumulators of Cu. They may be said to be poor bio-monitors of Cu.

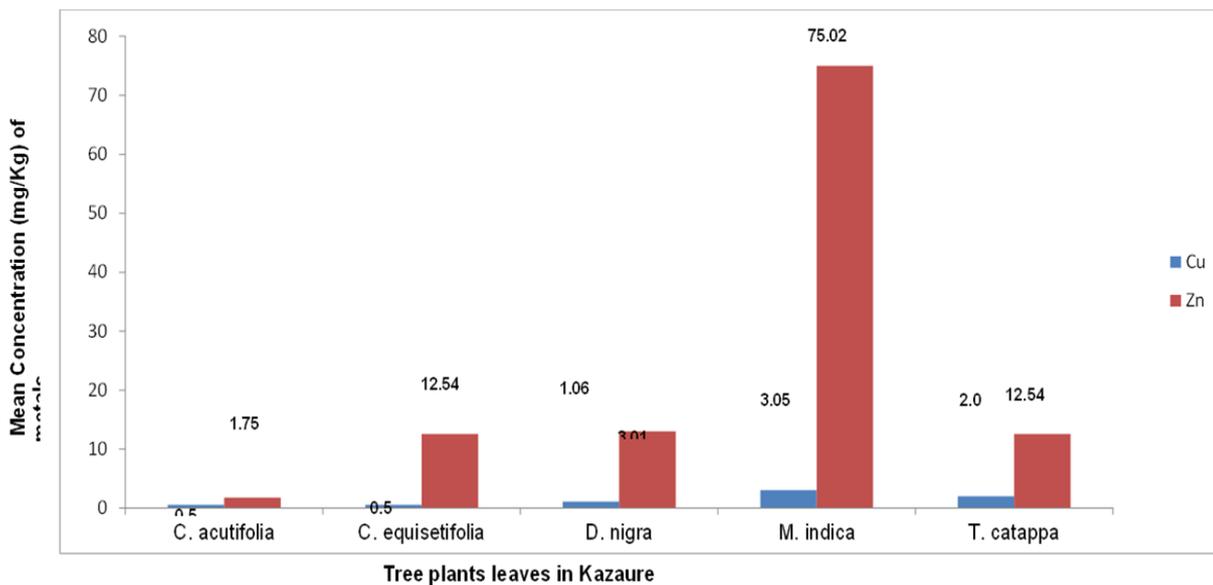


Fig. 3: Inhibitory effect of the levels of Zn over Cu among the tree plants in Kazaure

Iron is one the plant available mineral nutrients necessary for several physiological processes in plants notably photosynthesis (Salih and Aziz, 2018). The leaves sample of *C. equisetifolia* (199.92 mg/ Kg) maximally concerted Fe over other leaves samples while the leaves of *M. indica* (75.03 mg/ Kg) exhibited the least amount. The range of Fe in this study is greater than that (30.43 – 102.13mg/ Kg) reported by Salih and Aziz (2018). The level range of Fe (59.70 – 502.07 mg/ Kg) reported by Qadir and colleagues is on the higher side (Qadir et al., 2021). Fe is said to be toxic in plants at 300ppm (Salih and Aziz, 2018) and in this study the level of Fe is below this stated value. The outcome of the present findings is in agreement with the work of Olayiwola and Co (2021). Burd et al., (2000) reported the so-called critical concentration of Fe as 50 mg/Kg of dry matter. According to Djelic et al., (2021) Fe possessed a lethargic effect at a concentration range of 50 – 1000 mg/Kg which could ultimately leads to death. Although, the value observed in this work is higher than this critical level, no harmful effect orchestrated. Absorption of Fe by plant from soil is a function soil pH and redox potential, concentration as well as the proportion of other heavy metals present (Brković et al., (2021) the results of the present study buttress this stand. The Fe level reported in the present study testified that numerous elements present in the soil affect the concentration of Fe uptake by the studied plants. However, all the organs so considered displayed efficient bio-accumulation potential towards the bio-monitoring of Fe in Kazaure and its environs.

Nickel is highly essential in the metabolic pathways of higher tree plants (Salih and Aziz, 2018). The leaves sample of *T. catappa* (5.06 mg/ Kg) condensed the highest amount of nickel while *C. acutifolia* (0.40 mg/ Kg) recorded the least amount of the same metal. The Ni concentration range (18.45 – 37.93 mg/ Kg) observed by Salih and Aziz (2018) is greater than those announced in this study. The levels of Ni obtained in this work are almost the same as the environmental standard range 1.00 – 5.00 mg/ Kg (Salih and Aziz, 2018). According to Qadir et al., (2021), a lower concentration range of Ni (2.21 – 8.16 mg/ Kg) is determined in three species of tree plants. These values as unveiled by this work, presupposed that the concentration of Ni is not hazardous to the plants and indirectly the consumption of such plants pose no health risk to the biota of Kazaure and its environs. The FAO/WHO (2007) permissible limit for nickel is 1.50 mg/Kg. the levels of Ni is lower in *C. acutifolia* (0.40 mg/Kg), *D. nigra* (0.80 mg/Kg), and *M. indica* (0.90 mg/Kg), than the permitted limit set by FAO/WHO indicating no environmental pollution of the metal while those of *C. equisetifolia* (2.02 mg/Kg), and *T. catappa* (5.06 mg/Kg) are above the said limit revealing Ni metal pollution in Kazaure and its environs. The high amount of Ni recorded may be due to closeness of the tree plants to the road where human activities such vehicular trafficking and coal burning operations are evident (Al-Heety et al., 2021). However, all the reported values are not phytotoxic. Employing the yardstick of the set permissible limit of FAO/WHO, *C. equisetifolia* and *T. catappa* may be said to be hyperaccumulators of Ni. Thus, affirming their bio-monitoring potential of

environmental nickel. The fast-growing and high biomass quality of the duo confirmed their bio-accumulation potential (Brković et al. (2021).

Manganese is one of the mineral nutrients that are readily present in the plants. Manganese is largely present in the leaves sample of *C. equisetifolia* (46.02 mg/ Kg) and *C. acutifolia* (44.05 mg/ Kg) while the same metal is least present in the leaves of *M. indica* (4.03 mg/ Kg). The Mn concentration range (73.66 – 521.23 mg/ Kg) posited by Salih and Aziz (2018) is much superior over the results of this study. A somewhat lower range for Mn (29.71 – 58.51 mg/kg) is reported by Qadir and Co (Qadir et al., 2021). The levels of Mn in all tree plant species in the study area are smaller than the threshold micronutrient level in animal feeds of more than 70 mg/kg (Salih and Aziz, 2018). Brković et al. (2021) said the mean Mn contents in leaves in the normal range is 15-100 mg/Kg while FAO/WHO (2007) gave the permissible limit of 67 mg/Kg. otherwise the outcomes of this research posited lower concentrations of Mn across all the studied tree plants; *C. acutifolia* (44.05 mg/Kg), *C. equisetifolia* (46.02 mg/Kg), *D. nigra* (25.03 mg/Kg), *M. indica* (4.03 mg/Kg), and *T. catappa* (16.8 mg/Kg). These results indicate low bioaccumulation of Mn across the studied plant species. Particularly, *M. indica* is deficient in Mn as the reported value is below the lower range of the normal level of Mn in leaves of tree plant going by the findings of Brković et al. (2021). However, zero Mn pollution threshold is established among the tree plants in this study as the mean Mn concentration is below the permissible limit set by FAO/WHO. This may translate to non-phytotoxicity of the metal in the studied plants. Also, four of the tree plants displayed promising bio-accumulation prowess towards Mn. *C. acutifolia*, *C. equisetifolia*, *D. nigra* and *T. catappa* are excellent bio-monitors of Mn in Kazaure and its environs.

Lead is one of abundant toxic heavy metals, often classified as non-essential heavy metals. It is a member of the class of mutagenic, carcinogenic and those with toxic effects on reproduction (Haider et al., 2021). Anthropogenic activities are the main reservoirs of lead contamination, such as automotive transportation, industrial processes (Salih and Aziz, 2018). Lead is highest in the leaves sample of *T. catappa* (4.04 mg/ Kg) and the lowest amount is uncovered in the leaves of *M. indica* (1.02 mg/kg). However, the leaves samples of *C. equisetifolia* and *C. acutifolia* accumulated the same level of Pb (3.03 mg/ Kg). The concentration range of Pb (89.05 – 144.31 mg/ Kg) observed by Salih and Aziz (2018) is greater than those revealed in this study. The concentration range reported by Qadir et al., (2021) for Pb (9.54 – 16.40 mg/ Kg) is lower than the value given by Salih and Aziz. According to Kabata-Pendias & Pendias (2001), the concentration of Pb metal in a plant is considered to be normal within the range

of 0.1–10.0 mg/Kg. The concentration of Pb in the leaves samples of studied tree plants in this finding is within the normal range. The findings of the present work tally with the pronouncement of the results of the work conducted by Mariwy et al., 2024 on bioaccumulation of Pb in mangrove plants (*Rhizophora apiculata*). The FAO/WHO (2007) permissible limit for Pb is 0.20 mg/Kg. Plants absorb lead from the air mainly through the leaves and high traffic intensity is a major precursor of Pb in the environment (Lovynska et al., 2023). Also, numerous studies have shown that atmospheric deposition mainly affects the level of Pb in vegetation (Laptiev et al., 2024). It is evident from the results of the present study that all the leaves samples bioaccumulated Pb above lower level of the normal range of the metal but above the permissible limit set by FAO/WHO. Therefore, the values of Pb may be said to be non-phytotoxic because some works reported a value of 30 mg/Kg to be toxic (Lovynska et al., 2023). Meanwhile for the reported values to be well above the set permissible limit presume that the all leaves effectively bioaccumulate Pb. It may be finalized that all studied plant species are proficient bio-monitors of Pb in kazaure and its surroundings.

Zinc is also one of the phyto-available essential nutrients. When present in excessively large amount, it becomes toxic to plants generating unusual biochemical and physiological changes in the plants. Depending on the species of plant, the toxic level of Zn is given in the range 300 – 400mg/Kg (Salih and Aziz, 2018). The concentration of Zn in the leaves of *M. indica* (75.02 mg/kg) is highly intense while the amount of the same metal is least intense in *C. acutifolia* (1.75 mg/kg). The leaves samples of *C. equisetifolia* and *T. catappa* show equal level for Zn (12.54 mg/ Kg) bio-accumulation. The range of level of Zn in this work is largely small compared to the range (484.80 – 912.33 mg/ Kg) reported by Salih and Aziz (2018). The outcome of this work for Zn levels is in agreement to the study conducted by Qadir et al., (2021) in suburban regions of Delhi India. The FAO/WHO (2007) permissible limit for Zn is 100.00 mg/Kg. The level of Zn as determined in this study may indicate the apoplasmic nature of absorption or a barrier-free mechanism of bioavailability of Zn metal from the soil to the

roots and aboveground

Phytomass (Laptiev et al., 2024). Based on the findings of this work, the Zn bioconcentration is very low compared to the toxic level, thus its level is non-phytotoxic. The leaves of *M. indica* with the highest value of Zn are the most effective bio-monitor of Zn in the environs of Kazaure LGA.

Hyperaccumulation potential is the ability of plant parts to absorb, translocate and accumulate HMs in amounts more than those found in the environment (Gupta et al., 2016). In summary, plants are referred to as hyperaccumulators if their metal bioconcentration level is greater than 1000 mg/Kg and non-hyperaccumulators when the metal level is below 500 mg/Kg (Maestri et al., 2010). Based on these proportions, all the plants studied are non-hyperaccumulators. This is because on particular element basis, Fe is the largely concentrated HMs in the leaves of *C. equisetifolia* (199.92 mg/Kg). Additionally, considering the total metal levels in each tree plants, the highest value stands at 277.60 mg/Kg (Fig. 2) which is equally less than 500 mg/Kg. In a nutshell, be it individual or combined elemental basis, all the assayed tree plants leaves are non-hyperaccumulators of environmental HMs in the Kazaure and its environs.

The outcome of this study as displayed in Table 1 shows that the leaves of *D. nigra* is well suitable to bio-monitor Co, using the yardstick of specific leaves basis of tree plants. It should be recalled that all the trees are located in the same area, experiencing the same environmental impact (Fig. 1). Chromium, iron and manganese are best bio-monitored by the leaves of *C. equisetifolia*. The leaves of *M. indica* are proficient bio-monitors of Cu and Zn. The leaves of *T. catappa* exhibit great tendency in the bio-monitoring of lead and nickel.

Statistical analysis

Correlation coefficient: Spearman’s correlation was conducted at the confidence level of 95%

Table 2: Correlation coefficient values (r) between total heavy metal concentrations among tree plant species

	<i>C. acutifolia</i>	<i>C. equisetifolia</i>	<i>D. nigra</i>	<i>M. indica</i>	<i>T. catappa</i>
<i>C. acutifolia</i>	1.0000				
<i>C. equisetifolia</i>	0.8330*	1.0000			
<i>D. nigra</i>	0.9786**	0.9040**			
<i>M. indica</i>	0.8095*	0.5952	0.7381*	1.0000	
<i>T. catappa</i>	0.5952	0.6667	0.5714	0.6667	1.0000

r – Spearman Pearson- correlation coefficient: 0-0.3: no correlation; 0.3-0.5: poor correlation; 0.5-0.7: medium correlation; 0.7-0.9: high correlation *; 0.9-1.0: a very high statistically significant correlation **.

The total HMs levels in the pairs of *D. nigra* / *C. acutifolia* and *D. nigra* / *C. equisetifolia* portends a very high statistically significant correlation as displayed in Table 2. However, high correlation is observed in the total HMs levels in the pairs of *C. equisetifolia* / *C. acutifolia*, *M. indica* / *C. acutifolia* and *M. indica* / *D. nigra*. The remaining pairs of tree plants recorded medium correlation, as observed in *T. catappa* / *C. acutifolia*, *T. catappa* / *C. equisetifolia* , *T. catappa* / *D. nigra* , *T. catappa* / *M. indica*, *C. equisetifolia* / *M. indica*. Above all this statistical analysis suggests that all the tree plant leaves are potential biomonitors of HMs in the environs of Kazaure.

Table 3: Analysis of variance between metal concentrations in the leaves of tree plant species

	<i>C. acutifolia</i>	<i>C. equisetifolia</i>	<i>D. nigra</i>	<i>M. indica</i>	<i>T. catappa</i>	Mean
Co	12.01 ^c	5.03 ^e	20.00 ^b	12.02 ^b	2.52 ^f	10.32
Cr	0.95 ^f	8.56 ^d	3.06 ^e	0.60 ^g	0.73 ^h	2.78
Cu	0.50 ^g	0.50 ^h	1.06 ^f	3.05 ^d	2.00 ^g	1.42

Fe	92.52 ^a	199.92 ^a	100.02 ^a	75.03 ^a	185.02 ^a	130.50
Ni	0.40 ^g	2.02 ^g	0.80 ^g	0.90 ^f	5.06 ^d	1.84
Mn	44.05 ^b	46.02 ^b	25.03 ^c	4.03 ^c	16.80 ^b	27.19
Pb	3.03 ^d	3.03 ^f	3.03 ^e	1.02 ^e	4.04 ^e	2.83
Zn	1.75 ^e	12.54 ^c	13.01 ^d	75.02 ^a	12.54 ^c	22.97
Mean	19.40	34.70	20.75	21.46	28.59	

Notes: presented values were shown as mean; 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 ($P < 0.05$).

As shown in Table 3, there are significant differences in almost the HMs levels in *C. acutifolia* with the exception of Cu and Ni. Similar scenario ensued in *D. nigra* where there is no significant difference in the levels of Cr and Pb. Additionally, there exists no significant difference in the levels of Fe and Zn in the leaves of *M. indica*. The reverse is the case in *C. equisetifolia* where all levels of HMs bioaccumulated are significantly different. The same observation is seen in *T. catappa* as evident in *C. equisetifolia*. This analysis equally buttresses the fact that all the studied tree plant leaves are capable of biomonitoring HMs in Kazaure and its environs.

CONCLUSION

The present study successfully determined the levels of major atmospheric heavy metal particulates in Kazaure and its environs using the leaves of five named tree plants. The data obtained as a result of the research indicate almost significant differences in the levels of HMs bioaccumulated in the leaves of the plant species. Few of the HMs have their values above the permissible level. The duo of *C. equisetifolia* and *T. catappa* had the highest level of total HMs, thus are better biomonitors of the metals in the studied area. These tree plants can also be employed in the phytoremediation of the area. Our findings also maintained that none of the tree plants is hyperaccumulator judging by the outcomes of the present study. However, almost all the tree plants are potential biomonitors of HMs in Kazaure LGA. Considering the rising interest in the use of tree plant species in metropolitan green space systems to mitigate the negative environmental risks caused by uncompromising soaring levels of HMs, conduction of further research is pertinent to fill in the gaps related to the features of transportation, accumulation, and mechanisms of interaction of such HMs in various separate plant organs.

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