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ORIGINAL RESEARCH ARTICLE

Quantitative determination of heavy metals around schools and automobile workshops near frequented roads in Kaduna State, Nigeria

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ABSTRACT

Heavy metals are metallic elements with high density compared to other metals and are toxic even at minute concentrations. The concentration of these metals around schools and automobile workshops near frequented roads in Kaduna State, Nigeria, was reported in the present work. Soil samples were collected at varying distances from the major roads (0 – 10m) and at different depths (0 – 60cm). The elemental composition of the samples was determined using Next-Generation Cartesian Geometry Energy Dispersive X-Ray Fluorescence Spectrometer (NEX CG EDXRF) and the statistical correlation and clustering analysis were carried out using SPSS and Mini tab, respectively. The heavy metals Sn, Hf, Ta, V, Cr, Zn, Ir, Pt, Au, Mn, Fe, Co, Ni, Cu, Pb, Th, Ga, As, U, and Zr were considered in the analysis, and their concentrations were presented as Average ± standard deviation. Pearson correlation coefficient indicated different levels of relationships among the heavy metals, while Clustering analysis grouped the soil samples into three major clusters, further confirming the interrelationship among the samples. The concentrations of As, Pb, Cd, Co, Ni were found to be of serious health concern, considering that in almost all the zones in Kaduna state, their average concentrations were greater than the threshold provided by WHO/FAO. Findings from this study indicated that it is unsafe for children to play near schools /auto-mechanic workshops located along highways.

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INTRODUCTION

Heavy metals have been on the earth since the creation of the universe; however, in some instances, human activities aggravate their concentrations (Vitousek, *et al*., 1997; Bello *et al*., 2017; 2019a and b; Rahman & Singh, 2020). When solid wastes containing metals are released into the atmosphere and atmospheric deposition, heavy metals can travel great distances and be transferred to soils (Agoro, *et al*., 2020). Because they cannot degrade, heavy metals remain in the environment for an extended period and have hazardous consequences on nearby people (Tchounwou, *et al*., 2012; Ali, *et al*., 2013). Some heavy metals, even in trace amounts, are considered to be highly poisonous and dangerous, including arsenic (As), lead (Pb), cadmium (Cd), nickel (Ni), mercury (Hg), chromium (Cr) (VI), cobalt (Co), zinc (Zn), and selenium (Se) based on their toxicity profiles (Vhahangwele and Khathutshelo, 2018; Tchounwou, *et al*., 2012; AMAP/UNEP, 2013; Oludare & Opeyemi, 2019; Clemens, *et al*., 2013; Rahman, & Singh, 2020). Heavy metal soil pollution from car sources has been viewed as a severe environmental problem (Ogwo *et al*., 2015; Yusuf, *et al*., 2015; Laxmi, 2016; Nkwoada *et al*., 2018; Ogunkolu *et al*., 2019; Zwolak, *et al*., 2019; Adewole, & Uchegbu, 2010; Aloysius *et al*., 2013; Morka, *et al*., 2016; Rabe, *et al*., 2018). These metals are released as a result of fuel combustion, tire wear, oil leaks, and corrosion of metal automotive parts (Dolan, *et al*., 2006). Heavy metal pollution are primarily found in vehicle exhaust. Due to its inclusion in fuel as an antiknock agent, lead (Pb), cadmium (Cd), zinc (Zn), and nickel (Ni) are the most metal pollutants from heavy traffic (Simon et al., 2013; Ahmed et al., 2015). Regrettably, little research on heavy metals contamination of children's school playgrounds and auto mechanics sites along the roadside along the frequented road due to car exhaust in Kaduna state existed as at the time of this research. It is hypothesized that public/private schools and automobile workshops within a residential area near frequented roads present themselves as appropriate targets for assessing the heavy metal content of playground surface soil contamination since the occupants of the target site

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include children and infants. Hence, it is pertinent to determine the concentration of heavy metals around school playgrounds close to main/busy roads and automobile workshops in Kaduna State, Nigeria.

MATERIALS AND METHODS

The Study Area and sample collection

Kaduna State shares common boundaries with Zamfara, Katsina, Niger, Kano, Bauchi, and Plateau States and is located in the central region of northern Nigeria. The State and Abuja, the Federal Capital Territory, share a boundary to the southwest (Kaduna, 2019). A total of fourteen (14) local government areas from three geopolitical zones were chosen for the study out of the twenty-three local government areas (LGAs) in the state. The sampled areas were selected randomly bearing in mind the closeness of mechanic garage/schools to busy roads. Soil samples were collected at specified locations from road end. The top 0 -1.0cm surface soil samples were collected at varying distances ranging between (0 – 10m) and depths (0 – 60cm) with the help of auger machine from road end to residence schools and mechanic garages.

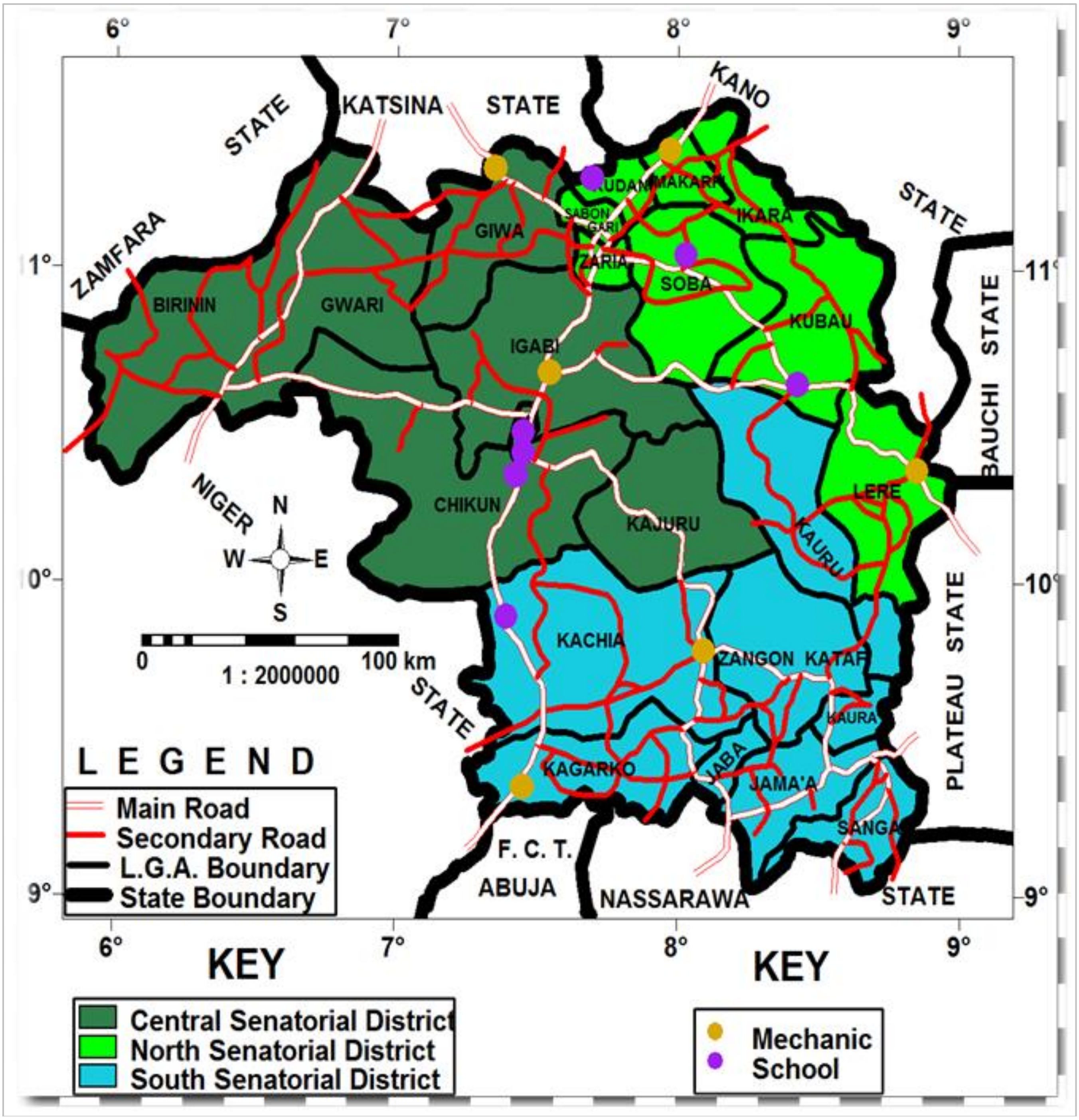

Fig 1.0: Sampling locations for Kaduna north, Kaduna central and Kaduna south

The focus on the top 1.0 cm surface soil is because it is the portion most accessible to local government areas from three geopolitical zones were chosen for the study out of the twenty-three local government areas (LGAs) in the state. The sampled areas were selected randomly bearing in mind the closeness of mechanic garage/schools to busy roads. Soil samples were collected at specified locations from road end. The top 0 -1.0cm surface soil samples were collected at varying distances ranging between (0 – 10m) and depths (0 – 60cm) with the help of auger machine from road end to residence schools/mechanic garages. The focus on the top 1.0 cm surface soil is because it is the portion most accessible to children and likely to cause an immediate hazard to the occupants or the target group and distance 0 – 10m form the children's playground. Collected samples were safeguarded from cross-contamination to maintain good accuracy and purity of samples.

Preparation and laboratory analysis of samples

The soil samples were gathered and sieved to grain size of 50 nm and stored in labeled double polythene bags sample storage plastics. The analysis was carried out in UTM Laboratory, Malaysia. In the laboratory, 3-5 grams of the sieved sample was poured into white circular cups of 7- 8 cm and a Prolene thin film pressed with a rod to make it compact (air tight) and then brought to an air-tight EDXRF chamber for examination. The elemental makeup of the samples was determined using NEX CG EDXRF MODEL with the brand name RIGAKU. The instrument is equipped with a silicon drift detector, a Pd X-ray tube for producing X-rays, and a fourteen (14) position sample chamber with a spin function. Additionally, to increase the sensitivity of trace element analysis by lowering background intensity, the device uses secondary targets in Cartesian Geometry for indirect stimulation. The study's secondary targets were Mo, Cu, Rx9, and Si. The fewer fundamental parameters technique (FP), a standard procedure, was used to analyze the samples (Omote *et al.*, 1995; Kataoka *et al.*, 2006). The Rigaku EDXRF system's operational features allow the development of "alpha corrections" or matching libraries to rectify FP-derived analytical data. In addition, to increase the sensitivity of the light elements, all PPP samples were performed in vacuum (Singh and Agrawal, 2012; Maruyama *et al.*, 2008).

A library calibration using pure elements was conducted to check for instrument drift in order to confirm the validity of the quantitative data from the EDXRF. Cu, Sn, SiO2, and a Multi-channel Analyzer (MCA) were the drift monitor samples utilized in this investigation, provided by the manufacturer. Additionally, the MCA was executed every day before any analysis began. In order to verify the accuracy of the analytical results, CRMs are also added to every set of soil samples that are analyzed using the EDXRF. Additionally, the following equation was used to obtain the EDXRF limit of detection (LOD) (Kadachi and Al-Eshaika, 2012 and Scott Rees Fees, 2019).

$$\mathbf{LOD} = \frac{3}{S}\sqrt{\frac{I_b}{T}}$$

Where, S is the sensitivity in counts per ppm, I_b is the background intensity and T is the counting time in seconds.

Data Exploration Using Cluster Analysis

SPSS version 23 was used to obtain the Pearson correlation coefficients for the three zones of Kaduna state. Mini tab statistical software was used to carry out the cluster analysis based on Ward's method. The result was presented in the form of a dendrogram, recognizing that outliers are almost always present in regional geochemical data sets. Because the outliers reveal crucial details regarding the quality of the data and unexpected behavior in the study area, they were not overlooked. However, because outliers can impair proximity measures and mask clustering tendencies, they can significantly impact cluster analysis. For this reason, both with and without outliers, cluster analysis was done. A dendrogram was used to display the clustering analysis result that was obtained using Ward's approach. Individual samples are positioned along a baseline known as the abscissa, and the fusion of each succeeding sample is plotted against rising values of the fusion coefficient or dissimilarity coefficient on the ordinate as the size of the group and the degree of within-group heterogeneity grows.

RESULTS AND DISCUSSION

Heavy metals concentrations in the vicinity of schools and auto mechanic workshops

Based on the definition of heavy metals, the following elements were identified as heavy metals and were subsequently taken in to consideration in all future analyses; V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Sn, Hf, Ta, Ir, Pt, Au, Pb, Th, U and Zr. In order to represent the concentrations of each heavy metal in a sample location, firstly, its average concentration was estimated from the concentrations obtained from 0m, 2m, 4m, 6m and 10m and standard deviation was calculated which serves as a measure of variability of the concentrations. Table 1, 2 and 3 presented the summary statistics of the heavy metals concentrations in the form of average ± standard deviation for Kaduna north, Kaduna central and Kaduna south zones respectively. The table presented the average background concentration of each heavy metal alongside the average concentrations of the schools and mechanical workshops for easy comparison.

Due to the differences in the elemental composition of the sampling sites as well as the land use pattern; Co, As, Sn, Hf, Ir, Pt, Au and U were not detected in all the samples collected from Soba school, Makarfi and Lere mechanical workshops in Kaduna North zone. This may be attributed to the natural composition of the soil as well as the fact that the intensity of the heavy emissions in the areas is minimal compared to the other zones in Kaduna state. Fe was recorded as the element with exceptionally high concentrations (in thousands) in all the samples analyzed, this was not surprising since it is a ubiquitous element and a macro nutrient. Therefore, the iron levels found in this study may be an additive outcome of lithological or crustal origin and human influences. Iron could also be responsible for the deterioration of car bodies and the wear on crankshafts. The waste produced in the research area's auto workshops, which includes solvent, hydraulic fluid, used lubricants, metal construction work, metal welding, and iron bending, may be the cause of the soil's increased iron concentration. Ni, Ta, Au, Ga, Sn, U, and As were elements that were found in relatively low concentrations, which was to be expected given that several of them are rare earth elements. Leachates from used motor oils include high copper concentrations, lead, and antimony.

The average concentrations of the selected heavy metals in Kaduna north zone-V, Fe, Co, Ni and Zr had their maximum concentrations Kudan school; whilst, Cr, Mn, Cu, Ga and As maximum concentrations were recorded in Makarfi mechanical workshops. Th was detected only in Kudan and Soba schools while U, Ir, Pt and Au were detected only Kudan School.

Table 1.0: Heavy metals concentrations (ppm) for samples from Kaduna north zone

	KUDAN SCH	SOBA SCH	MKRF MECH	LERE MECH	BGRD
HM	**Aver± S.D**	**Aver± S.D**	**Aver± S.D**	**Aver± S.D**	**Aver± S.D**
V	170.7±12.6	67.0±4.5	106.6±22.0	61.0±8.1	124.7±2.5
Cr	77.3±18.4	56.5±1.7	104.0±38.2	67.0±11.2	18.7±5.2
Mn	735.7±64.8	1110.0±146.4	2809.5±793.6	1230.2±73.4	4998.0±24.6
Fe	367638.8±232.4	25433.6±132.7	51317.5±287.2	156.3±108.6	440.5±32.8
Co	250.6±63.0	BDL	BDL	BDL	BDL
Ni	185.0±17.0	BDL	13.7±23.7	BDL	0.0
Cu	0.2±0.0	13.1±2.9	105.4±49.1	100.4±23.0	0.4±0.1
Zn	99.3±11.9	205.5±13.7	307.2±124.3	563.0±184.6	80.1±8.2
Ga	27.7±11.0	7.6±1.6	23.1±23.1	9.1±2.3	2.7±0.6
As	26.4±1.8	BDL	90.0±60.0	BDL	9.5±1.8
Sn	19.4±5.8	BDL	BDL	BDL	BDL
Hf	50.4±42.9	BDL	BDL	BDL	BDL
Ta	BDL	36.4±3.0	78.5±47.0	36.0±5.9	0.0±0.0
Ir	0.2±0.0	BDL	BDL	BDL	BDL
Pt	7.9±10.9	BDL	BDL	BDL	BDL
Au	8.3±7.3	BDL	BDL	BDL	BDL
Pb	47.9±27.0	124.8±22.4	1641.9±2363.7	BDL	20.4±2.7
Th	35.8±11.3	2.0±3.5	BDL	BDL	0.0
U	15.2±5.2	BDL	BDL	BDL	BDL
Zr	4608.8±601.1	2520.6±75.8	1407.7±717.6	BDL	7194.5±21.9

Ni was only detected in Kaduna north and Kaduna south schools in Kaduna central zone as 0.2ppm throughout. As was not detected in Kaduna north school. Co, Ir, Pt and Au were not detected in all the Giwa and Igabi mechanical workshops samples. Fe, Zr, Mn and Zn were noted to have comparatively higher concentrations compared to the other heavy metals considered in this work. Sn, Hf, V, Fe, Co, Ni, Ga, Th and Zr were observed to be maximum in samples from Chikun schools; Cr, As and T in Giwa mechanical workshop; Mn, Cu, Zn and Pb in Igabi mechanical garage. The least concentrations of the heavy metals were found to occur in: Cu and Ta in Kaduna north school, Mn, Zn, Pb in Chikun school, V in Kaduna south school, Cr, Hf, Co, Ni, As, Sn and Th in Igabi mechanical workshop. Similarly, Fe was recorded as the element with exceptionally high concentrations (in thousands) in all the samples analyzed, this was not surprising since it is a ubiquitous element and a macro nutrient. Elements observed to be of relatively low concentrations were Ni, Ga, Ta, Au, Sn, U, As which was expected since some of them are rare earth elements.

In the Kaduna south zone, Co, As, Sn, Hf, Ir, Pt, Au and U were not detected in all the Kachia local government school samples. The average concentration of the selected heavy metals in the sampling area under this zone was found to have the highest values thus- V, Cu, U in Kachia Mechanical workshop; Cr, Mn, Pb in Kachia school; Fe, Ga, As, Hf, Co, Ni, Zn, Ta, Th in Kauro school and Pt, Au and Zr in Kagarko school. V, Cr, As, Co, Ni, Cu, Zn, Sn, Hf, Ta, Pt, Au and Za had their least concentrations in Kagarko school while Mn, Ir, Pt, Au, Pb had theirs in Kauro school.

The world health organization (WHO) and the food and agriculture organization (FAO) have stipulated the thresholds limits of heavy metals concentration in soil thus: Zn-300 ppm, As-20 ppm, Pb-100 ppm, Cu-100 ppm, Cd-3 ppm, Cr-100 ppm,Co-50 ppm and Ni-50 ppm. The average concentrations obtained in this work for each heavy metal in both the schools and the auto mechanic workshops were compared in the form of ratio (quotient) with the threshold limits recommended by WHO/FAO. It was observed that As, Pb, Cd, Co, Ni were of serious health concern because in almost all the zones, there average concentrations replicates the threshold provided by WHO/FAO. The high levels of Pb in these locations proved to the overall high degree of environmental pollution with this metal and were easily linked in large part to the activities in these locations. The quantity of waste oil increases these levels of Pb, the presence of automobile fumes, and the outdated motor batteries that are carelessly abandoned by nearby battery chargers and auto mechanics. The amount of heavy metals in the soil at the auto-mechanic workplace in the research region varies according to how long the workshop has been operating there. The quantity of waste oil may increase these levels of Pb, the presence of automotive fumes, and the indiscriminate disposal of old motor batteries by battery chargers and auto mechanics in these areas. The studied auto-mechanic workshop could also be identified as a playground or close to residential areas where children play freely, and for children, ingestion of contaminated soil is the most significant pathway to Pb exposure. As a result, concern about Pb concentrations in auto-mechanic workshop soils may arise primarily due to this. Additionally, schools and auto repair shops had higher concentrations of heavy metals than the surrounding area did, including Cr, Cu, Zn, As, Pb, V, Mn, Fe, Ga, and Ta.

Table 2.0: Heavy metals concentrations (ppm) for samples from Kaduna central zone.

	K/NORTH SCH	**CHIKUN SCH**	**K/SOUTH SCH**	**GIWA MECH**	**IGABI MECH**	
HM	**Aver± S.D**	**Aver± S.D**	**Aver± S.D**	**Aver± S.D**	**Aver ±S.D**	**BGRD**
V	60.8±9.9	174.8±78.3	47.0±8.9	59.3±15.4	75.7±34.3	32.8±2.8
Cr	63.6±6.1	68.6±2.0	70.1±26.8	88.5±9.8	33.5±4.8	12.3±4.2
Mn	320.4±8.9	260.4±50.2	283.4±58.1	1845.8±334.6	2061.4±445.2	808.5±20.7
Fe	38718.8±6205.2	60178.8±202184	30478.8±7950.5	29978.8±2714.8	34353.4±4889.3	8645.5±212
Co	113.6±16.0	177.2±34.3	101.8±7.6	BDL	0.2±0.0	BDL
Ni	0.2±0.0	41.0±15.6	0.2±0.0	BDL	0.1±0.1	12.3±3.6
Cu	10.5±5.0	23.8±1.6	17.5±14.6	32.4±10.9	42.9±14.9	4.1±2.3
Zn	168.2±74.5	84.1±57.1	148.2±41.4	224.2±24.9	234.8±62.8	56.3±4.8
Ga	13.0±3.1	31.2±13.8	12.4±1.4	4.1±2.6	10.4±2.3	6.4±1.6
As	ND	5.1±4.2	2.5±3.3	10.6±16.6	0.1±0.1	0.0±0.0
Sn	15.3±2.9	17.2±1.6	14.3±1.3	0.2±0.0	0.2±0.0	BDL
Hf	41.1±11.9	50.3±8.0	33.8±2.4	0.2±0.0	0.2±0.0	BDL
Ta	0.2±0.0	7.9±10.8	0.2±0.0	147.9±195.6	25.3±16.3	23.7±2.2
Ir	8.3±2.5	8.2±1.7	6.2±5.3	BDL	BDL	BDL
Pt	6.1±8.3	11.2±1.8	4.9±6.6	BDL	BDL	BDL
Au	5.5±7.5	8.0±1.5	6.1±5.2	BDL	BDL	BDL
Pb	67.1±2.9	42.9±7.7	67.5±6.1	133.4±53.3	577.8±352.7	73.5±8.8
Th	20.8±5.7	31.3±8.1	14.3±2.6	BDL	0.0±0.0	0.0±0.0
U	10.7±2.5	10.1±2.2	10.7±1.5	ND	ND	ND
Zr	3112.8±171.7	3270.8±180.4	2872.8±185.6	351.4±144.1	2741.0±1413.1	3882.8±86.4

Key: HM-heavy metal, BDL-Blow detection Limit, sch-school vicinity, K/North- Kaduna north L.G, K/south- Kaduna south L.G, mech-mechanic workshop and BGRD-background.

Table 3.0: Heavy metals concentrations (ppm) for samples from Kaduna south zone

	KACHIA MECH	KACHIA SCH	KAURO SCH	KGARKO SCH	
HM	**Aver± S.D**	**Aver± S.D**	**Aver± S.D**	**Aver± S.D**	**BGRD**
V	103.5±20.6	89.9±29.3	76.4±52.5	43.7±1.8	24.0±2.8
Cr	80.0±22.4	94.1±19.8	85.9±44.5	42.4±13.0	23.0±8.6
Mn	434.3±182.3	2150.9±640.9	353.3±122.7	569.4±40.0	709.2±82.6
Fe	58059.9±21449.4	35058.9±8692.0	671798.8±273511.9	31178.8±7556.0	7373.0±122.
Co	181.9±78.1	BDL	191.0±37.4	115.7±22.2	BDL
Ni	13.3±16.9	8.4±14.5	18.6±4.1	0.2±0.0	15.2±3.2
Cu	28.9±14.1	39.1±5.9	14.9±6.7	12.9±2.3	1.9±0.6
Zn	204.9±49.8	169.8±87.3	247.0±49.1	162.0±21.6	33.1±2.8
Ga	22.4±15.5	10.4±5.3	29.8±7.5	14.6±4.5	2.7±0.3
As	11.2±1.9	BDL	301.8±129.4	3.6±4.8	2.5±0.6
Sn	21.3±10.7	BDL	37.0±15.3	14.5±2.9	BDL
Hf	47.5±11.6	BDL	301.0±92.1	40.0±3.8	BDL
Ta	30.8±2.6	57.3±24.6	369.9±1.8	0.2±0.0	3.4±0.8
Ir	18.6±13.2	BDL	0.2±0.0	7.7±2.1	BDL
Pt	7.3±4.4	BDL	0.2±0.0	7.3±1.6	BDL
Au	8.7±8.7	BDL	0.2±0.0	7.9±1.5	BDL
Pb	65.8±47.9	102.8±47.4	41.2±1.2	60.9±8.2	62.2±10.3
Th	23.3±13.9	8.8±12.4	952.2±651.4	15.5±1.3	BDL
U	27.6±6..6	BDL	7.5±6.4	6.3±1.9	BDL
Zr	2835.9±228.9	781.2±112.6	2167.8±1386.7	3132.8±54.4	BDL

Key: HM-heavy metal, BDL-Blow detection Limit, sch-school vicinity, mech-mechanic workshop and BGRD-background.

Correlation coefficients for heavy metals concentrations in the vicinity of schools and auto mechanic workshops

Table 4 presented the Pearson correlation coefficients between different pair of heavy metals in Kaduna north zone. Where positive correlation exists, it is an indication that the elements are from the same source and, negative correlation indicates the element are from different sources. Some of the heavy metals detected in this Zone were observed to have strong positively correlation with each other thus; Cr/Cu (0.75), Cr/Zn (0.84), Cr/Ga (0.93), Cr/As (0.84), Cr/Ta (1.00), Fe/Co (1.00), Fe/Ni (0.99), Cu/Zn (0.99), Cu/As (0.81), Cu/Pb (1.00), Zn/As (1.00), Zn, /Ta (0.88), Ga/As (1.00), Ga/Ta (0.88), Ga/Pb (0.99) and As/Ta (0.90). On the other hand, there was significantly strong negative relationship between: V/Cr (-0.8), Cr/Mn (-0.86), Mn/Co (-0.71), Mn/Ni (-0.75), Mn/Ta (-0.81), V/Cu (-1.00), V/Zn (-1.00), V/As (-1.00) and V/Pb (-1.00). The correlation coefficients clearly indicated that increase in Cr is associated with the increase Cu, Zn, Ga, As and Ta; increase in Fe is associated with the increase in Co and Ni; increase in Cu is associated with increase in Zn, As and Pb. On the other hand, increase in V concentration is associated with decrease in As, Pb, Zn, Cu and Cr and increase in Mn concentration is associated with decrease in Co, Ni and Ta.

Pearson correlation coefficients among the heavy metals in Kaduna central zone were presented in table 5. Some of the heavy metals detected in this Zone were observed to have strong positively correlation with each other thus; Cr/Fe (0.98), Cr/Cu (0.73), Cr/Zn (0.77), Cr/As (0.93), V/Cr (0.94), V/Fe (0.99), V/Ga (0.86), V/As (0.75), Mn/Cu (0.76), Mn/Zn (0.72), Mn/Pb (0.96), Fe/Co (0.75), Fe/Ga (0.79), Fe/As (0.83), Cu/As (0.93), Cu/Ta (0.80), Cu/Pb (0.90), Zn/As (0.95), Zn/Ta (0.76), Zn/Pb (0.88) and Ta/Pb (0.98). On the other hand, there was significantly strong negative relationship between: Mn/Co (-0.74), Mn/Ni (-0.98), Mn/Ga (-0.70), Ni/Cu (-0.88), Ni/Zn (-0.85) and Ni/Ta (-0.99). The correlation coefficients clearly indicated that increase in Cr is associated with the increase Fe, Cu, Zn and As ; increase in Fe is associated with the increase in Co, Ga and As; increase in Cu and Zn are associated with increase in Ta, As and Pb. On the other hand, increase in Mn concentration is associated with decrease in Co, Ni, Ga and increase in Ni concentration is associated with decrease in Zn and Ta.

Pearson correlation coefficients among the heavy metals in Kaduna south zone were presented in table 6. Some of the heavy metals detected in this Zone were observed to have a strong positively correlation with each other thus; V/Cr (0.94), V/Co (0.96), V/Cu (0.98), V/Zn (0.93), V/Ga (0.97),Cr/Cu (0.99),Cr/Ga (0.99), Cr/Pb 90.87), Mn/Fe (0.77), Mn/As (0.86), Mn/Ta (0.78), Fe/As

(0.99), Fe/Pb (0.91),Co/Pb (0.84), Cu/Zn (0.98),Cu/Pb (0.79), Zn/Ga (0.99), Zn/Pb (0.89), Ga/Pb (0.81), As/Ta (0.99), As/Pb (0.84) and Ta/Pb (0.91) On the other hand, there was significantly strong negative relationship between: Mn/Ni (-0.71), Ni/As (-0.97), Ni/Ta (-0.99) and Ni/Pb (-0.95). The correlation coefficients clearly indicated that increase in V is associated with the increase Cr, Co, Cu, Zn and Ga ; increase in Cr is associated with an increase in Cu, Ga and Pb; increase in Fe is associated with increase in As and Pb and, increase in Cu is associated with increase in Zn and Pb. On the other hand, increase in Mn concentration is associated with decrease in Ni and increase in Ni concentration is associated with decrease in As, Ta and Pb.

Table 4.0: Pearson correlation matrix for Kaduna north zone.

	V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As	Ta	Pb
V	1.00										
Cr	**-0.80**	1.00									
Mn	0.38	**-0.86**	1.00								
Fe	0.44	0.19	-0.66	1.00							
Co	0.38	0.25	**-0.71**	**1.00**							
Ni	0.32	0.31	**-0.75**	**0.99**	1.00						
Cu	**-1.00**	**0.75**	-0.31	-0.51	-0.39	1.00					
Zn	**-1.00**	**0.84**	-0.44	-0.38	-0.26	**0.99**	1.00				
Ga	-0.53	**0.93**	-0.99	0.53	0.63	0.47	0.58	1.00			
As	**-1.00**	**0.84**	-0.45	-0.37	-0.25	**0.99**	**1.00**	0.59	1.00		
Ta	-0.85	**1.00**	**-0.81**	0.09	0.22	**0.81**	**0.88**	**0.90**	**0.89**	1.00	
Pb	**-1.00**	0.74	-0.29	-0.52	-0.41	**1.00**	**0.99**	0.45	**0.99**	0.80	1.00

Table 5.0: Pearson correlation matrix for Kaduna central zone.

	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Ta	Pb
V	1											
Cr	**0.94**	1.00										
Mn	-0.23	0.11	1.00									
Fe	**0.99**	**0.98**	-0.10	1.00								
Co	**0.83**	0.59	**-0.74**	**0.75**	1.00							
Ni	0.02	-0.31	**-0.98**	-0.11	0.58	1.00						
Cu	0.46	**0.73**	**0.76**	0.57	-0.12	**-0.88**	1.00					
Zn	0.51	**0.77**	**0.72**	0.62	-0.06	**-0.85**	**1.00**	1.00				
Ga	**0.86**	0.64	-0.70	**0.79**	**1.00**	0.53	-0.06	0.00	1.00			
As	**0.75**	**0.93**	0.47	**0.83**	0.24	-0.65	**0.93**	**0.95**	0.30	1.00		
Ta	-0.17	0.17	**1.00**	-0.03	-0.69	**-0.99**	**0.80**	**0.76**	-0.65	0.53	1.00	
Pb	0.03	0.37	**0.96**	0.16	-0.54	**-1.00**	**0.90**	**0.88**	-0.48	0.69	**0.98**	1.00

Table 6.0: Pearson correlation matrix for Kaduna south zone.

	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Ta	Pb
V	1.00											
Cr	**0.94**	1.00										
Mn	-0.38	-0.05	1.00									
Fe	0.29	0.59	**0.77**	1.00								
Co	**0.96**	**1.00**	-0.11	0.55	1.00							
Ni	-0.38	-0.67	**-0.71**	-1.00	-0.63	1.00						
Cu	**0.98**	**0.99**	-0.20	0.47	**1.00**	-0.55	1.00					
Zn	**0.93**	**1.00**	-0.02	0.62	**1.00**	-0.69	**0.98**	1.00				
Ga	**0.97**	**0.99**	-0.16	0.50	**1.00**	-0.58	**1.00**	**0.99**	1.00			
As	0.14	0.46	**0.86**	**0.99**	0.42	**-0.97**	0.33	0.49	0.37	1.00		
Ta	0.27	0.58	**0.78**	**1.00**	0.53	**-0.99**	0.46	0.60	0.49	**0.99**	1.00	
Pb	0.66	**0.87**	0.44	**0.91**	**0.84**	**-0.95**	**0.79**	**0.89**	**0.81**	**0.84**	**0.91**	1.00

Clustering analysis for heavy metals concentrations in the vicinity of schools and auto mechanic workshops

The cluster analysis was applied to detect spatial similarity for grouping of the heavy metals concentrations in the premises of schools and auto mechanic workshops. The concentration of the various heavy metals in each of the samples studied were treated using cluster analysis (Ward's Method). The result of this treatment is presented in figure 1 in the form of a dendrogram consisting of four (4) different groups with an outlier clearly indicated.

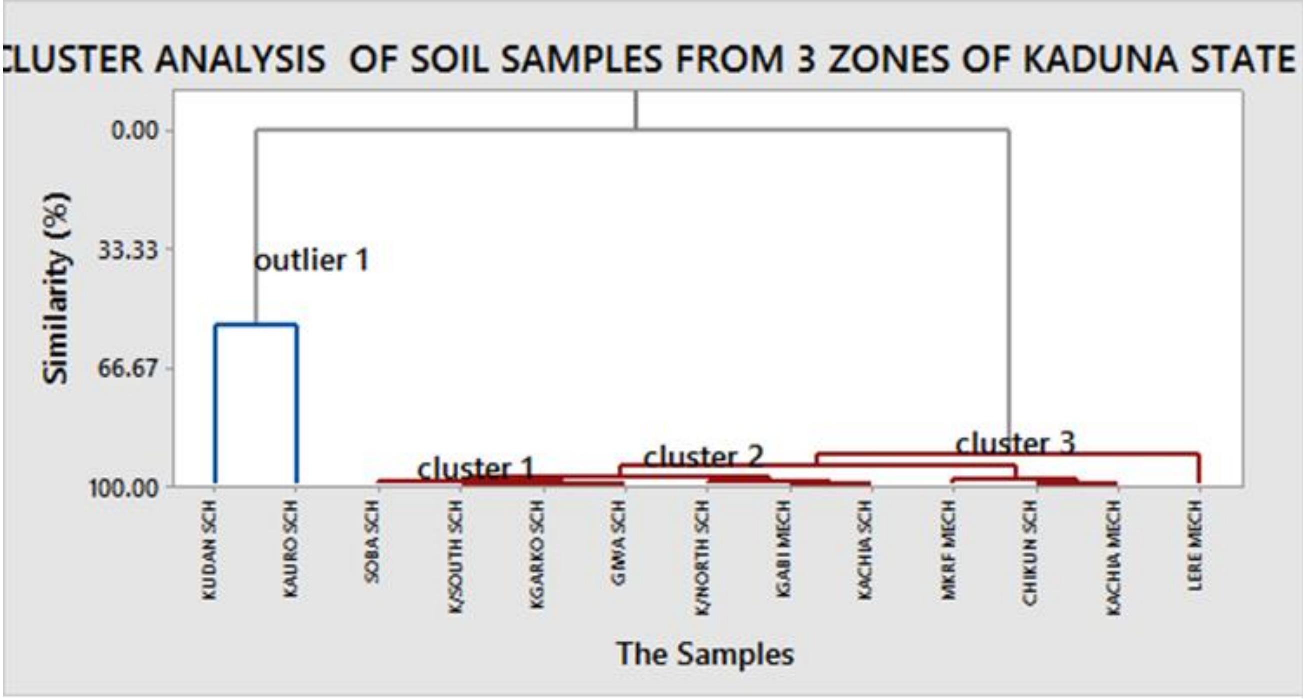

Fig 2.0: Cluster analysis with outliers

Because this outlier 1 has clearly affected proximity in measurement and has created obscure clustering tendencies, it was removed. The removal of this outlier has yielded a better grouping as shown in the next dendrogram in figure 2.

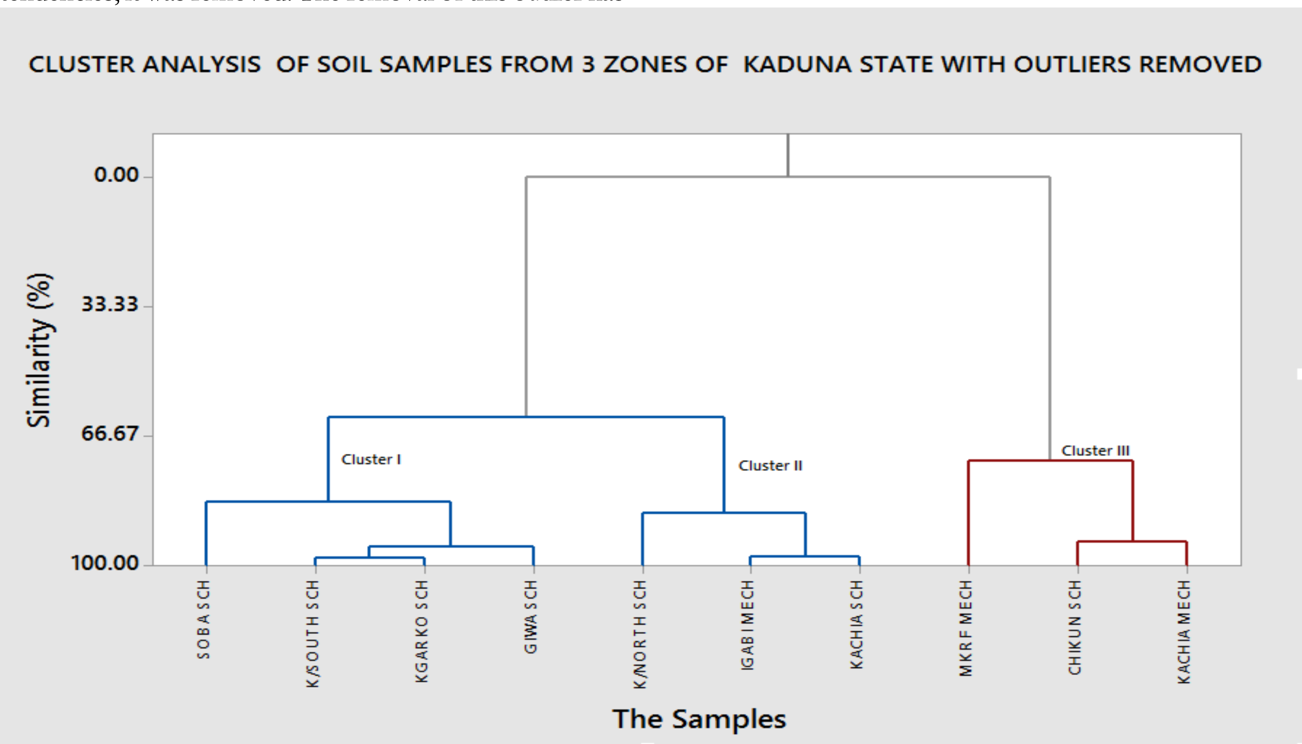

Fig 3.0: Cluster analysis without outliers

Three distinctive clusters exist, each containing samples with closely similar elemental composition which reflects similarity in the samples from those sites. Cluster I consists of samples from Soba, Kaduna South, Kagarko, and Giwa schools. It is worthy to note that Cluster I consists of samples from Kaduna North; South; and Central Zone. This suggest that soil from this location shows homogeneity.

Cluster II on the other hand consists of samples from Kaduna central and south zone, It consist samples from Kaduna north schools, Igabi mechanics and Kachia schools. while Cluster III consists of samples from Kaduna North; South; and Central Zone, consisting of samples from Makarfi mechanics, Chikun schools and Kachia mechanics. It can be seen from the dendrogram that the cluster analysis results were in agreement with the reported heavy metals pollution levels.

CONCLUSION

Heavy metals from soil samples around schools and auto mechanic workshops in Kaduna state at varying concentrations were determined. Majority of the elements (>80%) detected and analysed are not of interest in toxicity assessment and some are rare earth elements. These heavy metals levels may be attributed to the natural composition of the soil as well as the fact that the intensity of the heavy emissions is variable. The concentrations of As, Pb, Cd, Co, Ni were of serious health concern considering that in almost all the zones in Kaduna state, the average concentrations replicate the threshold provided by WHO/FAO. It is therefore concluded that it is not safe for children to be playing around the vicinity of schools located around auto-mechanic workshops and highways.

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REFERENCES

Adewole M.B. and Uchegbu L. U. (2010). Properties of Soils and Plants Uptake within the Vicinity of Selected Automobile Workshops in Ile-Ife Southwestern, Nigeria. *Ethiopian Journal of Environmental Studies and Management* (3)3, 30-35. **[Crossref]**

Agoro, M. A., Adeniji, A. O., Adefisoye, M. A., & Okoh, O. O. (2020). Heavy Metals in Wastewater and Sewage Sludge from Selected Municipal Treatment Plants in Eastern Cape Province, South Africa. *Water*, 12(10), 2746. 5. **[Crossref]**

Ali Z., Malik R.N., Qadir A (2013). Heavy metals distribution and risk assessment in soils affected by tannery effluents. *Chem. Ecol.,* 29(8), 676-692. 5. **[Crossref]**

Aloysius, Rufus, & John, (2013) Evaluation of heavy metals in soils around auto mechanic workshop clusters in Gboko and Makurdi, Central Nigeria. *Journal of Environmental Chemistry and Ecotoxicology*, Vol. 5(11), pp. 298-306. 5. **[Crossref]**

AMAP/UNEP (2013). Technical Background Report for the Global Mercury Assessment 2013 Arctic Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland.

Bello, S., Muhammad, B.G. and Bature, B (2017). Total Excess Lifetime Cancer Risk Estimation from Enhanced Heavy Metals Concentrations Resulting from Tailings in Katsina Steel Rolling Mill, Nigeria. *Journal of Material Sciences & Engineering.* 6:3. 5. **[Crossref]**

Bello, S., Nasiru, R., Garba, N. N. and Adeyemo, D. J (2019b). Quantification of pollution levels associated with heavy metals in Shanono and Bagwai artisanal gold mines, Kano state, Nigeria. *FUDMA Journal of Sciences (FJS). Vol. 3 No. 2, June, 2019, pp 97 – 102.*

Bello, S., Nasiru, R., Garba, N.N and Adeyemo, D.J (2019a). Carcinogenic and Non-carcinogenic health risk assessment of heavy metals exposure from Shanono and Bagwai artisanal goldmines, Kano State, Nigeria. *Scientific African*. 5. **[Crossref]**

Britannica, The Editors of Encyclopaedia (2019). "Kaduna". *Encyclopedia Britannica*,. Accessed 16 November 2022. **[Crossref]**

Clemens, S., Aarts, M. G. M., Thomine, S., & Verbruggen, N. (2013). Plant science: the key to preventing slow cadmium poisoning. *Trends in Plant Science, 18*, 92–99. 5. **[Crossref]**

Dolan, L. M. J. H. Van Bohemen, P. Whelan *et al.*, (2006). Towards the sustainable development of modern road ecosystem in The Ecology of Transportation: Managing Mobility for the Environment. J. Davenport and J. L. Davenport, Eds., vol. 10 of Environmental Pollution, pp. 275–331. 5. **[Crossref]**

Fees, S.; Applied Rigaku Technologies, Austin, TX, USA. Personal communication, 2019.

Kadachi, A.N. and Al-Eshaikh, M.A (2012). Limits of detection in XRF spectroscopy. *X-ray Spectrom.* 41, 350–354. 5. **[Crossref]**

Kataoka, Y.; Kawahara, N.; Hara, S.; Yamada, Y.; Matsuo, T.; Mantler, M (2006). Fundamental Parameter Method Using Scattering X-rays in X-ray Fluorescence Analysis; CPDS-International Centre for Diffraction Data: Newtown Township, PA, USA; Denver, CO, USA, 2006; pp. 255–260, ISSN 1097-0002.

Laxmi, K.S. (2016). Investigation of heavy metal contamination in the roadside soil at morena district in India, International Journal of Research - Granthaalayah, Vol. 4, No. 11: 72-76. 5. **[Crossref]**

Maruyama, Y.; Ogawa, K.; Okada, T.; Kato, M. Laboratory experiments of particle size effect in X-ray fluorescence and implications to remote X-ray spectrometry of lunar regolith surface. Earth Planets Space **2008**, 60, 293–297. 5. **[Crossref]**

Morka, Obiwulu,, Ataine, & Anthony, (2016). Soil contamination due to heavy metals within auto-mobile workshop clusters along Mariere by t-junction and orubor. (1) 1,Pg 18-22.

Nkwoada A.U.,Alisa C.O.& Amakom C.M. (2018) Pollution In Nigerian Auto-Mechanic Villages: A Review. IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT) 12.7 43-54.

Ogunkolu, Moses, Oyetunji & Abudllahi (2019) Assessment of Heavy Metal Contamination of Soil around Auto Mechanic Workshops in Anyigba, Kogi State.: 13 (1): 79-89

Ogwo, E., Prince, U. & Egedeuzu, C. (2015). Assessment of heavy metals in soil (A case study of a mechanic workshop in Kumin Mashi Kaduna State). Sky Journal of Soil Science and Environmental Management. 5. 85-90.

Oludare Hakeem Adedeji, Oluwafunmilayo O. Olayinka, and Opeyemi O. Tope-Ajayi,Spatial(2019) Distribution and Health Risk Assessment of Soil Pollution by Heavy Metals in Ijebu-Ode, Nigeria. J Health Pollut. 2019 Jun; 9(22): 190601. Published online 2019 May 20. **[Crossref]**

Omote, J.; Kohno, H.; Toda, K. X-Ray flfluorescence analysis utilizing the fundamental parameter method for the determination of the elemental composition in plant samples. Anal. Chim. Acta **1995**, 307, 117–126. **[Crossref]**

Rabe, J.M.1., Agbaji EB1, Zakka Y1, Muhammed HM and Rabe AM (2018). Assessment of Contaminated Soil with Some Heavy Metals in Selected Auto Repair Shops in Katsina North Western, Nigeria. *Journal of Waste Management & Xenobiotics*. **[Crossref]**.

Rahman Z and Singh VP. (2020). Bioremediation of toxic heavy metals (THMs) contaminated sites: concepts, applications and challenges. *Environ Sci Pollut Res Int*. 27(22):27563-27581. 5. **[Crossref]**

Simon, E. A., Vidic, M., Braun, I. F., & Tóthmérész, B (2013). Trace element concentrations in soils along urbanization gradients in the city of Wien, Austria. Environmental Science and Pollution Research, vol. 20, no. 2, pp. 917–924. **[Crossref]**

Singh, V and Agrawal, H (2012). Qualitative soil mineral analysis by EDXRF, XRD and AAS probes. *Radiat. Phys. Chem.* 81, 1796–1803. 5. **[Crossref]**

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy metal toxicity and the environment. *Molecular Clinical Environmental Toxicology, 101*, 133–164. 5. **[Crossref]**

Vhahangwele, M and Khathutshelo, L. M (2018). Environmental Contamination by Heavy Metals. **[Crossref]**

Vitousek, P. M., Mooney, H. A., Lubchenco, J., & Melillo, J. M. (1997). Human domination of Earth's ecosystems. *Science, 277*, 494–499. **[Crossref]**

Wu, G., Kang, H., Zhang, X., Shao, H., Chu, L., & Ruan, C. (2010). A critical review on the bio-removal of hazardous heavy metals from contaminated soils: issues, progress, eco-environmental concerns and opportunities. *Journal of Hazardous Materials, 174*, 1–8. **[Crossref]**

Yusuf, A.J., Galadima, A., Garba, Z.N.,& Nasir, I.,(2015). Determination of some Heavy Metals in Soil Sample from Illela Garage in Sokoto State, Nigeria. *Research Journal of Chemical Sciences*, ISSN 2231-606X.Vol. 5(2).

Zwolak, A., Sarzynska, M., Szpyrka, E. *et al.*, (2019). Sources of soil pollution by heavy metals and their accumulation in vegetables: a Review. *Water Air Soil Pollut.* 230. **[Crossref]**