

Ecological and human health risk assessments of Potentially Toxic Metals in soils around a private University in Ogun State, Nigeria

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Article info

Received 30/4/2024; received in revised form 5/9/2024; accepted 18/9/2024

DOI: [10.6092/issn.2281-4485/19459](https://doi.org/10.6092/issn.2281-4485/19459)

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Abstract

The environments are polluted with Potentially Toxic Metals (PTMs) due to natural and anthropological activities thereby leading to ecological threats to air, water, soil, plants, animals and humans. This research focuses on ecological and human health risk assessment of potentially toxic metals (Fe, Cr, Cd, Ni and Pb) around a private University in Ogun State. Fifty (50) top soils (0-15cm) were sampled from ten locations within the university. The physicochemical parameters were determined using standard methods, and the concentrations of the PTMs were determined using a Flame Atomic Absorption Spectrophotometer (FAAS; Buck Scientific, model 210) after digestion. The results obtained for physicochemical parameters indicated that they were within permissible limits. The mean concentration values of PTMs were: Fe 11805.65 ± 1327.95 mg/kg > Cr (22.89 ± 1.94 mg/kg) > Pb (15.41 ± 1.40 mg/kg) > Ni (1.43 ± 0.67 mg/kg) > Cd (0.04 ± 0.01 mg/kg). The average values of ecological risk for Enrichment Factor, Contamination Factor, Geochemical Index, Pollution Load Index PLI, and Potential Ecological Risk Index are 2.64, $2.69E+01$, $1.52E+00$, $1.42E-01$, and $8.08E+02$ respectively. Hazard Quotient ($HQ \leq 1$) and Hazard Index ($HI \leq 1$) for non-carcinogenic risk suggest that the soils are safe for lifetime exposure. The carcinogenic ($10^{-6} - 10^{-4}$) showed an associated risk for both adults and children. The study confirmed that the studied soil sample is pristine and poses neither an ecological nor human health risk. These scientific findings have provided valuable information for making suitable ecological management approaches to ameliorate the influence of potentially toxic metal pollution.

Keywords

Potentially toxic metals, University, pollution index, carcinogenic, health risk

Introduction

Soil is part of the terrestrial ecosystem where most human and agricultural activities are carried out. It consists of a mixture of mineral elements and organic matter capable of supporting plant life (Liu *et al.*, 2016; Olatunde *et al.*, 2020). It has equally played a vital role in receiving most of the natural and anthropogenic input due to improper management of waste from industrial or domestic sources. This leads to pol-

lution of soil and other soil-dependent materials such as vegetables, crops, and some micro-organisms. This also changes the physicochemical properties of the soil, thereby affecting microbial life, and imposing threats to the health of humans (Olatunde *et al.*, 2020). Discharges of wastewater that are poorly treated which contains potentially toxic metals, inorganic compounds, soluble salts, organic compounds, and pathogens are the major cause of soil contamination (Liu *et al.*, 2016). However, it has been observed that

consuming or using contaminated edible plants and vegetables in a contaminated environment could threaten human life (Budur *et al.*, 2018; Olatunde *et al.*, 2020). The transformation of potentially toxic metals present in soil and vegetation is from biomethylation to organometallic moieties or a solid form into either ionic moiety, they can bring about various health risks to the ecology, animals, and human beings via the food chain (Eziz *et al.*, 2018). Consequently, due to industrialization and expansion, soils are exposed increasingly to contamination with toxic organic and inorganic chemicals (Rodríguez-Eugenio *et al.*, 2018). Most metals in different ecological activities serve as important plant nutrients when below permissible limits and become potentially toxic elements (PTEs) above the permissible limits (Olatunde *et al.*, 2020). Ogundele *et al.* (2015) observed that concentrations of metals such as; Cr in plant (53.68 mg/kg), Cd in soil (0.37 mg/kg), Zn in soil (219 mg/kg), Cu in soil (80.13 mg/kg), Pb in soil (157.67 mg/kg), and Ni in soil (11.85 mg/kg) were above WHO permissible limits (WHO, 1996). Non-carcinogenic and carcinogenic risk assessments are major potential risks that have been identified as a germane and effective tool for the identification of health risks of potentially toxic metals, which is important in decision-making to reduce the level of pollution to ecology and minimize human exposure risk (Eziz *et al.*, 2018). The accumulation of potentially toxic metals such as Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni), Selenium (Se), Molybdenum (Mo), Zinc (Zn), Thallium (Tl), Antimony (Sb) in the soil is linked to applying numerous bio-solids like composts, livestock manures, and municipal sewage sludge to land (Wuana and Okieimen 2011). The International Agency for Research on Cancer (IARC) has classified Cadmium (Cd), Nickel (Ni), Chromium (Cr), and Arsenic (As) as group 1 carcinogens that are toxic to humans and ecology (IARC, 2018). Metals become heavy and toxic when they accumulate in large proportions and thus pose health effects, especially to humans. For instance, a high accumulation of Cr in humans causes non-carcinogenic health effects like acute poisoning through ingestion exposure, fever, diarrhoea, vertigo, toxic nephritis, liver damage and vomiting, coma, death, cancer, etc (ATSDR 2012; Briffa *et al.* 2020). Therefore, this study aims to measure the levels of potentially toxic metals in the soil around the University and their physicochemical properties to determine the potential human and ecological risk po-

sed by the potentially toxic metals to ascertain human and ecological safety in the university's environment. This is by comparing the determined concentration levels of potentially toxic metals with the thresholds provided by international standards permissible limits while providing appropriate pollution remediation strategies.

Materials and Methods

Study area

This Private University is an institution established in Ogun State in the Western part of Nigeria on Latitude $6^{\circ}53'38.39705''$ N and Longitude $3^{\circ}43'7.36975''$ E (Fig. 1). The Global Positioning System (Table 1) of the sampling points is depicted in the map. The map shows a general map of Nigeria, and the Ogun State map is extrapolated. The green points on the map indicate the location of all the sampling points in the university while the red point shows the control site. The sampling was done in student halls, school farm sites, cafeterias, car parks, laboratory areas, and staff quarters within the university.

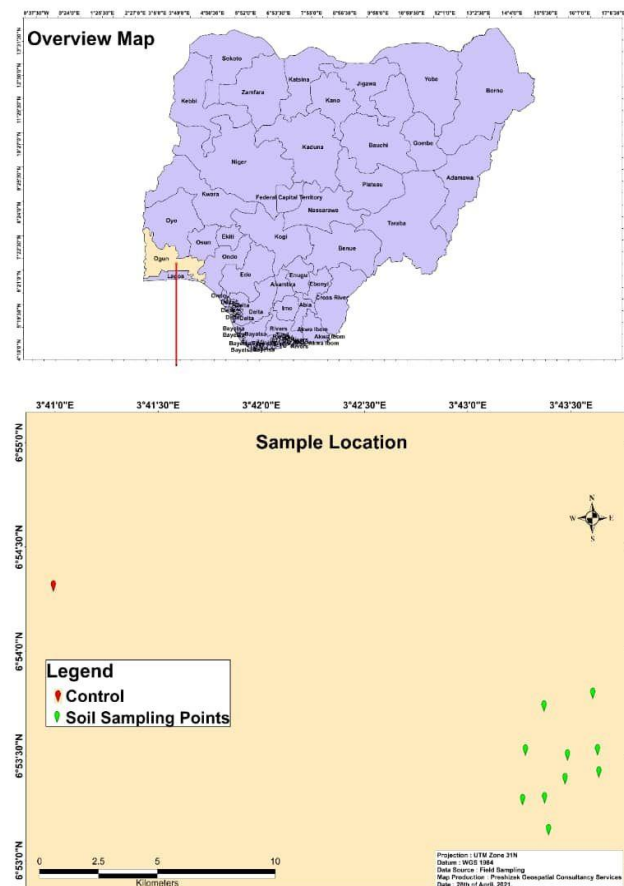


Figure 1. Map showing different sampling points

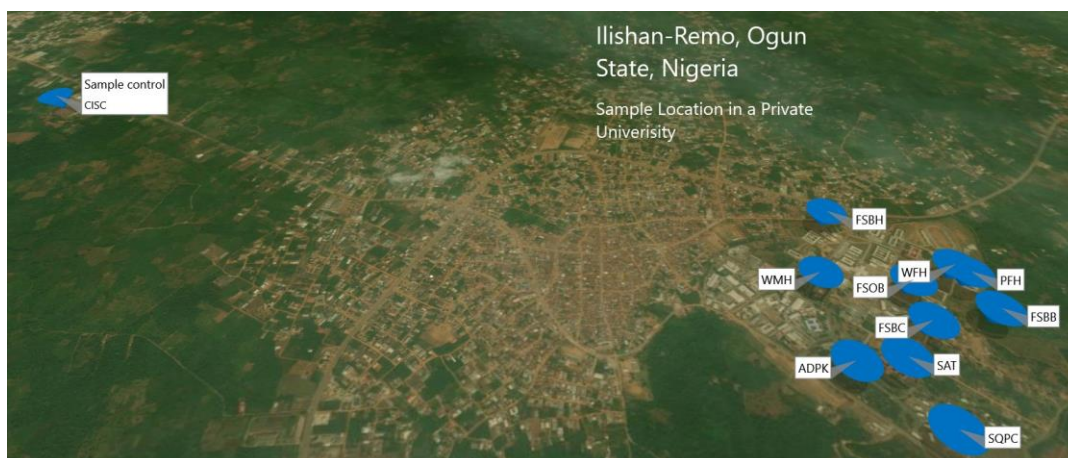


Figure 2
3D Map showing different sampling points

Location	Sample Codes	Latitude	Longitude
Farm Site 1	FSBB	N 6°53'25.104"	E 3°43'37.858"
Farm site 2	FSBH	N 6°53'44.076"	E 3°43'21.960"
Cafeteria	FSBC	N 6°53'23.181"	E 3°43'28.031"
Farm Site 3	FSOB	N 6°53'30.000"	E 3°43'28.764"
Male Hall 1	WMH	N 6°53'31.428"	E 3°43'16.530"
Female Hall 1	PFH	N 6°53'31.488"	E 3°43'37.482"
Female Hall 2	WFH	N 6°53'32.869"	E 3°43'36.126"
Science and Technology	SAT	N 6°53'17.754	E 3°43'22.080"
Car Park	ADPK	N 6°53'17.208	E 3°43'15.684"
Staff Quarters	SQPC	N6°53'08.538"	E 3°43'23.208"
Control sample	CSIC	N6°54'18.792	E 3°40'59.376"

Table 1
Sample study area and their Global Position System Locations within the University

Soil sampling and preparation

A total of fifty (50) soil samples were collected from ten sampling points within the university and five (5) control (with no anthropogenic activities) were sampled 5 km away from the university using a soil auger at 0-15 cm depth. The samples were air-dried, homogenized, and sieved through a 2-mm mesh to remove larger stones and other plant materials, and were stored in a polythene bag for further analysis.

Physicochemical properties of the soil

The physicochemical properties of the soil were determined using standard methods. The soil particle size (Bouyoucos 1962; Agbenin 1996), organic carbon (Walkey and Black, 1934), pH (Brady and Weil 2005), available phosphorus (Murphy and Riley, 1972), exchangeable bases (Okalebo *et al.*, 1993) and electrical conductivity (Mualem and Friedman, 1991) were assessed.

Soil digestion

3 g of the sieved soil sample was weighed and digested with aqua regia solution. A mixture of 15 mL of concentrated hydrochloric acid (HCl) and 5 mL of concentrated nitric acid (HNO₃) was added to the soil sample. The mixtures were allowed to stay overnight without heating in the fume cupboard. After 24 hours, the mixture was heated for 2 hours at 104°C. The digests were filtered after the addition of distilled water, and the filtrate was made up to the 100 mL mark with distilled water in a volumetric flask. The solution was transferred into sampling bottles for analysis and stored in the refrigerator to avoid degradation of the analyte (Olatunde *et al.*, 2020). The samples were analyzed using FAAS (Buck Scientific model 210). The detection limit (LOD) for the potentially toxic metals investigated was 0.01 mg/L, 0.04 mg/L, 0.05 mg/L, 0.04 mg/L, and 0.05 mg/L for cadmium, chromium, iron, lead, and nickel, respectively.

vely. The concentrations of heavy metals in mg/kg were determined using Equation [1]

$$\text{Concentration of heavy metals (mg/kg)} = \frac{\text{FAAS reading (mg/L)} - (\text{blank}) \times \text{Volume (L)}}{\text{weight of soil (kg)}} \quad [1]$$

Quality control

Plastic containers used for sample storage and glassware used in this analysis were washed with detergent and rinsed with warm water. This was soaked in a 10% (v/v) nitric acid solution overnight before being rinsed three times with deionized water, then covered with foil paper to avoid contamination, before storage inside a refrigerator. All analyses were done in triplicates.

Statistical analysis

In this study, potentially toxic metals analyses in the soil sample were done using descriptive statistical analyses which include mean, maximum, minimum, standard deviation, coefficient of variation, skewness, and kurtosis using the commercial Statistics Software Package SPSS (version 19 Inc., Chicago IL).

Ecological risk assessment of the soil

Many ecological indices were employed to estimate the contamination levels of the soil samples. These indexes included contamination factor (CF), contamination degree (CD), enrichment factor (EF), pollution load index (PLI), and risk index (RI). To determine the sources of pollution in the soil samples of the studied area, CF and EF were used. The EF expresses the impact of metals on the environment and is mathematically expressed as shown in Equation [2] (Nowrouzi and Poukhabbaz, 2014):

$$EF = \frac{(M/Fe)_{\text{Sample}}}{(M/Fe)_{\text{Background}}} \quad [2]$$

where $(M/Fe)_{\text{sample}}$ = ratio of metal and Fe concentration of the soil sample, and $(M/Fe)_{\text{background}}$ = the ratio of metal and Fe concentration of a background value.

The selected conservative metal concentration (background reference) in this research is Iron (Fe) because it exists naturally in high concentrations in the soil (Abraham and Parker, 2008). The contamination factor (CF) was estimated according to Alghamdi *et al.* (2018) using Equation [3]:

$$CF = \frac{C_{\text{Soil}}}{C_{\text{Background}}} \quad [3]$$

where C_{Soil} = mean metal concentration (mg/kg) in the soil samples taken; $C_{\text{Background}}$ = concentration (mg/kg) of metal in the background.

The international average concentration of metals in the soils was considered as the background values which are given as Cd (0.097 mg/kg), Cr (61 mg/kg), Fe (14,000 mg/kg, surrounding soil concentration), Ni (26.9 mg/kg) and Pb (26.00 mg/kg) (Jiao *et al.* 2015; Alghamdi *et al.* 2018). CF less than 1 indicates low contamination, $1 < CF < 3$ is moderate contamination; $3 < CF < 6$ is considerably contaminated and $CF > 6$ is very high contamination. The geoaccumulation index (I_{geo}) is expressed in Equation 4 (Yi *et al.*, 2016):

$$I_{\text{geo}} = \log_2 (C_n / 1.5 B_n) \quad [4]$$

where C_n and B_n is the concentration (mg/kg) of the potentially toxic metals (n) in the sample, and the background value in the average soil of element (n), respectively. I_{geo} consists of seven narrative grade levels which range from unpolluted to very polluted with class values of $I_{\text{geo}} < 1$, 0-1, 2-3, 3-4, 4-5, > 5 indicating Uncontaminated, Uncontaminated – Moderately contaminated, Moderately-Strongly contaminated, Strongly contaminated, Strongly-Extremely contaminated. respectively. (Yi *et al.*, 2016).

The Pollution Load Index (PLI) is calculated as indicated in Equation [5]:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad [5]$$

where CF is the contamination factor for every single metal and n is the number of potentially toxic metals. PLI index was divided into four-degree levels: $PLI < 1$ (grade 1), unpolluted; $1 \leq PLI < 2$ (grade 2), slight pollution; $2 \leq PLI < 3$ (grade 3), medium pollution; and $PLI \geq 3$ (grade 4), heavy pollution. (Li and Yang, 2008).

Health risk assessment of potentially toxic metals

In this study, the average chronic daily intake dosage (CDI_{dermal}) (mg/kg/day) of potentially toxic metals is calculated using the concentrations of potentially toxic metals that are mostly bioavailable (Luo *et al.*, 2012).

Non-carcinogenic risk estimation. To assess the human health risk assessment caused by the

potentially toxic metals present in the soil samples, the non-carcinogenic risk assessment was done using the two exposure pathways (dermal and ingestion) for children and adults respectively.

Potentially toxic metals intake through ingestion and dermal pathway. The ingestion dose chronic daily intake ($CDI_{\text{ingestion}}$) is ideally estimated using the equation of ingestion exposure pathway considering chronic exposure in Equations 6 and 7 (Budur *et al.*, 2018):

$$CDI_{\text{ingestion}} = \frac{(C_s \times IR \times EF \times ED)}{(BW \times AT)} \quad [6]$$

$$CDI_{\text{dermal}} = \frac{(C_s \times SA \times AF \times ABS \times EF \times ED)}{(BW \times AT)} \times 10^{-6} \quad [7]$$

HQ for exposure route of dermal and ingestion was calculated using Equation 8 (Alghamdi *et al.*, 2018):

$$HQ = \frac{CDI}{RfD} \quad [8]$$

where RfD = Reference dose

$$HI = HQ_1 + HQ_2 + HQ_3 + \dots HQ_n \dots \quad [9]$$

where C_s , IR, EF, ED, BW and AT represent metal concentration in soil (mg/kg), ingestion rate (kg/day), exposure frequency (days/year), exposure duration (years), body weight (kg), and average time (days), respectively. The $CDI_{\text{ingestion}}$ was estimated differently for adults and children due to differences in body weight and ingestion rate of soil. Exposure duration was 30 years for adults and 6 years for children (USEPA, 1997; Alghamdi *et al.*, 2018). More so, CDI_{dermal} , AF, SA and ABS are chronic absorbed daily intake (mg/kg-day), sediment-to-skin adherence factor (mg/cm²), skin surface area available for contact (cm²/event), and absorption factor (unitless), respectively. The reference dose (RfD) for the ingestion pathway was given as Fe (0.3), Cd (0.5), Ni (0.002), Pb (0.0035), As (0.3), and Cr (1.5) mg/kg/day while the reference doses for dermal pathway (RfD) are Fe (4.50 $\times 10^{-2}$), Cd (0.005), Ni (5.4), Pb (0.42), and Cr (0.015).

Carcinogenic risk quantification. The probability of an individual developing any form of cancer in their entire lifetime due to exposure to carcinogenic metals (Li, 2014). The cancer slope factor (SF) approach and individual cancer risk (ICR) were employed to calculate

the carcinogenic risk. The carcinogenic risk (CR) for ingestion of metals was calculated using Equation [10] (Qing *et al.*, 2015; Alghamdi *et al.*, 2018):

$$\text{Cancer risk} = CDI_{\text{ingestion}} \times SF \quad [10]$$

SF is the carcinogenic oral slope factor for a particular metal that represents the probability of developing cancer per unit exposure (mg/kg/day). Since Cr and Pb were investigated in this research and both have been classified as probable carcinogens for humans, their carcinogenic risk was evaluated (ATSDR, 2012; Alghamdi *et al.*, 2018). The values of SF used in the estimation are 0.5 and 0.0085 for Cr (VI) and Pb (II), respectively (Qing *et al.*, 2015; RAIS, 2018).

Results and Discussion

Physicochemical parameters of the soil samples

The physicochemical parameters of the samples are presented in Table 2. The pH value of the soil ranged from 5.19 ± 0.22 to 8.03 ± 0.57 with an average value of 6.79, which implies that the study area is weakly acidic to a weakly basic environment. The weakly acidic soil could be a result of the discharge from the laboratory around most of the sampling points. OC and TN values were of the range 1.89 ± 0.12 to 17.79 ± 1.76 g/kg and 0.12 ± 0.08 g/kg to 2.31 ± 0.55 g/kg, respectively. PFH has the lowest values for the two parameters and may be attributed to the low decomposition rate of the organic matter content of the soil in the area, including the lack of nitrogenous activities around the hall of residence (Ayeni *et al.*, 2008). The value of available P ranges from 6.11 ± 0.56 mg/kg (ADPK) to 55.48 mg/kg (FSBC). The rationale for high available P is the closeness of the FSBC site to the university cafeteria and the tendency to receive nutrient content from the food materials. Likewise, the FSBB site also showed a remarkable value of Available P which indicates a good enrichment factor for agricultural application on the farm land. On the other hand, the Soil K ranges from 0.36 ± 0.02 cmol/kg to 0.67 ± 0.02 cmol/kg which indicates good fertility of the farmland for the cultivation of agricultural products. The concentrations of exchangeable bases (Mg and Ca) are in the range of 1.12 ± 0.13 cmol/kg to 1.59 ± 0.15 cmol/kg and 2.91 ± 0.15 cmol/kg to 3.99 ± 0.56 cmol/kg respectively. This increase in the concentration of exchangeable bases suggests a good nutritive content for crop cultivation, increases microbial activities and improves the effects of exchangeable bases on soil

pH (Alex *et al.* 2020). The electrical conductivity (EC) ranges from $194.00 \pm 11.23 \mu\text{S}/\text{cm}$ to $423.00 \pm 11.24 \mu\text{S}/\text{cm}$ with an average of $314.73 \mu\text{S}/\text{cm}$. High OC and EC levels indicate high available nutrients and can be compared with the study of Olayinka *et al.* (2016). Alex *et al.* (2020) suggested that the high value of EC could be due to the presence of soluble salts. Cation exchangeable capacity (CEC) is the sum of all the exchangeable cations (Mg^{2+} , Ca^{2+} , K^{+} , Na^{+} , Al^{3+}). From this study, the CEC value ranges from $0.37 \pm 0.02 \text{ cmol}/\text{kg}$ to $0.58 \pm 0.04 \text{ cmol}/\text{kg}$ across the sampling sites with an average value of $0.50 \text{ cmol}/\text{kg}$. The high CEC values impact the value of OC by direct proportionality (Wild, 1996). Wild (1996) also reported that CEC values ranging from 2 – 6 cmol/kg

are indicative of kaolinitic minerals. These kaolinitic minerals are known to have low retention capacity and thus, toxic elements that find themselves in such soil through any means, will be leached out easily and thus would be a threat to water bodies, the ecology, and possibly humans as a whole (Tening *et al.*, 2014).

Potentially toxic metals

The concentrations of potentially toxic metals in all soil samples are presented in Table 3. High concentration was obtained for Fe in all the sampling sites (8220.00 ± 173.00 to $22700.00 \pm 479.42 \text{ mg}/\text{kg}$) with an average of $(11805.65 \text{ mg}/\text{kg})$, which is attributable to natural process as suggested by the enrichment factor analysis of this study and there are no anthropogenic activities as related to Fe. By comparison, it was

Table 2. Physiochemical properties and mean statistical analysis of physiochemical properties of the soil samples ($n=50$)

Sample sites	pH (H_2O)	Electric Conductivity ($\mu\text{S}/\text{cm}$)	Organic Carbon (g/kg)	Total N (g/kg)	P availability (mg/kg)	Exch. Acidity (cmol/kg)	Exch. H+ (cmol/kg)	Exch. Al+++ (cmol/kg)	Exch. Ca++ (cmol/kg)	Exch. Mg++ (cmol/kg)	Exch. K+ (cmol/kg)	Exch. Na+ (cmol/kg)	Sand (%)	Silt (%)	Clay (%)	Texture class USDA
WFH	6.74	384	10.5	1.16	8.88	0.35	0.30	0.05	3.15	1.19	0.41	0.33	71	11	18	LS
FSBH	7.74	314	4.96	0.55	17.2	0.45	0.35	0.10	3.80	1.26	0.48	0.41	74	13	13	LS
WMH	6.06	256	8.68	0.96	17.8	0.53	0.45	0.08	3.65	1.33	0.56	0.26	73	10	17	LS
PFH	8.44	364	0.62	0.07	5.68	0.48	0.35	0.13	2.74	1.03	0.49	0.34	76	10	14	LS
FSBB	6.22	211	11.5	1.26	40.3	0.50	0.40	0.10	3.58	1.21	0.58	0.47	71	13	16	LS
CSIC	7.75	369	11.2	1.23	10.0	0.42	0.35	0.07	2.73	1.12	0.61	0.41	70	11	19	LS
SAT	4.33	355	17.7	1.95	14.5	0.40	0.30	0.10	2.90	1.30	0.46	0.39	72	9	19	LS
ADPK	6.24	175	6.51	0.72	5.60	0.35	0.30	0.05	2.16	1.36	0.36	0.40	74	9	17	LS
FSOB	5.53	195	13.3	1.47	13.8	0.45	0.30	0.15	2.41	1.29	0.33	0.38	68	10	22	SL
FSBC	6.76	413	17.4	1.91	55.5	0.47	0.35	0.12	3.72	1.53	0.40	0.29	70	11	19	LS
SQPC	7.72	417	16.4	1.81	11.8	0.52	0.45	0.07	2.61	1.19	0.37	0.33	64	10	26	SL
Mean	6.79	315	11.2	1.42±	17.7	0.50			3.29	1.30			72.7±	11.5	15.8±	
±SE	±0.24	±11	±1.53	0.19	±3.65	±0.02			±0.13	±0.04			0.9	±0.37	1.06	
Kurtosis	0.70	-1.16	-0.62	0.88	2.46	1.82			-0.96	2.11			-0.26	0.29	2.74	
Skewness	-0.59	-0.22	-0.43	-0.64	1.71	-1.00			0.74	1.08			-0.34	-0.69	0.97	
Minimum	5.19	194	1.89	0.12	6.11	0.37			2.76	1.12			67	9	10	
Maximum	8.03	423	17.8	2.31	46.2	0.58			3.99	1.59			77	13	24	

Exch. = Exchangeable cations, LS = Loamy Sand, SL = Sandy Loam

Samples	Fe(mg/kg)	Cr(mg/kg)	Cd(mg/kg)	Pb(mg/kg)	Ni(mg/kg)	Table 3 Mean concentration (mg/kg) of Potentially toxic metals in the University soil (n=50)
Mean	11806±1328	22.9±1.9	0.04±0.01	15.4±1.4	1.43±0.67	
Kurtosis	3.03	1.76	11.0	-0.25	0.72	
Skewness	1.68	1.34	3.32	1.15	1.36	
Minimum	8223	16.8	BDL	11.5	BDL	
Maximum	22667	37.8	0.42	23.7	6.17	

found that Fe of SQPC (15700.00±331.50 mg/kg), CSIC (22700.00±479.42 mg/kg) and PFH (14400.00±296.20 mg/kg) sampling sites exceeded the natural background value (14,000 mg/kg) and the FAO/WHO permissible limits of 1000 mg/kg indicating that these three (3) sites might be affected by anthropogenic activities as constructions of the student's residence has been carried out over the years (FAO/WHO, 2001; Alex *et al.*, 2020). In Table 5, other comparison studies around the world were discussed. Cr ranges from 16.70±0.80 mg/kg - 37.80±1.60 mg/kg with an average of (22.89 mg/kg) and this threshold is greater than the range of value reported by Olatunde *et al.* 2020 (5.54 – 19.14 mg/kg) but lower than Gzik *et al.* (2003) (489 mg/kg). In Table 4, other comparison studies around the world were discussed. The concentrations of Cr at SQPC (26.80±1.00 mg/kg), PFH (24.70±1.20 mg/kg), FSBC (29.20±1.30 mg/kg), CSIC (37.80±1.60mg/kg) were greater than the natural background value (22.60 mg/kg). Compared with the National Environmental Standards and Regulations Enforcement Agency (NESREA), the Cr (average:22.89 mg/kg), is below the threshold of NESREA permissible limits of 100

mg/kg (NESREA, 2011) and FAO/WHO permissible limits of 100 mg/kg (FAO/WHO 2001). An increase in soil pH has been linked to the increase in the ability of Cr (VI) in soil to leach into the environment. (Wuana and Okieime, 2011). Chromium is associated with a common skin sensitization disease known as allergic dermatitis in humans (Wuana and Okieimen, 2011) and affects the bacterial diversity of the soil (Desai *et al.* 2009). Though it is best used in leather tanning, manufacturing of synthetic rubies, dye paints, alloys, metal ceramic, electroplating, and chromium salts are used to colour glass green but then its human health threats include; gastrointestinal ulceration, toxic nephritis, nausea, and vomiting, fever, diarrhoea, acute poisoning through ingestion, vertigo, liver damage, coma death. (Briffa *et al.*, 2020). The concentrations of Cd range from BDL – 0.42 ± 0.02 with an average of 0.04 mg/kg. This is lower than the values reported by Alex *et al.* (2020) (0.19 – 0.32 mg/kg) at a Municipal waste dumpsite, in Sunyani, Ghana, and also lower than Adedeji *et al.*, (2020) at Gateway Trailer Park, Ogere, Nigeria with an average of 2.35 ± 0.48 mg/kg. Cd average (0.04 mg/kg) is lower than Zhi-e *et al.* (2019) in the mining

Table 4. Potentially toxic metal concentrations of the University soil and other locations around the world

Study sites	Fe (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	References
University Soil	11806	22.9	0.04	15.4	1.43	Current study
Cement Factory, Ibese, Nigeria	-	19.1	1.06	2.89	4.96	Olatunde et al. 2020
Quarry site, Isiaqwu, Ebonyi, Nigeria	2654	-	0.23	213	-	Onyedikachi et al. 2018
Municipal waste dumpsite, Sunyani, Ghana.	78.0	-	0.29	0.54	-	Alex et al. 2020
Rustenburg, S. Africa	-	489	0.70	6.3	307	Gzik et al. 2003
Nizna Slana, Slovakia	-	83.2	0.73	44.5	43.7	Shuai et al. 2018
Urad Houqi, China	-	87.9	0.23	32.9	-	Fazekasová, and Fazekas, 2020

area of Xikuangshan, China with an average of 40.941 mg/kg. On comparing the mean concentrations of the university soil samples with their background international values, Cd of CSIC (0.42 ± 0.02) exceeded the natural background value (0.097 mg/kg) but lower than National Environmental Standards and Regulations Enforcement Agency (3.00 mg/kg) permissible level (NESREA, 2011; Eze *et al.*, 2020) and FAO/WHO (3.00 mg/kg) permissible level (FAO/WHO, 2001; Alex *et al.*, 2020). Chronic exposure to cadmium in animals has been linked to various depositions in kidneys thus causing kidney failure, fragile bones, and diseases of the lung due to absorption in the gastrointestinal tract of the lungs (Bernard, 2008). In plants, the key Cd gets into the plants through uptake and translocation processes from the soil. Xylem plays a major role in the transportation of Cd from roots to shoots. This makes it accumulates into tubers, legumes, fruits, grains, cereals, etc (Uraguchi *et al.*, 2009). The major pathway for the transportation of Cd to grain is the phloem. In Japan, the "Itai-Itai" disease is caused by excessive intake of Cd through contaminated foodstuff (Huang *et al.*, 2009). Pb concentrations in the soil range from 11.50 ± 0.63 - 23.70 ± 1.16 with an average of 15.41 mg/kg and is greater than the range of Olatunde *et al.* (2020) (range: 0.41 – 2.89 mg/kg) at Cement Factory, Ibese, Nigeria and Zhi-e *et al.*, (2019) with the average of 248.013 mg/kg in mining area of Xikuangshan, China but lower than Onyedikachi *et al.* (2018) (15–85 mg/kg) at Quarry site, Isiaqwu, Ebonyi, Nigeria. Comparing the mean concentration of Pb with the background international value, the mean concentration of Pb detected in the university soil fell below the natural background level (26 mg/kg). Compared with the National Environmental Standards and Regulations Enforcement Agency (NESREA), the threshold is below NESREA (164 mg/kg) permissible limits (NESREA, 2011; Eze *et al.* 2020) and FAO/WHO (50 mg/kg) permissible limits (FAO/WHO, 2001, Alex *et al.* 2020), suggesting that no adverse effect would occur, thereby making it eco-friendly. Chronic exposure to lead has been linked to various diseases and health problems such as dyslexia, weight loss, hyperactivity, birth defects, brain damage, psychosis, autism, allergies, mental retardation, paralysis, muscular weakness, kidney damage, and may finally lead to death (Martin and Griswold, 2009). Ni concentrations range from 0.03 ± 0.11 - 6.17 ± 0.35 with an average of 1.43 mg/kg. This result is greater

than the value of Olatunde *et al.* (2020) (0.92 – 4.96 mg/kg) but less than the report of Gzik *et al.* (2003) (307 mg/kg). Comparing the Ni average concentrations with their background international value, it was found that Ni concentrations are lower than the natural background level (26.9 mg/kg), also below NESREA (70 mg/kg) permissible limits (NESREA, 2011; Eze *et al.*, 2020) and FAO/WHO (35mg/kg), which suggest no potential adverse effect would likely occur due to its presence in the soil (FAO/WHO, 2001; Alex *et al.*, 2020). When it exceeds its maximum permissible level in the environment, it is hazardous and dangerous and has been known to cause various kinds of cancer within the bodies of animals, and mostly humans that reside close to refineries which include trash incinerators, power plants, that contaminates the air which later settles on the soil after undergoing precipitation reactions and presumably takes a long time to be eliminated from air (Briffa *et al.*, 2020).

Ecological risk assessment of soil

EF values range from 0.5 to 1.5 indicating that the potentially toxic metals pollution is from natural processes, whereas EF values >1.5 are most likely to be from anthropogenic activities (Yi *et al.* 2016). According to the calculation using equation (2), the soil enrichment factor ranges from 0.263 (Ni) – 2.64 (Cd) indicating that potentially toxic metal contamination is from natural processes except Cd which shows an anthropogenic activity (Table 5). The university soil contamination factor ranges from $6.27E-03$ (Cr) – $2.69E+01$ (Cd), and this indicates that the university soil is highly contaminated with Cd, thus making the soil susceptible to hazardous effects on ecological activities. The university geochemical index (I_{geo}) ranges from $-7.22E-01$ (Pb) – $1.52E+00$ (Cd). This suggests that the soil ranges from uncontaminated to moderately contaminated with Cd, which is likely to pose an ecological threat. This analysis measures the comprehensive contamination by all the metals and it's the sum of the contamination factors of the metals. The soil shows a low degree of contamination ($9.78E-03$) of all the metals detected across the sample sites. The modified degree of contamination of the soil (5.72) shows a high degree of contamination across the sample sites. According to the calculated PLI, the soil ($1.42E-01 < 1$) is in grade 1 indicating unpolluted. PERI is the summation of PERF for a single potentially toxic metal. No toxic response is available for Fe thus iron

Table 5. Ecological risk Assessment of the University's soil

Ecological risk factors	Mean Ecological Risk Factors of the Soil's Potentially Toxic Metals				
	Ni	Cr	Cd	Pb	Fe
Enrichment factor (EF)	2.63E-01	3.82E-01	2.64E+00	5.62E-01	-
Contamination Factor (CF)	9.78E-03	6.27E-03	2.69E+01	2.16E-02	1.62E+00
Geochemical index (I_{geo})	-2.71E+00	-1.27E+00	1.52E+00	-7.22E-01	1.12E-01
Potential ecological risk factor (PERF)	4.89E-02	1.25E-02	8.08E+02	1.08E-01	-
Contamination Degree (C_d)	Modified degree of contamination (MDC or mC_d)		Pollution load index (PLI)	Potential Ecological Risk Index (PERI)	
	9.78E-03	5.34E+02	1.42E-01	8.08E+02	

was not considered. As indicated PERF of all soil ranges from 1.25E-02 (Cr) – 8.08E+02 (Cd) which indicates a strong potential ecological risk level of a single metal (Cd). Considering the potential ecological risk index (PERI) level of 8.08E+02 suggests severe or strong potential ecological risk. Conclusively, PERF showed a strong ecological risk level of a single metal (Cd) while PERI suggests that the soil has severe or strong potential ecological risk. As discussed earlier, the potentially toxic metal enrichment in soil caused severe ecological risks by getting absorbed by various organisms present in the marine bodies, thus entering into the complex food chain indirectly (Dash *et al.*, 2019). The enrichment also has an impact on the performance of the soil enzymes (Singh *et al.*, 2020) and microbial biomass (Zhou *et al.*, 2015; Zhang *et al.*, 2016).

Non-carcinogenic risk assessment of the potentially toxic metals in the soil

The exposure pathways were considered on which ingestion exposure pathway is the most significant source of exposure to hazardous substances from sediments. The Hazard Quotient (HQ) for adults and children of the soil samples as calculated using the maximum metal in all the sample sites ranges from 1.15E-06 (Cd) – 0.10 (Fe) ($HQ \leq 1$) for adults and 5.40E-08 (Ni) - 0.97 (Fe) for Children. This suggests that both categories are safe for lifetime exposure and no adverse non-carcinogenic health effects will occur. Similarly, the soil samples showed HI (1.17E-01) < 1, for adults, indicating that no non – carcinogenic effects would occur for adults and likely may occur for children (1.05E+00) as shown in Table 6.

Table 6. Non-carcinogenic risk of different concentrations of potentially toxic metals, HQ and THI

Metals	Concentration (mg/kg)	CDI _{Ingestion}		CDI _{dermal}		HQ Ingestion		HQ dermal	
		Adults	Children	Adults	Children	Adults	Children	Adults	Children
Fe	11806±1328	0.03E+00	0.29E+00	2.84E-01	2.79E-03	0.97E+00	1.28E-02	1.25E-04	0.97E+00
Ni	1.43±0.67	8.45E-06	1.08E-10	6.48E-04	2.03E+00	5.40E-08	3.50E-03	1.10E+01	5.40E-08
Cr	22.9±1.9	3.25E-05	3.03E-04	2.97E-04	2.91E-06	3.22E-04	3.45E-05	3.22E-04	3.22E-04
Pb	15.4±1.40	5.18E-05	4.83E-04	4.73E-04	4.64E-06	8.66E-02	1.25E-04	1.22E-07	8.66E-02
Cd	0.04±0.01	5.75E-07	5.37E-06	5.21E-06	5.11E-08	1.07E-05	2.63E-08	2.58E-10	1.07E-05
		THI Ingestion				THI Dermal			
		Adults	Children	Adults	Children	Adults	Children	Adults	Children
		1.06E+00	1.65E-02	1.10E+01	1.06E+00				

Considering the average absorbed daily dose (mg/kg/day) of dermal exposure pathway (HQ_{dermal}), as stated in ingestion pathway exposure, CSIC having the highest metal concentration across all the sample points indicates $HQ < 1$ for adults and children, suggests no potential non-carcinogenic effect. FSBC having the highest metal (Ni) concentration shows no potential non-carcinogenic effect for adult's $HQ (3.50E-03) < 1$, while potential non-carcinogenic effect would likely occur for children as $HQ (1.10E+01) > 1$ in lifetime exposure. Comparing the average absorbed daily dose (ADD mg/kg/day) with the reference dose across the sample points of each metal for both adults and children, the thresholds are below the reference dose guideline values, suggesting that human health is not susceptible to non-carcinogenic risk. The Hazard Quotient (Table 6) of all the sampling points as calculated showed some variations. Ni in sample points FSBC ($1.10E+01$), and CSIC ($8.15E+00$) were $HQ > 1$ which indicates unsafe for lifetime exposure for children, therefore, potential non-cancer adverse effects will likely occur. Similarly, the non-carcinogenic effects posed by all the potentially toxic metals were assessed using the Hazard Index (HI) which is the summation of all the HQ of potentially toxic metals detected across the university soil and it's simply the contribution of all the detected potentially toxic metals in each sample point toward the non-carcinogenic effect of both adults and children, and as stated by (Qing *et al.* 2015), if $HI > 1$, then a chronic non-cancer effect would likely occur and will increase with an increase in HI thresholds, but then, when the

$HI < 1$, most probably no risk of non-carcinogenic effects would occur. The soil HI suggests that no chronic non-carcinogenic effects would likely occur for adults and children through both exposure pathways but any slight increase in the thresholds of all the metals detected will pose a chronic non-cancer threat.

Carcinogenic risk assessment of the potentially toxic metals in the soil

Assessment of carcinogenic risk is ideally a probability of an individual developing any form of cancer for a lifetime before ingestion route of exposure to carcinogenic hazards (Li *et al.*, 2014) Using individual excess lifetime cancer risk (IELCR) and Slope factor (SF), carcinogenic risk was estimated as stipulated in Table 7. The ingestion route of exposure was calculated for two potentially toxic metals; chromium and Lead as they are classified as probable causes of cancer in humans (ASTDR, 2007; 2012) and so, if the value of Risk Index $< 10^{-6}$, it indicates negligibility of carcinogenic risk from exposure while $RI > 10^{-6}$ indicates the risk of developing cancer in humans is likely to occur and if the RI is within the range from $10^{-6} - 10^{-4}$, it shows the tolerable risk to social stability and human health (Wu *et al.*, 2015). The analyzed soil sample points showed no carcinogenic risk under Chromium (VI) and Lead causing agents for both adults and children as they are within the range $10^{-6} - 10^{-4}$ indicating that the university community are not susceptible to cancer from Chromium and Lead causing agent for all population, thus, the thresholds are within tolerable limits of FAO/WHO.

Ingestion slope factor (mg/kg/day)		Carcinogenic risk			
		Lead		Chromium	
Lead (Pb)	Chromium (Cr)	Adults	Children	Adults	Children
0.0085	0.5000	2.76E-07	2.58E-06	7.96E-06	7.43E-05

Table 7
Carcinogenic risk of the university soil

Conclusions

This study assessed potentially toxic metals contaminations, ecological pollution, and health risk assessment caused by these metals. Potentially toxic metals detected in the University soil sites were in the order of $Fe > Cr > Pb > Ni > Cd$, which indicated natural contamination throughout the sample sites and was classified from non-polluted to moderately polluted. On comparing the mean concentration of

the university soil detected potentially toxic metals with FAO/WHO, Fe showed a threshold above FAO/WHO permissible limits due to natural process. Other metals (Cd, Ni, Pb, Cr) studied across the university sample sites were below FAO/WHO permissible limits. No significant effect of anthropogenic activities had an impact on the ecological assessment; however, the natural pollution load of most of the soil poses ecological threats the-

reby being contaminated with the detected potentially toxic metals. Human health risk assessment was assessed through ingestion and dermal exposure route and on calculating the estimation of ingestion HQ, the results suggested that no potential non-carcinogenic risk may occur on ingestion exposure but will likely occur for children through dermal exposure pathway for a lifetime while HI indicated that non-carcinogenic effects would occur for children and safe for adults. As in the dermal exposure route, HI of dermal showed ($HI > 1$) which suggests chronic non-carcinogenic effect would likely occur for children through lifetime exposure. For carcinogenic risk, both Chromium and Lead which are cancer-causing potentially toxic metals indicated no remote carcinogenic risk for both populations through ingestion exposure, as ($RI < 10^{-6}$) was found below guidelines values. Having studied, tested, analyzed, and compared the human health risk and ecological risk of this university soil with national and international guideline values, though no anthropogenic contamination was detected from natural activities causing a rise to contamination load of this university soil, it is recommended that further analysis on human health and ecological risk of soil and water should be carried out in a few years from now to ascertain the risk difference, then compared again with the thresholds of our local Environmental protection Agency here in Nigeria. Meanwhile, it is recommended that the university wastewater be pretreated for organic and inorganic contaminants before being released into the environment.

Acknowledgements

The authors wish to express their appreciation to Miss Leye Abioye in the Chemistry unit, Department of Basic Sciences, Babcock University for her support during the sampling and laboratory experiment.

Disclosure statement

Conflict of Interest: The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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