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Assessment of Heavy Metals in Agricultural Soils and Plant (*Vernonia amygdalina* Delile) in Port Harcourt Metropolis, Nigeria

William Azuka Iyama [1,2], Kingsley Okpara [1] and Kuaanan Techato [1,*]

1 Faculty of Environmental Management, Prince of Songkla University, Hat Yai, Songkhla 90110, Thailand; williamiyama@rschst.edu.ng (W.A.I.); okparakingsley777@gmail.com (K.O.)
2 Jaros Inspection Services Ltd. Laboratory, Rivers State University, Port Harcourt 5080, Nigeria
* Correspondence: kuaanan.t@psu.ac.th

Abstract: This study assessed the concentration of heavy metal, such as lead (Pb), cadmium (Cd), Chromium (Cr), iron (Fe), Nickel (Ni), and Silver (Ag), in *Vernonia amygdalina* Delile and agricultural soils of three university farms located in Port Harcourt, Nigeria. The soils and plants were taken randomly to form composite samples and analyzed for heavy metals by the use of atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF). The study stations were agricultural soils and *Vernonia amygdalina* Delile from the Ignatius Ajuru University of Education (I), River State University (R) and University of Port Harcourt (U). The soil samples recorded mean concentration ranges for Fe as 19.71 ± 1.77 (I)–27.24 ± 3.56 mg/kg (R) in soils and 12.95 ± 1.68 (R)–18.18 ± 2.02 mg/kg (U) for the bitter leaf samples. The mean range for Pb concentration in the soil and bitter leaf were 4.35 ± 0.87–6.80 ± 0.86 mg/kg and 0.24 ± 0.64–2.19 ± 0.74 mg/kg, while Cd concentration in the soil and bitter leaf were 0.46 ± 0.28–1.42 ± 0.40 mg/kg and 0.17 ± 0.22–0.42 ± 0.08 mg/kg, respectively. The respective mean ranges for Cr concentration in the soil and bitter leaf were 5.91 ± 1.14–8.77 ± 0.88 mg/kg and 4.04 ± 0.64–5.92 ± 0.69 mg/kg, while Ni in soil and bitter leaf were 0.54 ± 3.38–10.26 ± 3.50 mg/kg and 0.042 ± 1.42–3.30 ± 0.88 mg/kg, while Ag was negligible. Heavy metal levels in soils and *Vernonia amygdalina* followed the order Fe > Cr > Pb > Ni > Cd and Fe > Cr > Ni > Pb > Cd, respectively, and were lower than WHO/FAO and EPA, except Cd, which was higher in soil and in *Vernonia amygdalina*. The ecological risk factor (*ErF*) was comparatively lower in soils than in the plant, while pollution load index (*PLI*) showed high heavy metal retention capacities in *Vernonia amygdalina* due to more anthropogenic influences. The metal transfer factor (*TF*) was highest in Fe, followed by Cr > Cd > Ni > Pb, while Pb had the highest chances of cancer risks from the incremental lifetime cancer risk (*ILCR*), especially in both soil and plant (mean *ILCR*, 2.07×10^{-2} and 2.45×10^{-3}), while Cd had the least (mean *ILCR*, 9.64×10^{-5} and 3.36×10^{-5}). Anthropogenic activities must be regulated and monitored by government relevant agencies to reduce heavy metal inputs into soils and avoid excessive accruals in food chain.

Keywords: agricultural soil; *Vernonia amygdalina* Delile; heavy metal; pollution load index; cancer risk; transfer factor

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1. Introduction

Several research studies have shown that heavy metal contamination and pollution emanate principally from natural and anthropogenic activities [1,2]. Any metal considered toxic or hazardous may be called heavy metal; toxic heavy metals (THM), such as lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), and iron (Fe), contaminate agricultural soils and crops, such as garden vegetables, grains, and fruits, due to their concomitant and detrimental complications from their persistence and non-biodegradability [3,4]. By definition, heavy metals (HM) are metals of specific high densities greater than 5 g/cm^3 and of high molecular mass, transition metal, and of negative effects on the living things and the ecosystem [5]. According to Singh [6], it is irrespective of the weight, atomic mass, or density. Contamination of soils may emanate from heavy metal and metalloids accumulation through many anthropogenic activities, ranging from heavy metal disposal to deposition in the air [7]. Heavy metals are causes of environmental pollution from different from dictionary of Chemistry. The main sources of toxic metals are anthropogenic inputs and industrial wastes [8]. Currently, pollution has increased due to increasing anthropogenic inputs ranging from burning of fossil fuels to exhaust emissions, which were noted as major sources of metallic burden in the atmospheric [7,9]. Research showed that different automobiles released various kinds of hazardous metals into the ecosystem [10].

According to Khan et al. [3], soil can act as either a sink or source. There are myriads of pollution, such as soil pollution, affecting living organisms, which include the crops. Chemical features of soils are dependent on the kind of weathered rocks (e.g., the mafic and ultramafic classes) in study areas leading to contamination of both soil and crops [1,11,12]. *Vernonia amygdalina* Delile being a staple diet can act as buffer during digestion processes and may contain both essential and non- essential metals [12–14]. Metals, such as Cd, Cr, Pb, Ni, and Fe, can be toxic and, when accumulated over time, can be detrimental to human health [3,15]. Food contaminated by Cd can result in acute and chronic health challenges, such as artery problems and others [12,16,17]. Ingestion of Ni can cause cardiac arrest, fatigue, heart issues, and respiratory diseases [4]. Exposure to Pb and Cd (most abundant HMs in vegetables) can pose various health challenges, such as heart, kidney, and bone diseases. Therefore, obtaining the levels of these HMs in the soil and plant (*Vernonia amygdalina*) can help in estimating their concentration in the edible leaf part [18].

Study revealed that *Vernonia amygdalina* leaf has high mineral content and is used as a vegetable [19]. Bitter leaf is of either grey or brown colored bark, a rough texture, and is flaked [20]. *Vernonia amygdalina* is medicinal and contains both essential and toxic metals over a wide range of concentrations [21,22].

Studies on *Vernonia amygdalina* to determine concentrations of Cd, Pb, Cr, Ni, and Ag on garden soils from these tertiary institutions have not been done especially looking at the health risks using transfer factor (*TF*), contamination factor (*CF*), pollution load indices (*PLI*), enrichment factor (*EF*), ecological risk factor, chronic daily intake ingestion, hazard index (*HI*), and carcinogenic analysis [12,23–25]. Hence, this study will evaluate the level of heavy metals of interest from the locations (Fe, Pb, Cr, Cd, Ni, and Ag) and determine the levels of ecological and health risks impacts. The government pressure and focus on farming by the citizens increases the need to grow this plant even at subsistence level; hence, the adjacent soil content must be known to in monitoring, prevention, and control of contamination and subsequent pollution.

2. Materials and Methods

2.1. Study Stations

The research study was done on three campuses: Uniport (U), Rivers State University (RSU, R), and the Ignatius Ajuru University of Education (IAUE, I). The map of the sampling locations appears in Figure 1 whose locations were determined using geographic positioning system (GPS). The control stations have the following coordinates: I (4°48′42″ N, 6°56′40″ E), R (4°48′20″ N, 6°59′16″ E, and U (4°53′56″ N, 6°54′15″ E), as shown in the figure below.

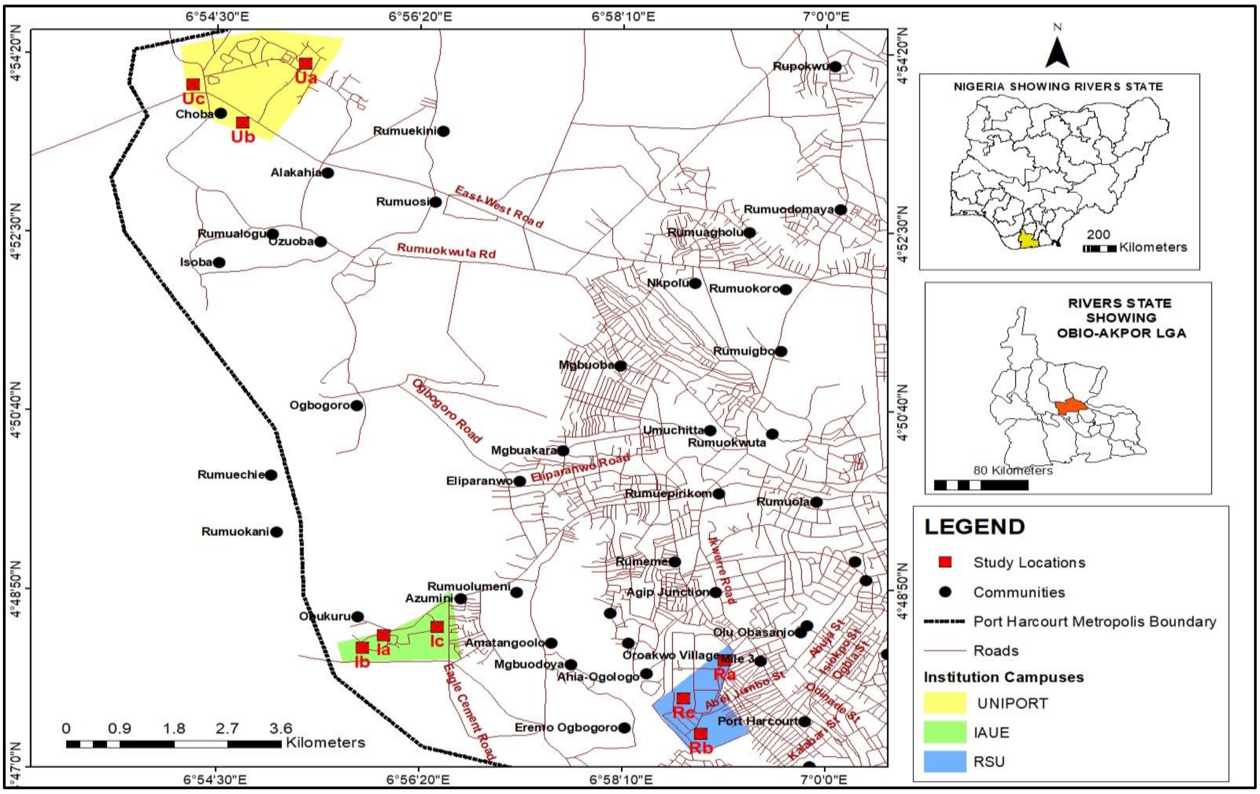


Figure 1. Map of the study locations, I, R, and U (source: Digitized from Ministry of Lands/Survey, Port Harcourt).

2.2. *Sampling and Pre-Treatment Procedures*

2.2.1. Soil Sampling

Samples of soils were taken randomly from a depth of 0–15 cm using the stainless steel auger from three locations. Each soil sample was prepared by firstly collecting many sub-soil samples around each sampling site, followed by thorough mixing of the samples to form the composite sample (1 kg) using the quartile technique. The sample was then sealed in a clean polyethylene bag and transported to the Jaros Inspection Services Ltd., Laboratory, KM 2 Iwofe Road, Rumueprikom, P.M.B.6150, Port Harcourt, Rivers State, (+234-33486693) Nigeria. After oven-drying (at 105 °C) for six hours, the soil samples were grounded mechanically and passed through a 1.18-mm sieve and stored for further analysis.

2.2.2. *Vernonia Amygdalina* Delile Sampling

The samples from bitter leaf were taken from the three study sites of I, R, and U (n = 36 samples from 4 study stations) at the same points where the soil samples were collected. The bitter leaf was taken from the three sampling spots, while the controls were outside the campuses. These were then put into separate polythene bags and labeled accordingly. They were then taken immediately to the laboratory for further handling and analysis. The samples of the vegetable were thoroughly washed with both tap water and de-ionized water to remove air pollutants. Finally, the samples were oven-dried at 105 °C for 48 h to remove moisture and pulverized. This was achieved by the use of agate pestle and mortar. Similarly, sieving was done using a 0.5 mm mesh size sieve to obtain a uniform particle size. Each sample was labeled and stored in a dry plastic container that had been pre-cleaned with concentrated nitric acid (HNO_3) to prevent contamination prior to analysis (X-ray fluorescence spectrometer). The determination of heavy metal was done in accordance with standard procedures.

2.3. Extraction Procedures

2.3.1. Agricultural Soil Extraction

The collected soil samples were extracted using the wet digestion method (WDM). Afterwards, thorough digestion of the representative soil samples was done. One gram (1 g) dried powdered soil was put into a 50 mL conical flask, and, later, a 15 mL sample digested in 10 mL of 1:1 HNO_3:H_2SO_4 mixture, heated to 95 °C to dry, and thereafter refluxed for 10 min without boiling. After cooling, 5 mL of concentrated HNO_3 was once again added and refluxed for 30 min till brown fumes were produced. The solution was vaporized to about 5 mL on mantle set at 95 °C with a watch glass over it. After cooling the resulting sample, 2 mL of H_2O and 3 mL of 30% H_2O_2 were added, and the solution was placed on the heating mantle to start the oxidation of peroxide until effervescence subsided. The vessel was cooled and the acid-peroxide digestate heated to about 5 mL at 95 °C. Later, 10 mL of concentrated hydrochloric acid (HCl) was added to the sample digest, and the solution was placed on the heating source and refluxed for 15 min at 95 °C. The Whatman No. 42 filter paper was used to filter the obtained digestate, put into a 100 mL volumetric flask, and then made up to the mark with distilled water. Finally, the filtrate was taken for analysis. Heavy metal analysis was done using the Atomic Absorption Spectrophotometer (ASTMD 1971/4691) (SAI Global Standards, Chicago, IL, USA), solar thermos elemental flame atomic absorption spectrometer, model SE-71096 made in Germany with detection limit of 0.001 $mg \cdot kg^{-1}$ at Jaros Inspection Services Ltd., Iwofe Road, Port Harcourt, Nigeria. The AAS was fitted with specific lamp of a particular heavy metal, while the other conditions were the same [26].

2.3.2. *Vernonia Amygdalina* Delile Extraction

Then, 2.0 g of *Vernonia amygdalina* Delile, 15 mls of perchloric ($HClO_4$), and trioxonitrate V acid solution were mixed in the ratio of 1:4. After been left overnight, cold digestion was done and heated on hot plate until a transparent solution was observed, but at different temperatures. After cooling, the digested samples were filtered using the What man filter paper No. 42, then diluted up to 100 mL by volume using highly purified deionized water, and stored at room temperature for further analytical procedures.

2.4. Analytical Procedures

Sample preparations and analysis utilized high grade chemicals of high spectroscopic purity of 99.9% (Merck Darmstadt, Darmstadt, Germany). To obtain high standards, solutions of Fe, Pb, Cd, Cr, Ag, and Ni were prepared diluting their respective 1000 mg/L standard solutions (Fluka Kamica, Busch, Switzerland). The final analysis for both soils and *Vernonia amygdalina* extracts were done using atomic absorption spectrophotometer AAS (Perkin Elmer AAS-700, Darmstadt, Germany). To determine accuracy and precision, blank reagents and standard reference materials (SRMs) of the studied heavy metals were used for digestion. To ascertain quality assurance, each sample batch was analyzed in triplicate under standard conditions at 95% confidence level. The instrumental conditions and detection limits for selected HMs are based on standard conditions. Appropriate quality assurance procedures and precautions were taken to ensure the reliability of the results. Samples were carefully handled to avoid cross-contamination. Deionized water was used throughout the study. Reagent blank determinations were used to apply corrections to the instrument readings. For validation of the analytical procedure, repeated analyses of the samples against internationally certified plant standard reference material (SRM) of the National Institute of Standard and Technology were used, and the results were found to lie within ±1% of the certified values. Measurements were made using standard hollow cathode lamps for Pb, Cd, Cr, and Ni. The limit of detection (LOD) of the analytical method for each metal was calculated as being triple the standard deviation of a series of measurements for each solution. The concentration of which is distinctly detectable above the background level. These values were 0.001, 0.001, 0.001, and 0.002 mg/kg for Pb, Cd, Cr, and Ni, respectively. In addition, the limit of quantification (LOQ) of the element was determined; these were calculated as 0.003, 0.003, 0.003, and 0.007 mg/kg for Pb, Cd, Cr, and Ni, respectively.

2.5. Research and Sampling Designs

The pure experimental (experimental with control) and cross-sectional survey designs (samples were taken at different points in time) were adopted for the study.

2.6. Statistical Analysis

The mean, standard deviation, analysis of variance (one-way ANOVA), *t*-test, and Pearson's product moment correlation coefficient were used to determine the spatial relationships in the study stations and concentrations, as well as also for that between two different stations, respectively, at 95% confidence level ($p \leq 0.05$). Similarly, different health risk assessment models and graphs were used to illustrate existing trends around the three campuses to ascertain the health implications.

2.7. Risk Assessment Models

1. Transfer Factor (*TF*)

The results for soil and the bitter leaf were employed to determine the transfer factor (*TF*) as given in the following equation [27].

$$TF = \frac{[Heavy\ metals]bitter\ leaf\ \mathrm{mg{\cdot}kg^{-1}}}{[Heavy\ metal] \times soil\ \mathrm{mg{\cdot}kg^{-1}}} \tag{1}$$

where $[Heavy\ metals]bitterleaf\ \mathrm{mg{\cdot}kg^{-1}}$ = Concentration of heavy metal in bitter leaf ($\mathrm{mg{\cdot}kg^{-1}}$); $[Heavy\ metal] \times soil\ \mathrm{mg{\cdot}kg^{-1}}$ = Concentration of heavy metal in the soil ($\mathrm{mg{\cdot}kg^{-1}}$).

2. Contamination Factor (*CF*):

The Contamination Factor (*CF*) is calculated using Equation (2) and shows site specific contamination of toxic substances [28].

$$CF = \frac{C_m(sample)}{C_m(background)} \tag{2}$$

where $C_m(sample)$ = metal concentration at a contaminated site; $C_m(background)$ = concentration of a given element in background sample. The *CF* is based on 4 categories of contamination: Low ($CF < 1$), moderate ($1 < CF < 3$), considerable ($3 > CF < 6$), and very high ($CF > 6$) [29].

3. Pollution Load Index (*PLI*):

This can be determined using Equation (3) [30].

$$PLI = (CF1 \times CF2 \times CF3 \ldots CF_n)^{1/n} \tag{3}$$

where *CF* = contamination factor, *n* = number of study metals, C_{metal} = metal pollutant concentration in soil; $C_{background}$ = metal background value.

4. Enrichment Factor (*EF*):

This can be evaluated using Equation (4).

$$EF = \left(\frac{C_{metal}}{C_{normalizer}}\right) / (C_{metal}/C_{normalizer})control \tag{4}$$

where C_{metal} and $C_{normalizer}$ are concentrations of heavy metal and normalizer in soil and control, respectively. *EF* value is used to differentiate magnitude of contamination resulting from either the natural or human influence [31].

5. Ecological Risk Factor (E_rF) and Potential Ecological Risk Factor (RI):

The E_rF and RI can be calculated using Equations (5) and (6), respectively [32].

$$ErF = TR \times CF \tag{5}$$

where TR = toxic response factor, and CF = contamination factor.

$$RI = \sum ErF \tag{6}$$

Interpretations of ErF and RI are as follows; $ErF < 40$ and $RI < 150$ is low risk; $40 \leq ErF < 160$ and $150 \leq RI < 300$ is moderate risk; $80 \leq ErF < 160$, $300 \leq RI < 600$ is considerable risk; $160 \leq ErF < 320$ is high; $ErF \geq 320$ and $RI \geq 600$.

6. Chronic Daily Intake (CDI_{ing}) via ingestion:

The result could be obtained using Equation (7) below.

$$CDIing = C_{soil} \times Ring \times EF \times \frac{ED}{BW} \times AT \times 10^{-6}. \tag{7}$$

R = Rate of ingestion (100 mg/day in adult and 200 mg/day in children), EF = exposure frequency, ED = exposure duration (24 years in adults and 6 years in children), BW = body weight of the individual exposed (70 kg in adults, 15 kg in children), AT = averaging time in days (365 $\times$ ED adult/children) (Reference dose (R_fD) for metals are: Fe = 0.7, Pb = 0.0035, Cd = 0.001, Cr = 0.003, and Ni = 0.0008) [33].

7. Hazard Quotient (HQ):

HQ is determined using Equation (8). If the $HQ < 1$, no obvious risk, but, if $HQ > 1$, then, risk is obvious.

$$HQ = \frac{CDI}{RfD} \tag{8}$$

CDI = chronic daily intake, and RfD is the oral reference dose for the metal (mg kg^{-1} of body weight per day); RfD = estimate of a daily oral exposure for the human population which does not cause deleterious effects during a lifetime, generally used in EPA's non-cancer health assessments, and values of RfD for Cd (0.001 mg kg^{-1} per day), Ni (0.02 mg kg^{-1} per day), and Cr (1.5 mg kg^{-1} per day) were taken from Integrated Risk Information System [34]. The value of RfD for Pb (0.0035 mg kg^{-1} per day) was taken from known WHO [34] standards. The average Bo was taken as 70 kg for adults [34], and 19.25 kg for children 0–6 years old [35].

8. Hazard Index (HI):

The hazard index can be calculated using Equation (9). $HI < 1$ means no risk from non-carcinogenic effects; $HI > 1$ means adverse health effects possible and has probability of effects increasing with the increases in the HI value.

$$HI = \sum HQ = HQFe + HQCd + HQCr + HQNi \tag{9}$$

9. Carcinogenic Analysis ($ILCR$)

The $ILCR$ is calculated using Equation (10), and it is defined as the incremental probability of a person developing any type of cancer over a lifetime as a result of twenty-four hours per day exposure to a given daily amount of a carcinogenic element for seventy years [36]. Equation (10) is commonly used for the calculation of the lifetime cancer risk.

$$ILCR = CDICSF \tag{10}$$

where CSF is the cancer slope factor, and CSF for the metals is Cd—0.38, Cr—0.5, Pb—0.0085, and Fe—0 [34], and CDI is the chronic daily intake. The permissible limits are considered to be 10^{-6} and $<10^{-4}$ for a single carcinogenic element and multi-element carcinogens [37].

3. Results and Discussions

The summary of results is shown in Table 1; Table 2 shows that for both soils and the *Vernonia amygdalina* leaf (bitter leaf). The soil samples recorded mean concentration ranges for Fe as 19.71 ± 1.77 (I)–27.24 ± 3.56 (R) in soils across the stations and 12.95 ± 1.68 (R)–18.18 ± 2.02 (U) for the bitter leaf samples. The mean ranges for Pb concentration in the soil and bitter leaf were 4.35 ± 0.87 (R)–6.80 ± 0.86 (I) and 0.24 ± 0.64–2.19 ± 0.74, respectively. The mean ranges for Cd concentration in the soil and bitter leaf were 0.46 ± 0.28 (I)–1.42 ± 0.40 (U) and 0.17 ± 0.22 (U)–0.42 ± 0.08 (U), respectively. The mean ranges for Cr concentration in the soil and bitter leaf were 5.91 ± 1.14 (R)–8.77 ± 0.88 (U) and 4.04 ± 0.64 (U)–5.92 ± 0.69 (I), respectively. These stations recorded respective concentration ranges of Ni for the soil and bitter leaf as 0.54 ± 3.38 (I)–10.26 ± 3.50 (R) and 0.04 ± 1.42–3.30 ± 0.88 (R). The mean ranges of concentration for Ag were 0.001 ± 0.00 (I)–0.00 ± 0.00 (R, soil) and 0.00 ± 0.00 (I)–0.00 ± 0.00 (I, bitter leaf).

Table 1. Mean concentration of heavy metals in soils of campuses (I, R, U).

	Sample Stations						
Heavy Metals(mg/kg)	**I**	**Control (Ic)**	**R**	**Control (Rc)**	**U**	**Control**	**Mean (I, R, U)**
Fe	19.71 ± 1.77	22.51 ± 2.25	27.24 ± 3.56	27.57 ± 2.37	19.69 ± 1.78	20.55 ± 2.50	22.21
Pb	6.80 ± 0.86	7.36 ± 1.20	4.35 ± 0.87	5.35 ± 0.46	5.60 ± 0.01	6.40 ± 1.40	2.98
Cd	0.46 ± 0.28	0.50 ± 0.24	0.71 ± 0.11	0.75 ± 0.21	1.42 ± 0.40	2.40 ± 0.50	0.87
Cr	8.77 ± 0.88	8.78 ± 0.56	5.91 ± 1.14	6.56 ± 0.56	7.89 ± 0.26	8.20 ± 1.20	7.52
Ni	0.54 ± 3.38	0.48 ± 3.50	10.26 ± 3.50	11.15 ± 0.20	5.14 ± 0.12	5.50 ± 0.05	5.31
Ag	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00

Table 2. Mean concentration of heavy metals in *Vernonia Amygdalina* of campuses (I, R, U).

	Sample Stations						
Heavy Metals(mg/kg)	**I**	**Control (Ic)**	**R**	**Control (Rc)**	**U**	**Control (Uc)**	**Mean**
Fe	14.86 ± 0.33	15.50 ± 0.50	12.95 ± 1.68	13.23 ± 0.54	18.18 ± 2.02	19.20 ± 1.00	15.33
Pb	0.98 ± 0.11	1.20 ± 0.20	0.24 ± 0.64	13.23 ± 0.54	2.19 ± 0.74	2.40 ± 0.50	1.14
Cd	0.17 ± 0.10	0.35 ± 0.25	0.32 ± 0.01	0.37 ± 0.05	0.42 ± 0.08	0.54 ± 0.26	0.30
Cr	5.92 ± 0.69	6.15 ± 0.50	4.88 ± 0.05	5.10 ± 0.03	4.04 ± 0.64	4.50 ± 0.45	4.95
Ni	0.04 ± 1.42	0.10 ± 1.60	3.30 ± 0.88	3.59 ± 0.10	2.80 ± 0.53	3.20 ± 0.10	2.05
Ag	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00

3.1. Heavy Metal Concentration in Both Soils and Vernonia Amygdalina (Bitter Leaf)

Total Fe concentration in the soil fell within WHO/FAO safe limit of 300 mg·kg^{-1} [38]. Concentration of Fe recorded is far below that for soils of Illela Garage in Sokoto State, Nigeria in oil impacted soil of the Niger Delta, and Abattoir soils, in Port Harcourt, Nigeria [39,40]. Relatively, high concentration found in RSU is likely due to natural Fe content in soil, especially for both RSU and IAUE, which lie on very similar terrain of soil structure and texture. Averagely, Fe content in both soils and plants is usually high in soil and selected medicinal plants and could emanate from agricultural practices [40,41].

The soil sample result recorded higher Pb concentration in IAUE (I), followed by Uniport (U), before RSU (R). These results were under similar ranges with those observed in drain soils in Kaduna, Nigeria [42]. These results were though lower than those recorded in earlier works [40,43]. These were higher than average concentrations observed in Kano gardens 1.60 ± 0.53 mg/kg [44]. This may be likened to the anthropogenic inputs, such as vehicle servicing and repair activities, found around these stations. Increased accumulation of Pb in the human system leads to several medical conditions, including biodiversity loss of lower organisms [45]. Lead (Pb) contaminant may be as a result of adjacent traffic activities and polluted atmospheric precipitation and use of agrochemicals easily assessed by plant absorption [46,47]. Soils affected by Pb could be ingested by children through the inhalation of dust ($PM_{2.5}$) containing Pb, resulting to cardiovascular and respiratory complications [48,49].

The results for Cd were higher than the lower range limit but lower than the upper range limits in earlier research by Mohammmed and Folorunsho [42] in Makera Drain soils, Kaduna, Nigeria, but absolutely lower than those recorded by Fosu-Mensah et al. [43] in their similar study, but in similar range with the work of Edet and Ukpong [50], on the concentrations of likely toxic metals elements and total hydrocarbon in soils of Niger Delta Region, Nigeria. The concentration of Cd was higher than those earlier recorded in Pakistani soils [12]. Cadmium (Cd) was mixed with 15 mL perchloric acid ($HClO_4$) and trioxonitrate V acid (HNO_3) solution using the respective ratio of 1:4 [3,51]. Cadmium (Cd) concentrations were higher than those found in common ranges of soils (0.01–0.7 mg/kg) but lower than threshold values [25,52,53]. This can be traced to the presence of dumpsite around the study site where abandoned batteries from domestic wastes are disposed. Amini et al. [54] reported best average for Isfahan as 1.79 mg/kg, while Fakhri et al. [25] had average range of 0.42–2.22 mg/kg in China, which were above those recorded in this research study attributed to soil type, prevalent air pollutants from differential industrial activities, and staple food waste and type. The health implication of elevated Cd level, especially as an endocrine disruptor and carcinogenicity in humans, cannot be underestimated [55,56]. The mean concentrations of Cd were lower than the threshold limit of 1.4 mg/kg as prescribed by UK but within the 0.8 mg/kg level by Dutch's guideline [57]. According to Wuana and Okieimen [8], Cd is bio-persistent but has some toxicological functions, so, once absorbed by any organism, it remains resident for many years. The concentration of Cd remains a threat from the study results.

The Cr concentrations showed that all the stations sampled have values below the target value ranges and intervention limits for soils, as well as for plants [58,59]. These were though above those recorded in soils and plants in Pakistan [12]. The results were generally lower than those earlier recorded by Nafiu et al. [60] on the vertical distribution of heavy metals in wastewater-irrigated vegetable garden soils of three West African cities but higher than the lower range limits observed in Calabar [50]. Though the relatively lower concentration of Cr observed in sample site does not reflect its association with parent granite and ultramafic rocks, as earlier reconfirmed by Mohammed and Folorunsho [42], other human inputs must be of great concern. The primary sources of Cr-contamination are human and industrial activities, such as electroplating processes and poor waste disposal [61]. The higher the concentration of Cr in IAUE soil types, the higher the probability of more anthropogenic inputs for the study areas. These results are lower than those obtained by Yusuf et al. [62] in Sokoto sampled soils and similar to those obtained by Ezejiofor et al. [63] on the study of environmental metals pollutants load of a densely populated and heavily industrialized commercial city of Aba, Nigeria. These relatively lower values than the standard limits are indication of man-made inputs which must be checked to avoid gradual accumulation and threat to life of both plants and organisms, including humans.

Nickel (Ni) concentration in the study was far lower than those observed in earlier research works [43,64]. These results were though lower (Ni) in station I but higher in terms of the upper limit ranges (R and I) by Lawal and Audu [44] Kano, Nigeria, and Edet and Ukpong [50] in Calabar. According to Masona et al. [65], wastewater increases heavy metal concentrations in soils, which agrees with the earlier research result of Schmidt [66], that toxic heavy metals, and especially Ni, is commonly found in high concentrations. The most common application of Ni is as additive in steel and other metal production processes, but the major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating [67]. Nickel (Ni) can be released into the atmosphere by various processes and industries, such as power plants and trash incinerators, which accumulates on ground surfaces after precipitation reactions, and Ni is persistent in the atmosphere [8]. The soils recorded relatively higher concentrations of Ni at the IAUE location than the others, and all the stations sampled have values below the intervention limits for soils, as well as for plants [59,68]. This may be due to anthropogenic activities, which are more common around U and I but not in R, due to site soil properties being near the main capital city, where only vehicular, mechanic workshops, and atmospheric pollutions are likely possible.

According to Saeki et al. [69], the Ag values ranged from 0.27 to 6.89 mg kg^{-1}, which were much higher than the values of the unpolluted soils and also within the range of the results of this study, especially the lower limit of 0.27 mg/kg. The concentrations of Ag were negligible as the range was 0.00–0.00.

3.2. Assessment of Pollution Indices and Health Risk Assessment for Heavy Metals in Soils and Bitter Leaf (Vernonia amygdalina)

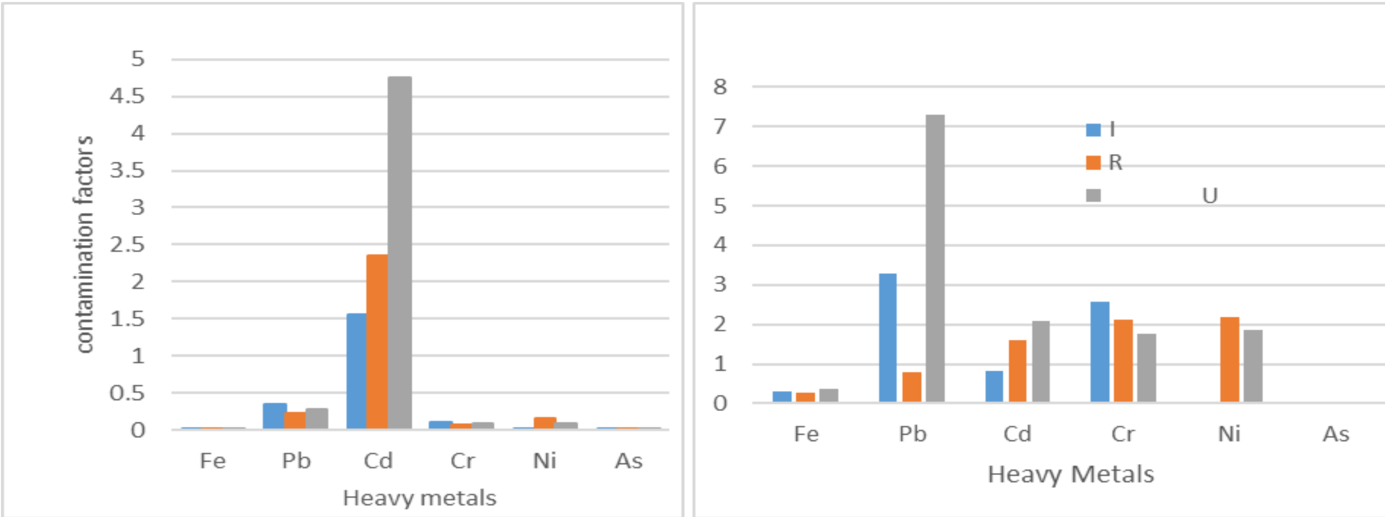
3.2.1. Contamination Factor (*CF*)

The soil contamination factor (*CF*) shows the following ranges in Table 3: Fe (0.0004–0.0006), very slight contamination; Pb (0.22–0.34), slight and moderate contamination; Cd (1.55–4.75), moderate and severe pollution; Cr (0.07–0.10), Ni (0.01–0.15), and Ag showed very slight contaminations, whereas, in bitter leaf, Fe (0.27–0.38) was of moderate contamination; Pb (0.79–3.27) recorded very severe contamination to severe pollution from vehicular emissions; Cd (0.83–2.095) showed very severe contamination to slight and moderate pollution due to indiscriminate battery disposal around the gardens; Cr (1.757–2.576) showed very severe contamination to moderate pollution; and Ni (0.028–2.197) showed very slight contamination to moderate pollution, while Ag recorded very slight contamination. These results were in consonance with those of earlier, similar research studies [70,71]. The presence of heavy metal in plant parts have been attributed to reckless use of land, leading to contamination [72,73]. The order of *CF* for the soil study area in metal composition was Cd > Pb > Cr > Ni > Fe > Ag, while, for the bitter leaf, it was Pb > Cr > Cd > Fe > Ni > Ag. The trend of heavy metal contamination in both soils and *Vernonia amygdalina* is shown in Figure 2 below.

Table 3. Contamination factor (*CF*) for heavy metals in soils and *Vernonia amygdalina* Delile of campuses (I, R, U).

		Sample Stations		
Heavy Metals (mg/kg)	**I**	**R**	**U**	**Mean**
Fe	0.0004 (0.310)	0.0006 (0.270)	0.0004 (0.379)	0.0005 (0.320)
Pb	0.3400 (3.273)	0.2200 (0.790)	0.2800 (7.297)	0.2800 (3.787)
Cd	1.5500 (0.830)	2.3500 (1.595)	4.7500 (2.095)	2.8833 (1.507)
Cr	0.1000 (2.576)	0.0700 (2.120)	0.0900 (1.757)	0.0657 (2.151)
Ni	0.0100 (0.028)	0.1500 (2.197)	0.0800 (1.865)	0.0080 (1.363)
Ag	<0.001 (<0.001)	<0.001 (<0.001)	<0.001 (<0.001)	<0.001 (<0.001)

Background values: Fe = 47,000; Pb = 20; Cd = 0.3; Cr = 90; Ni = 68; Ag = 533, WHO [34].



(**a**) **In soils** (**b**) **in *Vernonia amygdalina***

Figure 2. Trend of heavy metal (in mg·kg^{-1}) contamination in soils (**a**) and *Vernonia amygdalina* (**b**).

3.2.2. Pollution Load Index (*PLI*)

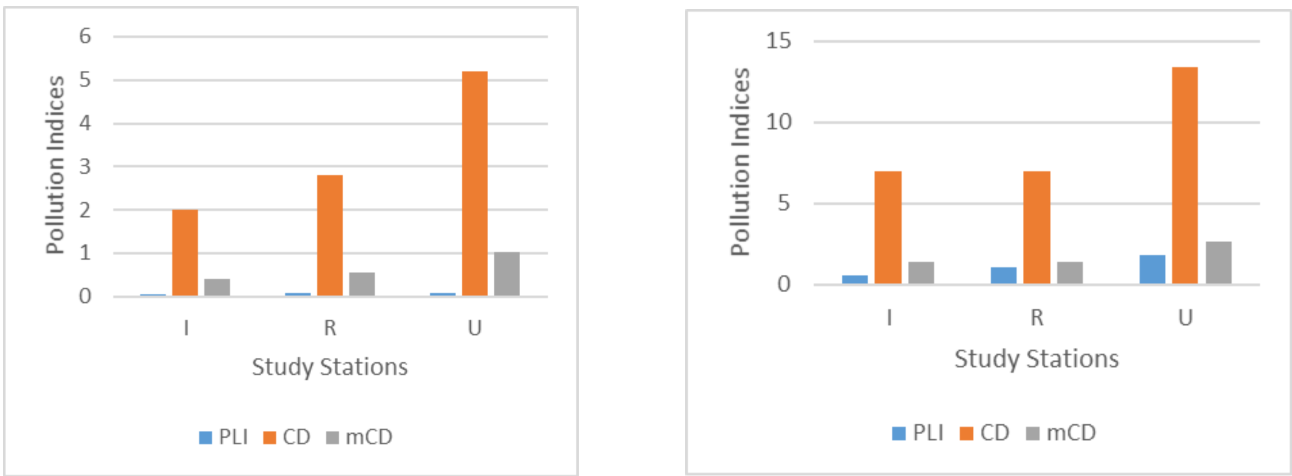
Comparatively, the campuses recorded more *PLI* values in the bitter leaf than in the soil, whose ranges were 0.046–0.08 for soil and 0.571–1.802 for bitter leaf, showing that the bitter leaf has more heavy metal retention capacities. *PLI* indicates deterioration level of soil due to heavy metal accumulation [74]. This may be attributed to both soil-root system flow and anthropogenic input, such as vehicular emissions and open incineration of fossils, which is common around the study region, Niger Delta. Spatially, Uniport had highest *PLI* values, while the least was in IAUE. This may be connected to the more population, human activities, and water logged soil terrain present in Uniport. The *PLI* values for almost all the stations and campuses were <1, showing baseline levels of low metal pollutions, which indicated permissible soil quality except for Uniport (1.802) and RSU (1.096) in bitter leaf [30]. This was in disagreement with results obtained in similar studies in South Africa, where 95% of samples had $PLI \geq 1.5$ [75]. This is an indication that the natural concentration has been distorted, hence there being more anthropogenic input in Uniport [76]. This is a threat to the ecosystem, such as water, organisms, and human health, of the area nearest to the stations. The *PLI* order for heavy metals in the soil was I > R > U, while bitter leaf was I < R < U.

3.2.3. Transfer Factor (*TF*)

The *TF* showed reduced concentration with values within range of 0.05–0.092, as shown in Table 4. The *TF* for Fe in the bitter leaf was in the range of 0.045 to 0.092 mg kg^{-1} but was highest in station U (0.92) and least in R (0.45); *TF* for Pb was of 0.05 to 0.39 mg kg^{-1} range but was highest for U (0.39) and least in R (0.05); Cd ranged from 0.29 to 0.45 but highest in R (0.45) and least in U (0.29); Cr ranged from 0.51 to 0.83 mg kg^{-1} but highest in R (0.83) and least in U (0.51); and Ni was ranged 0.08–0.54, where U (0.54) was highest and I (0.08) recorded the least. The *TF* results showed Fe and Cr were more variable and higher, in tandem with those earlier observed in soils and leaves of bitter leaf in Lagos, Nigeria [13,77]. According to Kumar et al. [78], high values *TF* indicate low retention capacity. Similarly, *TF* above 1 indicates hyper-accumulation, especially in soils, according to Eze and Ekanem [79], but values of 0.1 indicated that plant was excluding metals from its tissues, while the *TF* values of 0.2 indicated the probability of metal contamination by anthropogenic activities [80]. The *TF* values obtained from studied bitter leaf showed indications of poor accumulation of heavy metals in leaves of the bitter leaf, suggesting affinity of metal to the soil colloids, hence preventing bitter leaf from entry into the metals [77,81]. The relatively low *TF* result obtained for bitter leaf in this study is consistent with earlier finding by Ogundele et al. [77], for most plants species. Similarly, Ni and Fe are plant essential elements, and most plants have the potential to keep them [82]. The occurrence of heavy metals in the ecosystem is catastrophic to plant and organisms, including humans, as a result of their bio-accumulating tendency and toxicity [83,84]. Trend of soil heavy metals in plants, pollution index, and transfer factor are illustrated in Figures 2–4, respectively.

Table 4. CDI_{ing} for the Soils in both adults (A) and children (C).

	Sample Stations		
Heavy Metals	**I**	**R**	**U**
Fe	A (2.7 × 10^{-5}) C (2.5 × 10^{-4})	A (3.7 × 10^{-5}) C (3.5 × 10^{-4})	A (2.7 × 10^{-5}) C (2.5 × 102^{-4})
Pb	A (9.0 × 10^{-6}) C (2.5 × 10^{-5})	A (6.0 × 10^{-6}) C (5.6 × 10^{-5})	A (8.0 × 10^{-6}) C (7.2 × 10^{-5})
Cd	A (6.0 × 10^{-7}) C (6.0 × 10^{-6})	A (1.0 × 10^{-6}) C (9.0 × 10^{-6})	A (2.0 × 10^{-6}) C (1.8 × 10^{-5})
Cr	A (1.2 × 10^{-5}) C (1.1 × 10^{-4})	A (8.0 × 10^{-6}) C (7.6 × 10^{-5})	A (1.1 × 10^{-5}) C (1.0 × 10^{-4})
Ni	A (7.0 × 10^{-7}) C (2.5 × 10^{-6})	A (1.4 × 10^{-5}) C (1.3 × 10^{-4})	A (7.0 × 10^{-6}) C (6.6 × 10^{-5})



(**a**) soils (**b**) (*Vernonia amygdalina Delile*)

Figure 3. Pollution indices across study stations in soils (**a**) and *Vernonia amygdalina* Delile (**b**).

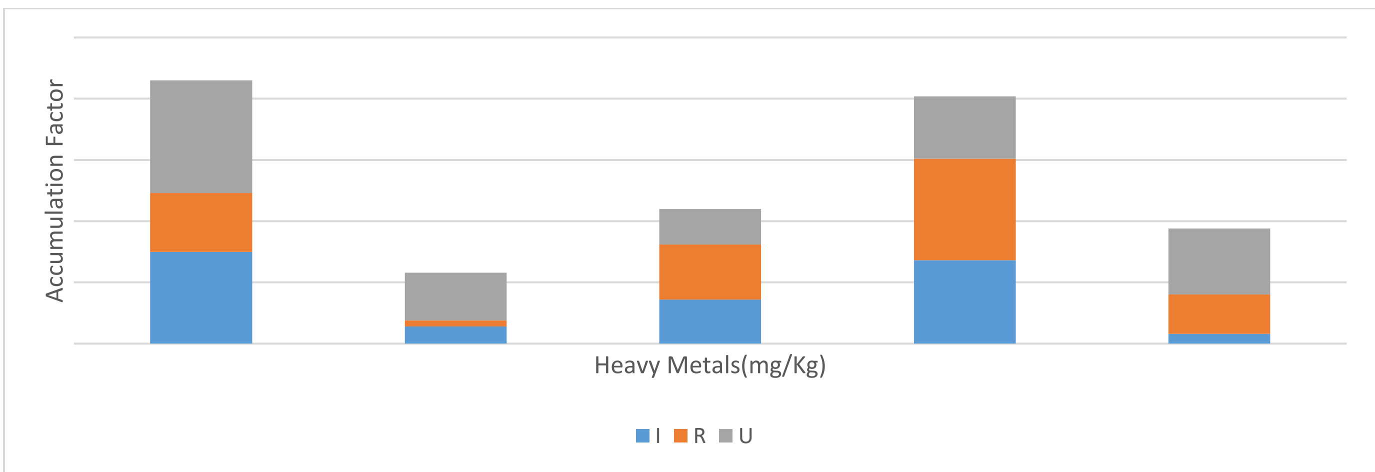


Figure 4. Transfer Factor (*TF*) for the study metals.

3.2.4. Chronic Daily Intake (CDI_{ing}) for Both Soils and Bitter Leaf in Adults and Children

Table 4 shows that adults have the least CDI_{ing} values in all the stations compared to those of the children in the agricultural soil. These values were also lower than those recorded for Ni, Cr, Cd, and Pb [85]. The acceptable range for CDI_{ing} is 10^{-6}–10^{-4} which showed that most values obtained for both children and adults were within range, except for station I (Cd and Ni) in adults for the soil. Similarly, Table 5 shows that all the stations recorded CDI_{ing} values within the acceptable range, according to Liang et al. [85], except for stations I (Cd, Ni in adults and Ni in children), R (Pb, Cd in adults), and U (Cd in adults) for the bitter leaf samples (*Vernonia amygdalina* Delile). The chronic daily intake dose was also the heavy metal intake of noxious substances during the exposure period [85]. The chronic and acute health effect on ingestion of Cd and Ni as they accumulate in living bodies cannot be over-emphasized [15,17]. This may be attributed to anthropogenic inputs as corroborated in similar research studies [3,86].

Table 5. CDI_{ing} for *Vernonia amygdalina* in both adults and children.

	Sample Stations		
Heavy Metals	**I**	**R**	**U**
Fe	A (2.0×10^{-5}) C (1.9×10^{-4})	A (1.8×10^{-5}) C (1.7×10^{-4})	A (2.5×10^{-5}) C (2.3×10^{-4})
Pb	A (1.3×10^{-6}) C (1.3×10^{-5})	A (3.0×10^{-7}) C (3.0×10^{-6})	A (3.0×10^{-6}) C (2.8×10^{-5})
Cd	A (2.0×10^{-7}) C (2.1×10^{-6})	A (4.0×10^{-7}) C (4.1×10^{-6})	A (6.0×10^{-7}) C (5.4×10^{-6})
Cr	A (8.0×10^{-6}) C (7.6×10^{-5})	A (6.7×10^{-5}) C (6.2×10^{-5})	A (5.5×10^{-6}) C (5.2×10^{-5})
Ni	A (6.0×10^{-8}) C (5.4×10^{-7})	A (4.5×10^{-6}) C (4.2×10^{-5})	A (3.8×10^{-6}) C (3.6×10^{-5})

3.2.5. Health Risk (*HQ* and *HI*)

The hazard quotient (*HQ*) and hazard index (*HI*) for both soil and bitter leaf are shown in Table 6; Table 7. This indicated risk from non-carcinogenic effects ($HI > 1$). Additive effects can emanate from the exposure of man to more than one pollutant [87]. The *HI* for heavy metals in adults and children for the *Vernonia amygdalina* Delile across the stations for I, R, and U were 1.67, 16.24; 14.46, 83.6; and 8.56, 79.7, respectively. Hazard index (*HI*) can be used to estimate the likely impacts of these additive effects [88]. The *HI* were above 1, indicating high risk factor, which was the opposite of results by Xue et al. [89] and Isiuku and Enyoh [87], on the monitoring and modeling of heavy metal contents in vegetables collected from markets in Imo State, Nigeria. The *HI* obtained were all greater than 1 ($HI > 1$), showing that negative risks to human health are of immediate concern, as detrimental effects gradually emanate from long-time consumption of these bitter leaf vegetables [89,90]. This may be due to additive effects showing that agricultural soils were contaminated [91]. The *HI* index is a useful tool in the assessment of overall non-carcinogenic risk caused by additive effects of toxicants [85]. The highest *HI* was found in children (222) at station R, while the least was in adults (3.77) at station I. The results calculated for *HI* in heavy metals were all above safe limits, hence not being risky (all $HI > 1$) [4,12]. The overall result is similar to those of Khan et al. [12] in Swat District for agricultural soils and crops, but higher than those earlier reported [3,13]. The *HI* trend for heavy metals is shown in Figure 5.

Table 6. Hazard Quotient (*HQ*) for both adults and children in soils.

	Sample Stations		
Heavy Metals	**I**	**R**	**U**
Fe	(5.57×10^{-6}) (5.14×10^{-4})	(7.57×10^{-5}) (7.14×10^{-4})	(5.57×10^{-5}) (5.14×10^{-4})
HQ/*HI*	(1.48×10^{-6}) (1.42×10^{-5})	(3.0×10^{-6}) (3.2×10^{-6})	(3.7×10^{-6}) (3.7×10^{-6})
Pb	(0.74) (7.14)	(0.49) (4.57)	(0.65) (6.00)
HQ/*HI*	(0.20) (0.20)	(0.02) (0.02)	(0.04) (0.04)
Cd	(0.60) (6.00)	(1.00) (9.00)	(2.00) (18.0)
HQ/*HI*	(0.16) (0.17)	(0.04) (0.04)	(0.13) (0.13)
Cr	(1.33) (12.3)	(0.90) (8.33)	(1.23) (11.0)
HQ/*HI*	(0.35) (0.34)	(0.04) (0.04)	(0.08) (0.11)
Ni	(1.10) (10.8)	(22.5) (200)	(11.0) (104)
HQ/*HI*	(0.29) (0.30)	(0.90) (0.90)	(0.74) (0.75)

Table 7. Hazard Quotient (*HQ*) for *Vernonia Amygdalina* in both adults and children), respectively.

	Sample Stations		
Heavy Metals	**I**	**R**	**U**
Fe	(4.14×10^{-5}) (3.86×10^{-4})	(3.71×10^{-5}) (3.43×10^{-4})	(5.14×10^{-4}) (4.71×10^{-4})
HQ/*HI*	(2.48×10^{-5}) (2.38×10^{-6})	(2.57×10^{-6}) (4.10×10^{-6})	(6.0×10^{-5}) (5.9×10^{-6})
Pb	(0.11) (1.06)	(0.02) (0.25)	(0.25) (2.29)
HQ/*HI*	(0.07) (0.07)	(1.38×10^{-3}) (2.99×10^{-3})	(0.03) (0.03)
Cd	(0.57) (6)	(0.11) (11.7)	(1.71) (15.43)
HQ/*HI*	(0.34) (0.37)	(7.61×10^{-3}) (0.14)	(0.20) (0.19)
Cr	(0.9) (8.33)	(7.33) (6.67)	(0.6) (5.67)
HQ/*HI*	(10) (9.8)	(0.51) (0.08)	(0.07) (0.07)
Ni	(0.09) (0.85)	(7) (65)	(6) (56.3)
HQ/*HI*	(0.05) (0.05)	(0.48) (0.78)	(0.71) (0.71)

HI in *Vernonia amygdalina* for adult and children(I) is 1.67, 16.24; (R) is 14.46, 83.6; (U) is 8.56, 79.7.

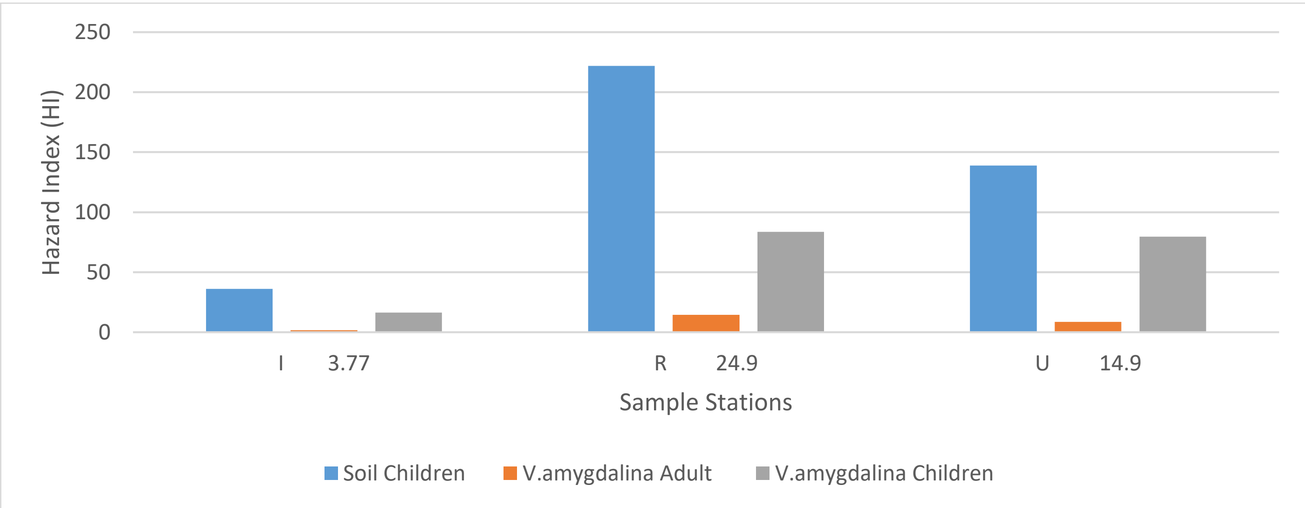


Figure 5. Spatial Hazard Index trend for both soil and *Vernonia amygdalina*.

The total hazard index (THI or TTHQ) in the stations were all greater than 1, suggesting that the heavy metal health risks of exposure through bitter leaf consumption from these soils were comparatively above safe limits, hence being of great risk and negative to earlier research studies on different vegetable species [81,91]. THI was high and of great risk probably due to increased use of land for agricultural purposes introducing foreign agents, such as fertilizers and pesticides.

3.2.6. Carcinogenic Risk Analysis

Cancer in humans can be increased by heavy metals, such as Pb, Cd, Cr, and Ni, especially prolonged exposure to low concentrations of these toxic metals [92]. Therefore, using Pb, Cr, Cd, and Ni as carcinogens, the exposure of the residents were assessed based on the CDI values. The carcinogenic risk assessment for adults and children for both soil and *Vernonia amygdalina* is shown in Table 8; Table 9. Heavy metals whose *ILCR* is $<1.0 \times 10^{-6}$ are assumed insignificant; hence, the cancer risk could be neglected, but, above 1.0×10^{-4}, it is taken as a harmful and troublesome cancer risk result. This study revealed that Pb (soil) has the highest chances of cancer risks, especially in children (mean *ILCR*, 2.0×10^{-2}), while Cd has the least (mean *ILCR*, 3.36×10^{-5}). For *Vernonia amygdalina*, Pb has the highest chances of cancer risks (mean *ILCR*, 2.45×10^{-3}), while Cd had the least (mean *ILCR*, 3.362×10^{-5}). The implication of these results was that there is potential risk of cancer emanating from the impact of contaminants through the ingestion route by accumulation in both soil and *Vernonia amygdalina* Delile.

Table 8. Incremental Lifetime Cancer Risk (*ILCR*) in soil for children and adults.

	Sample Stations		
Heavy Metals	**I**	**R**	**U**
Fe	(0) (0)	(0) (0)	(0) (0)
Pb	(1.06×10^{-3}) (2.94×10^{-3})	(7.06×10^{-4}) (6.59×10^{-3})	(9.41×10^{-4}) (8.47×10^{-3})
Cd	(1.58×10^{-6}) (1.58×10^{-5})	(2.63×10^{-6}) (2.37×10^{-5})	(5.26×10^{-6}) (4.74×10^{-5})
Cr	(2.4×10^{-5}) (2.2×10^{-4})	(1.6×10^{-5}) (1.52×10^{-4})	(2.26×10^{-5}) (2.2×10^{-4})
Ni	(7.69×10^{-7}) (2.75×10^{-6})	(1.54×10^{-5}) (1.43×10^{-4})	(7.69×10^{-6}) (7.25×10^{-5})

CSF $(mg \cdot kg^{-1} \cdot day^{-1})^{-1}$; Fe = 0.0; Pb = 0.0085; Cd = 0.38; Cr = 0.5; Ni = 0.91: Permissible limit for single element $= 10^{-6} < 10^{-4}$.

Table 9. Incremental Lifetime Cancer Risk (*ILCR*) for *Vernonia amygdalina* Delile in both adults and children.

	Sample Stations		
Heavy Metals	**I**	**R**	**U**
Fe	(0) (0)	(0) (0)	(0) (0)
Pb	(1.53×10^{-4}) (1.53×10^{-3})	(3.53×10^{-5}) (3.53×10^{-4})	(3.53×10^{-4}) (2.8×10^{-5})
Cd	(5.26×10^{-7}) (5.53×10^{-6})	(1.05×10^{-6}) (1.08×10^{-5})	(1.58×10^{-6}) (1.42×10^{-5})
Cr	(1.6×10^{-5}) (1.52×10^{-4})	(1.34×10^{-4}) (1.24×10^{-4})	(1.1×10^{-5}) (1.04×10^{-4})
Ni	(6.59×10^{-8}) (5.93×10^{-7})	(4.94×10^{-6}) (4.62×10^{-5})	(4.18×10^{-6}) (3.96×10^{-5})

3.2.7. Enrichment Factor (EF)

All the stations in both soil and bitter leaf showed extremely high EF as all were greater than 40 but were relatively higher in the bitter leaf samples than as found in the soils, as shown in Table 10. For the soil samples, Uniport (U) recorded the highest in Cd (11,302), but Pb (18,709) in bitter leaf was highest in the same, Uniport. The least EF in soil was found in Ni (I) and also for the bitter leaf (I). These values were lower than those of Edith-Etakah et al. [93], on the soils of the Kette-Batouri Region, Eastern Cameroon. The highest EF of Cd (soil) and Pb (bitter leaf) in the same station is an indication of increase pollution potentials and more activities within the location, such as high vehicular and pollutant emissions, likely to endanger human health, though not as effective as those recorded earlier in separate studies on heavy metals through three exposure routes [91].

Table 10. Enrichment Factors (*EF*) for the soil and *Vernonia amygdalina* samples.

	Sample Stations			
Heavy Metals	**I**	**R**	**U**	**Mean**
Fe	-	-	-	-
Pb	191 (10,229)	88 (2821)	157 (18,709)	145 (10,586)
Cd	3683 (2594)	4057 (5696)	11,302 (5372)	6347 (4554)
Cr	232 (8049)	113 (7570)	209 (4504)	185 (6708)
Ni	19 (88)	260 (7848)	180 (4783)	153 (4240)

3.2.8. Ecological Risk Factor (E_rF) and Risk Index (*RI*)

The results of *ErF* are shown in Table 11 for soil and bitter leaf, respectively. The E_rF and *RI* in soils were all, respectively, less than 40 but not as much as 150 (40 < E_rF or *RI* < 150), showing low risk factor, but the bitter leaf samples had moderate risk for Cd in station R and U, at 47.85 and 62.85, respectively. The *ErF* showed relatively lower values in all the stations in soils for the Pb, Cd, Cr, and Ni compared to those of the bitter leaf except station U (Cd, 41.7 in soil) and very low in bitter leaf for I (Ni, 0.14). The higher values of *ErF* were found in soil within the range of 40 ≤ *ErF* < 80 (U, Cd-41.7) and in bitter leaf for Cd (R-47.85, U-62.85), hence requiring further studies, as it shows both soil and bitter leaf samples were of moderate potential ecological risks, as agreed upon in other related similar studies [94,95]. These values were relatively lower than those recorded in abandoned and active dumpsites in Lagos of range, 43.86–732.4 [23].

Table 11. Ecological Risk Factor (E_rF) and Potential Ecological Risk Factor (*RI*) for the soil and *Vernonia amygdalina* Delile.

	Sample Stations			
Heavy Metals	**I**	**R**	**U**	**Mean**
Fe	-	-	-	-
Pb	1.70 (16.37)	1.10 (3.95)	1.400 (36.49)	1.40 (18.94)
Cd	46.50 (24.90)	70.50 (47.85)	142.5 (62.85)	86.5 (45.20)
Cr	0.20 (5.15)	0.14 (4.24)	0.180 (3.51)	0.17 (4.30)
Ni	0.05 (0.14)	0.75 (10.99)	0.400 (9.33)	0.40 (6.82)
RI (Risk Index)	48.45 (46.56)	72.49 (67.03)	144.5 (112.18)	88.48 (75.26)

3.3. Statistical Analysis and Inter-Metal Correlation

The respective mean (mg/kg), median (mg/kg), minimum (mg/kg), maximum (mg/kg), and standard deviation for Fe, Pb, Cd, Cr, and Ni were 15.33, 14.86, 12.95, 18.18, 2.65; 1.14, 0.98, 0.24, 2.19, 0.99; 0.90, 0.319, 0.17, 0.42, 0.13; 4.95, 4.88, 4.04, 5.92, 0.94; and 2.05, 2.80, 0.04, 3.30, and 1.75, as shown in Table 12. Figure 6 shows the parametric and spatial variations in heavy metals, and the three locations of 1, 2, 3, 4, 5, 6 represent Fe, Pb, Cd, Cr, Ni, and Ag, respectively.

Table 12. Statistics of Fe, Pb, Cd, Cr, and Ni in both *Vernonia Amygdalina Delile* and soils in the study stations.

				Statistics (Bitter Leaf)	
Heavy Metals (mg/kg)	**Mean**	**Median**	**Min**	**Max**	**SD**
Fe	15.33	14.86	12.95	18.18	2.65
Pb	1.14	0.98	0.24	2.19	0.99
Cd	0.90	0.319	0.17	0.42	0.13
Cr	4.95	4.88	4.04	5.92	0.94
Ni	2.05	2.80	0.04	3.30	1.75
				Statistics (soil)	
	Mean	**Median**	**Min**	**Max**	**SD**
Fe	22.21	19.71	19.70	27.24	4.35
Pb	5.59	5.60	4.35	6.80	1.23
Cd	0.86	0.71	0.46	1.42	0.50
Cr	7.52	7.89	5.91	8.77	1.47
Ni	5.31	5.14	0.54	10.26	4.86

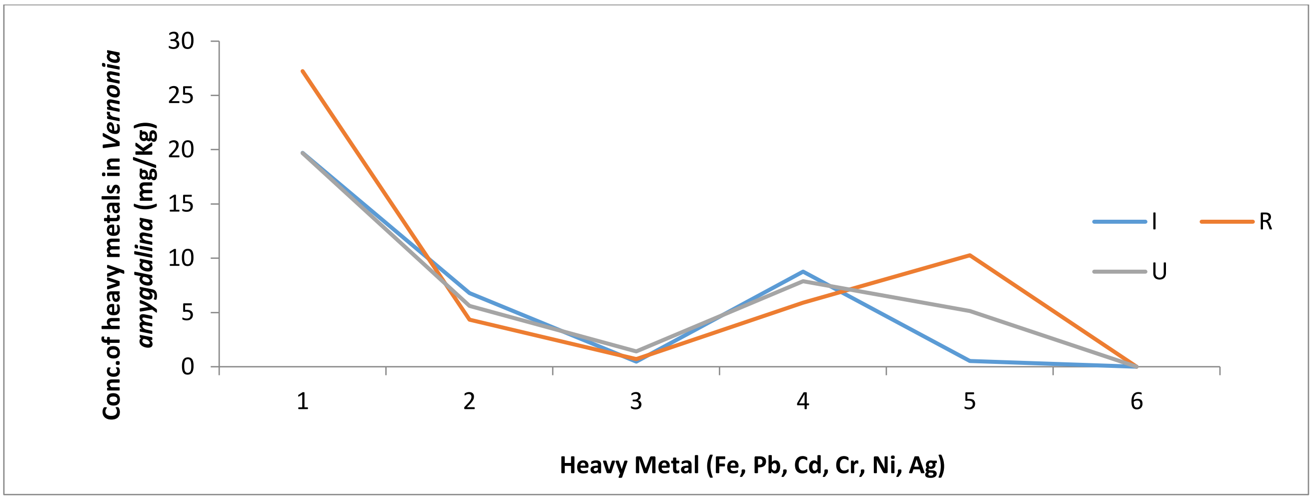


Figure 6. Spatial variation of heavy metals in *Vernonia amygdalina*.

One-way ANOVA result showed that there were no significant differences and correlation (f-ratio = 0.05; p-value = 0.95 $p < 0.05$) in the levels of heavy metals in the study soils of the stations. Similarly, t-test was used to compare the heavy metal contents of both garden soil and *Vernonia amygdalina* (t = −0.73; p-value = 0.24), which also gave no significant difference between the levels of the soil and *Vernonia amygdalina* Delile, indicating that soil-plant heavy metal uptake was efficient similar to that of Fakhri et al. [25], on probabilistic risk assessment of Pb and Cd in Iran. There was no significant correlation existing within the three study stations, both in soil and bitter leaf samples, in contrast to the significant positive correlation in greenhouses [96]. The negative values for metals gave credence to the non-contaminated soil and bitter leaf, similar to earlier research on pollution status of heavy metals and risks within sediments in China [97]. The concentration of Fe in soil and *Vernonia amygdalina* Delile were found to be of strong negative correlation using 2-tailed Pearson's Product Correlation coefficient, r (16) = −0.78, $p < 0.05$. Conversely, Pb and Cr recorded weak positive correlations of r (16) = 0.39, $p < 0.136$ and r (16) = 0.36, $p = 0.167$, indicating that both heavy metals increase in concentration simultaneously, though weak but not significant at $p < 0.05$, respectively. Similarly, the soil and *Vernonia amygdalina* recorded strong positive correlations for Cd and Ni of r (16) = 0.92, $p < 0.000$

and r (16) = 0.92, $p < 0.00$, and significant at $p < 0.05$, respectively, meaning that, as the concentrations of Cd and Ni increases, so does that of the vegetable.

4. Conclusions

This study showed that the studied soils and *Vernonia amygdalina* Delile plant recorded some heavy metal concentrations that require adequate monitoring to avoid values above permissible limits. The health risk index for Cd showed risk from non-carcinogenic effects as almost all the stations recorded HI > 1 values for the plant and *Vernonia amygdalina*. This was due to projected bioaccumulation and CDI_{ing} for Cd. The ecological risks (*ErF* and *EF*) recorded for Cd in bitter leaf poses a potential threat. The increasing population explosion is a threat due to limited food supply; hence, garden farming must be encouraged, especially by the tolerable heavy metal levels found within these university campuses. The study showed that there is potential risk of cancer from the contaminants through the ingestion route due to accumulation in both soil and *Vernonia amygdalina* Delile, though highest chances in children (mean *ILCR*, 2.07×10^{-2}), but Cd has the least (mean *ILCR*, 3.36×10^{-5}). For *Vernonia amygdalina*, Pb has the highest chances of cancer risks (mean *ILCR*, 2.45×10^{-3}), while Cd has the least (mean *ILCR*, 3.362×10^{-5}).

There is the ardent need for regular monitoring to ascertain optimum concentration which may have concomitant negative effect on plant and humans. Similarly, the need to monitor the anthropogenic activities around these areas, especially air pollution due to the illegal crude oil refining, is of necessity. The number of heavy metals considered in this work may not be enough to draw vivid conclusion on heavy metal impact; hence, others, such as copper, arsenic, cobalt, zinc, etc., should also be monitored. The absorption of heavy metals through other routes other than ingestion should be evaluated.

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