



ECOLOGICAL AND HUMAN HEALTH RISKS OF TOXIC METALS IN SOILS UNDER DIFFERENT LAND USES IN MAKURDI, NIGERIA



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Abstract: The study assessed the levels, ecological and human health risks of mixed contaminants (toxic metals and petroleum hydrocarbons) in soils under different land uses in Makurdi, Nigeria. Composite surface soil samples at auto-repair site, abattoir, waste dumpsite and farmland, all located in Makurdi were characterized physicochemically and assayed for Cd, Cu, Ni, Pb, Zn and total petroleum hydrocarbon (TPH) concentrations. Ecological and human health risk indices were calculated from corresponding contaminant concentrations and relevant reference data. The surface soils were predominantly sandy and alkaline (pH 7.1 – 8.4) with contaminant concentrations (mg/kg) in the ranges: Cd (0.42 – 1.80), Cu (2.50 – 37.28), Ni (6.20 – 440.30), Pb (3.22 – 82.78), Zn (57.33 – 131.14) and TPH (1.36 – 355.10). Results of ecological risk indices showed the auto-mechanic, abattoir, dumpsite and farmland {PLI (1.75 x 10⁰, 4.33 x 10⁰, 8.32 x 10⁻¹ and 5.07 x 10⁻¹), EF (6.03 x 10⁻¹, 8.63 x 10⁻¹, 5.69 x 10⁻¹ and 4.57 x 10⁻¹), PERI (3.27 x 10², 4.37 x 10², 7.64 x 10¹ and 1.45 x 10¹), Cd (5.85 x 10¹, 7.59 x 10¹, 1.00 x 10¹ and 2.17 x 10⁰), PI_{avg} (1.17 x 10¹, 1.52 x 10¹, 2.01 x 10⁰ and 4.35 x 10⁻¹), PI_{Nemerow} (3.52 x 10¹, 4.75 x 10¹, 2.94 x 10⁰ and 6.60 x 10⁻¹)}, respectively. These values implied that except for the farmland, soil at the auto-mechanic, abattoir and dumpsite were of low quality. Results of human health risk assessment for the four soil samples showed that there are no adverse non carcinogenic health effects expected due to exposure for the three exposure routes at the abattoir soil with respect to Cd, Zn, Pb, Cu and Ni. However, ingestion cancer risks for children {abattoir (8.48 x 10⁻³), auto-mechanic (4.89 x 10⁻⁴), dumpsite (1.19 x 10⁻⁴), and farmland (4.89 x 10⁻⁴)} and adults {abattoir (9.08 x 10⁻⁴)} due to exposure to Ni exceeded the acceptable range (10⁻⁶ to 10⁻⁴), with that of children higher than adults. Corrective and preventive measures and further research areas have been suggested.

Keywords: Ecological risks, toxic metals, human health indices, mixed contaminants, soil

Introduction

Soil pollution is a result of the buildup of a wide range of chemical compounds created either by natural or human activities in an amount that is harmful to human health and the ecosystem (George *et al.*, 2014).

In Makurdi Metropolis of Benue State, several portions of lands have been contaminated through unregulated human activities such as the several auto-mechanic sites, dumpsites for both industrial and domestic wastes, abattoirs scattered within the town, and the current trend of unprofessional use of pesticides on farmlands by local farmers. The net result is large scale contamination of the receiving soils and subsequent leaching of some of the contaminants into the groundwater, which may act as a source of water supply for domestic use of inhabitants of the localities. This loss of soil and water quality may cause health hazards and death of humans, livestock and aquatic life forms, crop failure and loss of aesthetics (Audu *et al.*, 2013).

The fertility of the soil may also be adversely affected by the impact of human activities on the physico-chemical properties of the soil such as pH, conductivity, soil organic matter (SOM), bulk density, cation exchange capacity and soil texture. Conductivity indicates the presence of harmful salts in the soil. SOM has much influence on physical, chemical and biological processes of the soil (Johnston *et al.*, 2009). The cation exchange capacity of soil is the maximum amount of cations that 100 g of dry soil can absorb (Gzar, *et al.*, 2014). It is the soil's ability to react with positively charged molecules. It refers to how well colloidal materials of soils are able to give off the ions surrounding their negatively charged surface for other highly positively charged ions from a solution system that these particles swims in (Brown and Lemon, 2018). The higher the CEC, the higher the negative charge of the soil and the more cations that can be held. It is the total capacity of a soil to hold exchangeable cations. CEC is a critical component of soil properties influencing soil structure stability, nutrient availability, pH and soil's reaction to amelioration procedures, and hence it does regulate the

movement of potentially toxic metals (PTMs) in soil (Pam *et al.*, 2013).

Ecological risk assessment

In identifying and managing risks at contaminated sites, consideration is given to spectrum of contaminant concentrations. The level of concern associated with those concentrations depends on the likelihood of exposure to soil contaminants at levels of potential concern to human health or to ecological receptors (NMED, 2015). Quantitative methods usually used in assessing soil contamination include metal pollution index, contamination factor, enrichment factor, pollution load index, index of geo-accumulation, degree of contamination, average of pollution index, potential ecological risk index (PERI) and Nemerow pollution index.

The metal pollution index (MPI) is used to determine which metal poses the highest threat to a soil environment. It is also important in calculating some of the complex pollution indices such as the Nemerow pollution index and pollution load index (Kowalska *et al.*, 2018). It is expressed as:

$$MPI = \frac{\text{Concentration of metal in soil}}{\text{reference soil (control)}} \quad (1)$$

Contamination factor enables the assessment of soil contamination taking into account the PTMs content from the surface of the soil and their background levels. It is expressed as:

$$CF = \frac{C_{\text{metal}}}{C_{\text{background}}} \quad (2)$$

where C_{metal} is the concentration of a single metal in the soil and $C_{\text{background}}$ is the metal concentration in pre-industrial reference level for the metal (Gong *et al.*, 2008; Abdullah *et al.*, 2015).

Pollution load index (PLI) is a potent tool in PTM pollution evaluation for each site and is expressed as:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (3)$$

where: n = number of metals and CF = contamination factor. The PLI value higher than 1 indicates the samples have been polluted while the PLI value less than 1 indicates no pollution occurred.

Enrichment factor (EF) is defined as:

$$EF = \frac{(C_i/C_{ie})_s}{(C_i/C_{ie})_{RS}} \quad (4)$$

where C_i is the content of element i in the sample of interest or the selected reference sample, and C_{ie} is content of immobile element in the sample or the selected reference sample.

Geo-accumulation Index (I_{geo}) is an indicator used to assess the presence and intensity of anthropogenic contaminant deposition on surface soil. This index of potential contamination is determined by normalizing PTM concentration in the topsoil with respect to its reference concentration. Index of geo-accumulation is calculated using the following expression:

$$I_{geo} = \log_2 \frac{C_i}{1.5C_{ri}} \quad (5)$$

where C_i is the measured concentration of the examined metal i in the soil, and C_{ri} is the geochemical background concentration or reference value of the metal i .

The degree of contamination (Cd) is generally defined as the sum of all the contamination factors for a given set of soil pollutants divided by the number of analyzed pollutants (Sivakumar *et al.*, 2016). It is expressed as:

$$C_d = \sum_{i=1}^m C_f^i \quad (6)$$

where C_f^i is the single index of contamination factor, and m is the number of the heavy metal species. Risk is low when $C_d < m$, moderate when $m \leq C_d < 2m$, considerable when $m \leq C_d < 4m$ and very high when $C_d > 4m$.

An average of pollution index (PI_{Avg}) is used to estimate the soil quality (Kowaska *et al.*, 2018) and thus communicate to the public how polluted the environment currently is or how polluted it is forecasted to become. It is defined as:

$$PI_{Avg} = \frac{1}{m} \sum_{i=1}^m P_i \quad (7)$$

where P_i is the single pollution index of heavy metal i , and m is the number of the heavy metal species. A PI_{Avg} value >1.0 indicates low quality soil due to contamination.

PERI is another precise method applied to evaluate the harm of PTMs in the soils. It does not only reflect the single impact of PTMs to ecological environment but also takes into consideration the different background values of the geography and combines environmental chemistry with biological toxicology and ecology (Guo *et al.*, 2010). It comprehensively considers the concentration, the toxic level,

the synergy and ecological sensitivity of PTMs (Jiang *et al.*, 2014). It is expressed as:

$$PERI = \sum_{i=1}^m Er^i \quad (8)$$

A Nemerow pollution index ($PI_{Nemerow}$) is usually applied to assess the quality of soil environment widely and is expressed as:

$$PI_{Nemerow} = \sqrt{\frac{(\frac{1}{m} \sum_{i=1}^m P_i)^2 + P_{i_{max}}^2}{2}} \quad (9)$$

where P_i is the single pollution index of heavy metal i ; $P_{i_{max}}$ is the maximum value of the single pollution indices of all heavy metals, and m is the number of the heavy metal species. The soil environment is a considered a safety domain when $PI_{Nemerow} < 0.7$, precaution domain when $0.7 \leq PI_{Nemerow} < 1.0$, slightly polluted domain when $1.0 \leq PI_{Nemerow} < 2.0$, moderately polluted domain when $2.0 \leq PI_{Nemerow} < 3.0$ and seriously polluted domain when $PI_{Nemerow} > 3.0$

Human health risks assessment

Human exposure and health risk assessment is a process of estimating the possibility that humans who may be exposed to contaminants in the environment now or in the future will experience negative health effects and the nature and severity of the adverse health effect. Human health risk indices usually considered are hazard quotient and cancer risks. The hazard quotient (HQ) for metals with non-carcinogenic effects and cancer risk (CR) for metals with carcinogenic effects, are calculated based on their corresponding chronic daily intake (CDI), reference dose (RfD), and slope factor (SF) values (Urrutia *et al.*, 2017; Luo *et al.*, 2012). Metal toxicological characteristics have already been reported (USDOE, 2011; USEPA, 2011a, 2011b; USEPA, 2002; WHO, 2008; IARC, 2017). The ratio of the potential exposure to contaminants and the level at which adverse effects are not expected is referred to as the hazards quotient (HQ). If HQ is >1 , then adverse health effects are possible due to exposure. On the other hand, if HQ is <1 , then no expected adverse health effect due to exposure.

To calculate the hazard quotient (HQ), the CDI for each element and exposure pathway is divided by the corresponding reference dose, (equation 10) for systemic toxicity. For carcinogens the CDI is multiplied by the corresponding slope factor to produce a level of excess lifetime cancer Risk (Equation 11).

$$HQ = \frac{CDI}{RfD} \quad (10)$$

$$CR = CDI \times SF \quad (11)$$

Though interactions between some metals might result in their synergistic manner (Luo *et al.*, 2012), it is usually assumed that all the metal risks are additive, hence it is possible to calculate the cumulative non-carcinogenic hazard expressed as the Hazard Index (HI), (Equation 12), and carcinogenic risk expressed as the total cancer risk (Equation 13).

$$\begin{aligned}
 HI &= \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{dermal} \\
 &= \frac{CDI_{ing-nc}}{RfD_{ing}} + \frac{CDI_{inh-nc}}{RfC_{inh}} + \frac{CDI_{dermal-nc}}{RfD_{dermal}} \\
 (12) \quad &= \frac{CDI_{ing-nc}}{RfD_{ing}} + \frac{CDI_{inh-nc}}{RfC_{inh}} + \frac{CDI_{dermal-nc}}{RfD_{ing} \times ABS}
 \end{aligned}$$

$$\begin{aligned}
 TCR &= \sum CR = CR_{ing} + CR_{inh} + CR_{dermal} \\
 &= \frac{CDI_{ing-ca} \times SF_{ing}}{ABS} + \frac{CDI_{inh-ca} \times IUR}{ABS} + \frac{CDI_{dermal-ca} \times SF_{ing}}{ABS} \quad (13)
 \end{aligned}$$

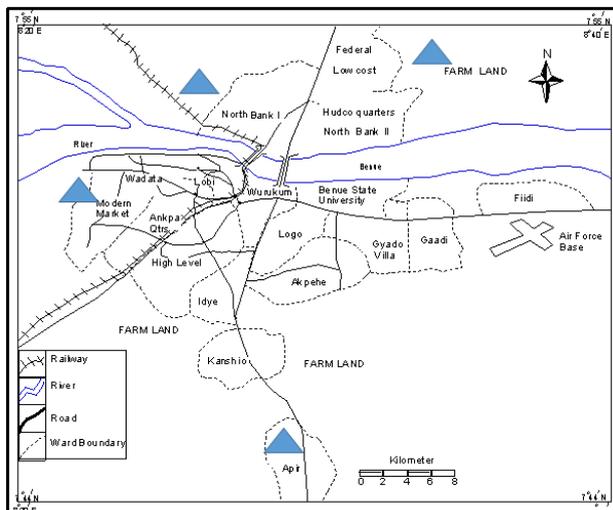
The greater is the value of HQ and total hazard index (THI) above 1, the greater is the level of concern since the accepted standard is 1.0 at which there will be no significant health hazard (Grzetic and Ghariani, 2008; Lai *et al.*, 2010). The probability of experiencing long-term health hazard effects increases with the increasing THI value (Wang *et al.*, 2012; Ogunkunle *et al.*, 2013).

Many researches in Makurdi have been geared towards determination of concentration of PTMs and a few cases of organic contaminants in the soils around these activity sites (Iorungwa *et al.*, 2013; Pam *et al.*, 2013; Akan *et al.*, 2013; Aguru and Alu, 2015; Ubwa *et al.*, 2013; Leke *et al.*, 2011). This study assessed the potential ecological and human health risks of some potentially toxic metals (PTMs) in soils around auto-mechanic site, abattoir, solid wastes dumpsite and farmland.

Materials and Methods

Study area and sample collection

Makurdi (7°44'0" - 7°55'0" N, 8°20'0" - 8°40'0" E) is the capital of Benue State, north central Nigeria. The study locations in Makurdi were the Abattoir at Wadata, the mechanic village at Apir, solid waste dumpsite along NASME Zungu road and a farmland located in northbank. The map of the area is as shown in Fig. 1.



Source: Akpen *et al.* (2018)

Fig. 1: Map of Makurdi, Nigeria Showing Study Areas

Composite samples were taken from each study location at a depth of 0-20 cm (topsoil) each composite sample was a mixture of 10 subsamples collected using stainless hand trowel and placed in sealed and labelled polyethylene package and immediately taken to the laboratory for further analysis.

Physicochemical and heavy metal analysis

Each of the soil samples was air-dried in the laboratory and then finely powdered using porcelain mortar and sieved to < 2 mm and then thoroughly mixed and homogenized prior to analysis. Standard methods were employed to determine physicochemical attributes of the soil. Atomic absorption spectrophotometer (AAS) was used for determination of Cd, Ni, Pb, Zn and Cu. Gas chromatography flame ionization detector (GC-FID) was used for total petroleum hydrocarbons (TPH). For each sample, 5 g of soil was digested with aqua regia (HCl/HNO₃, 3:1 v/v) in a 95°C water bath for 2 h. Quality assurance and quality control (QA/QC) were conducted by using reagent blanks, replicates, and standard reference materials (GBW07427). The triangle of soil texture shown in Fig. 2 was used to determine the textural class of the soil samples.

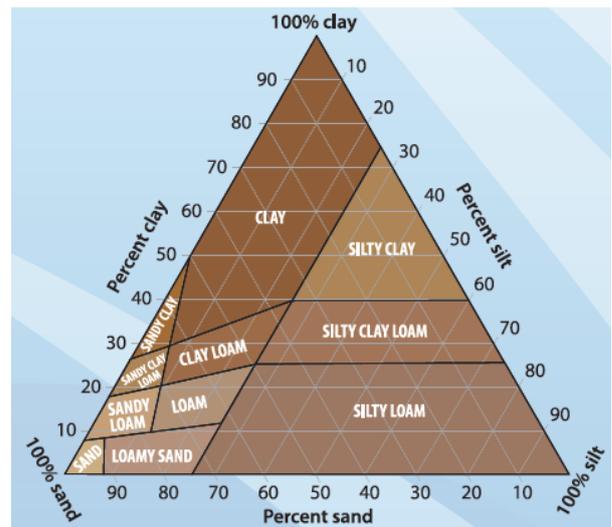


Fig. 2: Triangle of soil texture

Ecological risk indices

Ecological indices such as metal pollution index, potential ecological risk index (PERI), contamination factor, pollution load index, enrichment factor, geoaccumulation index, degree of contamination, average pollution and Nemerow pollution indices were determined using the models described in equations (1) – (9). The values of metal pollution index of soil greater than 1 (> 1), and those less than (< 1) define the pollution range (< 0.10 as very slight contamination, 0.10 – 0.25 as slight contamination, 0.26 – 0.50 as moderate contamination, 0.51 – 0.75 as severe contamination, 0.76 – 1.00 as very severe contamination, 1.10 – 2.00 as slight pollution, 2.10 – 4.00 as moderate pollution, 4.10 – 8.00 as severe pollution, 8.10 – 16.00 as very severe pollution and > 16.00 as excessive pollution). Potential ecological risk is low when PERI < 150, moderate when 150 ≤ PERI < 300, considerable when 300 ≤ PERI < 600 and very high when PERI > 600.

Human health risk indices

Human health indices such as hazard quotient (HQ), cancer risk (CR), hazard index (HI) and total cancer risk (TCR) were determined using the models described in equations (10) – (13).

Results and Discussion

Physicochemical attributes of soil from the study areas are presented in Table 1. The textural analysis using the triangle of soil texture (Fig. 2) for the soil samples are indicated in Table 1. Ecological risk indices determined in this work are presented in Tables 2 – 10. And the Human health risk indices are presented in Tables 11 – 15.

Physicochemical attributes of soils from study areas

The results showed range of pH values 7.10 ± 0.20 to 8.40 ± 0.20 . The highest value was obtained for soil samples taken from auto-mechanic site, while the lowest was obtained for soil samples taken from abattoir. The pH value of 8.40 ± 0.20 implies that the soil at the auto-mechanic site is mildly alkaline. This result is relatively higher than the pH value (6.36 ± 0.37) reported by Pam *et al.* (2013) in a similar study. pH is an important soil parameter because it influences solute concentrations and sorption of contaminants in the soil. High pH values reduce availability and mobility of some PTMs in the soil and low pH values usually favour distribution and transport of PTMs in soil. The relatively high pH value at the mechanic site could be as a result of use of carbides for welding of vehicle exhausts and other metal parts scattered around the site. This pH value is slightly above the favourable pH condition (6.20 – 7.50) that enhances availability of nutrients for most plants. Values of pH obtained for soil samples from Abattoir, solid waste dumpsite and farmland use fall within the optimum pH range for plant growth. The pH trend is such that auto-mechanic>farmland>dumpsite>abattoir.

Conductivity is another important soil characteristic as it indicates the presence of harmful salts in the soil resulting from low rainfall and high evaporation. The specific conductivity (μScm^{-1}) of the soil samples were in the range 40.00 ± 2.00 to 1770.00 ± 15.00 . The lowest value was obtained for soil samples taken from the farmland, while the highest value was obtained for soil samples taken from abattoir. The conductivity values obtained in this work for dumpsite, abattoir and auto-mechanic were relatively higher than the values ($142.00 \mu\text{Scm}^{-1}$) obtained by Amadi, (2011), in an assessment of the effect of Aladimma dumpsite on soil and groundwater in Owerri, Imo State, Nigeria ($110 \mu\text{Scm}^{-1}$) obtained by Chukwu and Anuchi (2016) in an assessment of the impact of abattoir wastes on the physicochemical properties of soil within Port Harcourt metropolis; and ($11.05 \mu\text{Scm}^{-1}$) obtained for soils around welding workshop by Funtua *et al.* (2017) when they evaluated heavy metals level of soil in old Pantaka market area of Kaduna, Nigeria. The sampling season, the nature of the soil and the analytical procedures employed may have contributed to the variation in the results. Specific conductivity of the samples are in the order abattoir>dumpsite>auto-mech>farmland.

Organic matter (%) in the soil samples were in the range 1.011 ± 0.002 to 4.113 ± 0.003 . Soil samples taken from abattoir have the highest value while the soil samples taken from farmland gave the lowest value. Organic matter of top soil is usually in the range of 1 to 6% (Magdoff and Harold, 2009), hence the value of the SOM in the sample compares favourably. It however followed a trend abattoir>auto-mech>dumpsite>farmland.

Bulk density is an indicator of the level of soil compaction. It reflects the soil's ability to function for structural support, water and solute mobility, and soil aeration. The ideal soil bulk density for plant growth in a sandy soil such as the type of soil obtainable at the sampling sites is should be less than 1.6 gcm^{-3} and root growth is prohibited as bulk density increases to 1.8 gcm^{-3} (Arshad *et al.*, 1996). The results of bulk density (gcm^{-3}) obtained for the samples under study were in the range 1.12 ± 0.02 to 1.55 ± 0.03 . The soil samples taken from abattoir recorded the lowest value, while the soil

samples taken from the farmland recorded the highest value. In all cases the results compare favourably with plant growth requirement. The mean results (g/cm^3) fall within the range in a trend farmland (1.55)>dumpsite (1.42)>Auto-mech (1.38)>abattoir (1.12).

Soil texture as an important soil attribute influences the rate of infiltration of storm-water. The percentage of sand, clay and silt determines the textural class of a soil. Table 4 shows textural analysis of the four soil samples with auto-mech having 85.88% sand, 11.84% clay and 2.28% silt; abattoir having 86.04% sand, 7.68% clay and 6.28% silt; dumpsite having 92.04% sand, 5.84% clay and 2.16% silt; farmland having 90.16% sand, 7.68% clay and 2.16% silt. The triangle of soil texture (Fig. 2) shows the textural class names associated with various percentage combinations of sand, clay and silt. The textural class names obtained when the results of soil samples under study were superimposed on the textural triangle were sandy-loam, loamy-sand, sandy and sandy for auto-mechanic site, abattoir, dumpsite and farmland, respectively.

The CEC values in the samples were 5.732, 8.066, 2.965 and 3.645 meq/100g for auto-mechanic site, abattoir, dumpsite and farmland respectively with a trend abattoir>auto-mech>farmland>dumpsite. Organic matter has a very high CEC. The highest value obtained in abattoir soil sample is most likely due to the higher percentage of silt and organic matter content as compared to the other three soil samples. Auto-mech has a relatively higher percentage of clay and higher pH. It has been reported that CEC increases with increasing pH and soils with a higher clay fraction tends to have a higher CEC, these factors explains why the CEC for auto-mech soil sample is higher than those of dumpsite and farmland, the latter two soil samples have more percentage of sand in their texture. This agrees with reports from similar studies that sandy soils have lower CEC than loamy soils. Soils with low CEC are more likely to develop deficiencies in K^+ , Mg^{2+} and other cations while soils with high CEC are less susceptible to leaching of these cations (Brown and Lemon, 2018). The result obtained for auto-mechanic compares favourably with the value (6.15 ± 2.79) reported by Pam *et al.* (2013), for same site.

Table 1: Physico-chemical attributes of soil from the study areas

Soil Attributes	Auto-Mechanic Mean \pm SD	Abattoir Mean \pm SD	Dumpsite Mean \pm SD	Farmland Mean \pm SD
pH	8.40 \pm 0.20	7.10 \pm 0.20	7.20 \pm 0.10	7.60 \pm 0.10
Conductivity ($\mu\text{S/cm}$)	240.00 \pm 9.00	1770.00 \pm 15.00	820.00 \pm 3.00	40.00 \pm 2.00
Organic matter (%)	1.69 \pm 0.01	4.11 \pm 0.00	1.32 \pm 0.00	1.01 \pm 0.00
Bulk density (g/cm^3)	1.38 \pm 0.03	1.12 \pm 0.02	1.42 \pm 0.00	1.55 \pm 0.03
Sand (%)	85.88 \pm 0.01	86.04 \pm 0.04	92.04 \pm 0.01	90.16 \pm 0.01
Clay (%)	11.84 \pm 0.02	7.68 \pm 0.02	5.84 \pm 0.02	7.68 \pm 0.02
Silt (%)	2.28 \pm 0.02	6.28 \pm 0.02	2.16 \pm 0.01	2.16 \pm 0.02
Texture class	Sandy loam	Loamy sand	Sandy soil	Sandy soil
CEC (meq/100g)	5.73 \pm 0.01	8.07 \pm 0.00	2.97 \pm 0.00	3.65 \pm 0.01
TPH (mg/kg)	355.10 \pm 0.04	113.05 \pm 0.05	5.62 \pm 0.02	1.36 \pm 0.02
Cd (mg/kg)	1.00 \pm 0.10	1.80 \pm 0.10	0.42 \pm 0.01	0.51 \pm 0.01
Pb (mg/kg)	82.78 \pm 0.03	70.40 \pm 1.40	16.45 \pm 0.04	3.22 \pm 0.02
Ni (mg/kg)	16.25 \pm 0.05	440.30 \pm 2.30	6.20 \pm 0.10	25.40 \pm 0.30
Zn (mg/kg)	75.46 \pm 0.06	131.14 \pm 1.14	74.16 \pm 0.10	57.33 \pm 0.20
Cu (mg/kg)	28.74 \pm 0.02	37.28 \pm 1.16	22.37 \pm 0.03	2.50 \pm 0.01

*SD = Standard deviation

Table 2: Metal pollution index for soils from the study areas

Metal	MPI	Significance
Auto Mechanic Site		
Cd	1.56 x 10 ⁰	Slightly polluted
Pb	4.84 x 10 ¹	Excessively polluted
Ni	5.45 x 10 ⁰	Severely polluted
Zn	1.44 x 10 ⁰	Slightly polluted
Cu	1.60 x 10 ⁰	Slightly polluted
Abattoir		
Cd	2.61 x 10 ⁰	Moderately polluted
Pb	3.80 x 10 ⁰	Moderately polluted
Ni	6.54 x 10 ¹	Excessively polluted
Zn	1.96 x 10 ⁰	Slightly polluted
Cu	2.12 x 10 ⁰	Moderately polluted
Dumpsite		
Cd	1.31 x 10 ⁰	Slightly polluted
Pb	3.64 x 10 ⁰	Moderately polluted
Ni	2.05 x 10 ⁰	Moderately polluted
Zn	1.65 x 10 ⁰	Slightly polluted
Cu	1.38 x 10 ⁰	Slightly polluted
Farmland		
Cd	2.20 x 10 ⁻¹	Slightly contaminated
Pb	5.13 x 10 ⁻¹	Moderately contaminated
Ni	8.24 x 10 ⁻¹	Severely contaminated
Zn	4.66 x 10 ⁻¹	Moderately contaminated
Cu	1.53 x 10 ⁻¹	Slightly contaminated

Table 3: CF of toxic metals in soils from the study areas

Metal	CF	Classification
Auto-Mechanic		
Cd	3.33 x 10 ⁰	Slightly contaminated
Pb	4.87 x 10 ⁰	Moderately contaminated
Ni	8.13 x 10 ⁻¹	No contamination
Zn	1.08 x 10 ⁰	suspected contaminated
Cu	1.15 x 10 ⁰	suspected contamination
Abattoir		
Cd	6.00 x 10 ⁰	Moderately contaminated
Pb	4.14 x 10 ⁰	Moderately contaminated
Ni	2.20 x 10 ¹	Severely contaminated
Zn	1.87 x 10 ⁰	suspected contaminated
Cu	1.49 x 10 ⁰	Suspected contaminated
Dumpsite		
Cd	1.40 x 10 ⁰	Suspected contamination
Pb	9.68 x 10 ⁻¹	No contamination
Ni	3.10 x 10 ⁻¹	No contamination
Zn	1.06 x 10 ⁰	suspected contamination
Cu	8.95 x 10 ⁻¹	No contamination
FarmLand		
Cd	1.70 x 10 ⁰	suspected contamination
Pb	1.89 x 10 ⁻¹	not contamination
Ni	1.27 x 10 ⁰	suspected contaminated
Zn	8.19 x 10 ⁻¹	No contamination
Cu	1.00 x 10 ⁻¹	No contamination

Table 4: I-geo for toxic metals in soils from the study areas

Metal	I _{geo}	Classification
Auto-Mechanic		
Cd	5.89 x 10 ⁻²	Between unpolluted to moderately polluted
Pb	5.01 x 10 ⁰	Extremely polluted
Ni	1.86 x 10 ⁰	Moderately polluted
Zn	-6.07 x 10 ⁻²	Unpolluted
Cu	9.41 x 10 ⁻²	Between unpolluted to moderately polluted
Abattoir		
Cd	7.98 x 10 ⁻¹	Between unpolluted to moderately polluted
Pb	1.34 x 10 ⁰	Moderately polluted
Ni	5.45 x 10 ⁰	Extremely polluted
Zn	3.83 x 10 ⁻¹	Between unpolluted to moderately polluted
Cu	5.01 x 10 ⁻¹	Between unpolluted to moderately polluted
Dumpsite		
Cd	-1.93 x 10 ⁻¹	Unpolluted
Pb	1.28 x 10 ⁰	Moderately polluted
Ni	4.53 x 10 ⁻¹	Between unpolluted to moderately polluted
Zn	1.34 x 10 ⁻¹	Between unpolluted to moderately polluted
Cu	-1.20 x 10 ⁻¹	Unpolluted
Farm Land		
Cd	-2.77 x 10 ⁰	Unpolluted
Pb	-1.55 x 10 ⁰	Unpolluted
Ni	-8.64 x 10 ⁻¹	Unpolluted
Zn	-1.69 x 10 ⁰	Unpolluted
Cu	-3.29 x 10 ⁰	Unpolluted

Total petroleum hydrocarbons (TPH) in soils from study areas

The mean concentration of TPH obtained in the soil samples in this study are presented in Table 1. The results showed that 355.10 ± 0.04, 113.05 ± 0.05, 5.62 ± 0.02 and 1.36 ± 0.02 mg/kg were recorded for auto-mechanic site, abattoir, dumpsite and farmland, respectively. TPH values follow the trend auto-mech>abattoir>dumpsite>farmland. Anthropogenic activities in auto-mechanic site involve use and inappropriate disposal of petroleum products such as grease, oils, lubricants and fuels on the soil. This may be related to the higher value obtained in the auto-mechanic soil sample. Activities in abattoir also involve use of fuel and burning of tires to roast animals, and these have contributed to the relatively higher value obtained in abattoir soil sample. Alinnor and Nwachukwu (2013) reported that similar study which was carried out in an auto-mechanic site in Lagos, Nigeria produce TPH value of 362.6 mg/kg. The result in this study compares favourably. The toxicity of TPH in soil has been established by DPR in Nigeria at concentration range >1000 mg/kg (Alinnor and Nwachukwu, 2013). This study shows that all four soil samples have TPH concentrations below the toxicity limit. However, it is important to monitor the trend especially at the auto-mechanic and abattoir sites because some of the components of TPH such as benzene and naphthalene have chronic carcinogenic effect, more so that Eneji *et al.* (2017) had reported the presence of naphthalene in soil around auto-mechanic workshop in Makurdi.

Potentially toxic metals (PTMs)

Results of PTMs obtained in this study are presented in Table 1. The concentrations of Cd (mg/kg) in soil samples from the four locations were in the range 0.42 ± 0.01 to 1.8 ± 0.05. Abattoir soil recorded the highest value and dumpsite soil recorded the lowest value. Pb concentrations (mg/kg) were in the range, 3.22 ± 0.02 to 82.78 ± 0.03. The highest value was obtained in the soil samples taken from auto-mechanic while

the lowest value was obtained in the soil samples taken from the farmland. Values for Ni (mg/kg) were in the range 6.2 ± 0.1 to 440.3 ± 2.3 . The concentration of Ni was highest in abattoir soil samples and lowest in the dumpsite soil samples. Zn concentrations (mg/kg) were in the range 57.33 ± 0.2 to 131.14 ± 1.14 . Zn concentration was lowest in soil samples taken from farmland and highest in abattoir soil samples. While Cu concentrations (mg/kg) were in the range 2.5 ± 0.01 to 37.28 ± 1.16 . Concentration of Cu was lowest in farmland soil samples and highest in abattoir soil samples.

Potentially toxic metals (PTMs) concentrations (mg/kg) in auto-mech soil (Table 1) follows the trend: Pb (82.78)>Zn (75.46)>Cu (28.74)>Ni (16.25)>Cd (1.00), this slightly deviated from the trend Zn>Pb>Cu>Ni>Cd reported by Pam *et al.* (2013), however the general trend which put Pb and Zn at higher concentration is still discernible. The higher values observed for Pb and Zn could be attributed to inappropriate disposal of petroleum products such as used of lubricants, fuels and specialty products, batteries which are no longer in use, welding work, painting and dumping of alloy materials at the site. Pb concentration observed in auto-mechanic in this study is lower than those reported by Pam *et al.* (2013) and Beetseh and Ocheje, (2013) but higher than values reported by Leke *et al.* (2011) in similar studies on auto-workshops in Makurdi. Factors such as sampling methodology as well as analytical techniques employed and variation in human activities at the sites could have been responsible for the differences. Ni concentration in this study compares favourably with the value reported by Pam *et al.* (2013). Cd concentration in this study compares favourably with the one reported by Leke *et al.* (2011). The presence of these PTMs (Ni and Cd) could be attributed to unused nickel-cadmium batteries disposal at the site. Cu concentration is lower than the values reported by both Pam *et al.* (2013) and Leke *et al.* (2011). Pb, Cd and Ni are priority PTMs and need to be monitored.

PTMs concentrations (mg/kg) in abattoir (Table 1) followed the trend Ni (440.30)>Zn (131.14)>Pb (70.40)>Cu (37.28)>Cd (1.80). Ande *et al.* (2017) had reported a trend showing Ni>Cu>Pb while Cd was not detected in a similar study on soil around Wurukun abattoir. Olayinka *et al.* (2017) reported a trend showing Zn>Pb>Cd in another study on abattoir soil in Abeokuta. It does appear that the trend is somewhat erratic. However, Ni concentration maintains the lead in the abattoir soils in Makurdi. Higher concentrations of all the metals were observed in this study than those reported by Ande *et al.* (2017) for Wurukun abattoir soil. These higher values may be connected to the higher level of activities around the Wadata abattoir which is almost inside the highly populated Wadata market generating PTMs containing wastes. Waste vehicle tires together with petroleum products are burnt to roast the animals being processed at the abattoir, the blood and undigested materials as well as the burnt materials are washed onto the soil while animal dung littered everywhere around the abattoir. Kalu *et al.* (2015) had reported the presence of Ni, Cd, Cu and Pb in cattle hides while Nwude *et al.* (2010) reported presence of Zn, Pb, Cu and Cd in the blood of cows at slaughter houses. All these are responsible for concentrations of these PTMs in abattoir soil. Of the four sampling locations in this study, abattoir recorded the highest value of Cd, this can be attributed to disposal of unsold vegetables particularly spinach and fruits from the market around the abattoir, also meat organs like kidney, liver and lungs which may be disposed could contribute to enhanced level of Cd in abattoir soil.

The concentrations of PTMs in the solid waste dumpsite is in the order Zn>Cu>Pb>Ni>Cd. This trend conforms to the trend Zn>Cu>Pb reported by Amadi (2011) and the trend Zn>Cu>Pb>Cd reported by Amadi *et al.* (2012) in similar

studies in Owerri. The trend also compares favourably with those Zn>Pb>Cu>Cd and Zn>Cu>Pb>Cd reported by Anhwange *et al.* (2012) for dumpsite soil samples in two seasons within makurdi metropolis. The highest value of Zn at the dumpsite could be traced to large amount of zinc coated materials disposed at the site. Zn dust can also be removed from the air by rain and snow into the soil (Anhwange *et al.*, 2012), and these could raise the Zn level in the soil. There is no reported evidence that Zn is carcinogenic to human, however, chronic effects of large amounts of zinc in the body may result to anemia, nervous system disorders, damage to the pancreas and deficiency in "good" cholesterol (Anhwange *et al.*, 2012). The presence of copper in the dumpsite soil is not unconnected to the disposal of waste electrical cables and fittings at the site. The presence of Pb in the dumpsite soil sample can be attributed to dumping of lead glazed ceramics and plumbing materials. The presence of Cd in the soil sample from the dumpsite can be traced to the disposal of cigarette filters, trace level of Cd can also be found in jewelries, plates, stained glasses (Anhwange *et al.*, 2012), and these could contribute to the presence of Cd in the dumpsite soil. The presence of Nickel in the solid waste dumpsite can be linked to disposal of household metal wares, electronics wastes, rechargeable batteries, power tools and condemned CD plates. The concentrations of PTMs in the soil sample taken from farmland use in Northbank were in the order: Zn>Ni>Pb>Cu>Cd. The presence of these PTMs could be attributed to natural sources as well as composts made from organic materials in solid wastes which inevitably contain these metals. Pb and Cd can be hazardous to animals and humans at relatively low concentrations and hence should be closely scrutinized when applying municipal composts to agricultural soils. Most leafy vegetables and spinach can readily take up Cd from soil (Hussain *et al.*, 2016). This could explain why the lowest value of Cd was observed. The presence of Ni is not unconnected to metal wares such as knives, axes and other farm implements containing nickel used and dumped on the land.

Ecological risks assessment

The results of MPIs for the selected potentially toxic metals (PTMs) for soils under different land uses in Makurdi, Nigeria and their respective significance are presented in Table 2. The results show that at the auto-mechanic site, the soil was slightly polluted with Cd with MPI value of 1.56×10^0 , Pb value was 4.84×10^1 indicating that the soil was excessively polluted with Pb. Ni show a severe pollution with an MPI value of 5.45×10^0 , the soil was slightly polluted with Zn and Cu having MPI values of 1.44×10^0 and 1.60×10^0 , respectively. At the Wadata abattoir site, the results showed 2.61×10^0 , 3.80×10^0 , 6.54×10^1 , 1.96×10^0 and 2.12×10^0 for Cd, Pb, Ni, Zn and Cu, respectively. Cd, Pb and Cu indicated moderate pollution; Ni polluted the soil excessively while the soil showed slight pollution with respect to Zn. At the solid waste dumpsite, the soil show slight pollution with regards to Cd, Zn and Cu having MPI values of 1.31×10^0 , 1.65×10^0 and 1.38×10^0 , respectively, while Pb and Ni moderately polluted the soil with MPI values of 3.64×10^0 and 2.05×10^0 , respectively. At the farmland, Cd and Cu slightly contaminated the soil with 2.20×10^{-1} and 1.53×10^{-1} MPI values, respectively; Ni severely contaminated the soil with MPI values of 8.24×10^{-1} , while Pb and Zn moderately contaminated the soil with MPI values of 5.13×10^{-1} and 4.66×10^{-1} , respectively. Analysis of the MPIs in the four sampling sites for the PTMs shows that Cd follows the trend: abattoir > auto-mech > dumpsite > farmland, this trend is a function of the reference values of Cd at the various sites. Pb is in the order: Auto-mech > abattoir > dumpsite > farmland. Ni follows the trend: abattoir > automech > dumpsite > farmland. The trend for Zn is abattoir > dumpsite > auto-mech > farmland. While Cu

is in the order abattoir>auto-mech>dumpsite>farmland. The MPI values for all the PTMs indicated that they pose negative effect on the soils around the auto-mechanic, abattoir and dumpsites with abattoir>auto-mechanic>dumpsite, but at the farmland, there was no negative effects on the soil. Amadi *et al.* (2017) utilized pollution indices to assess the quality of soil around Madaga gold mining site in Niger State, Nigeria, their MPI values for Cd, Pb, Cu, Zn and Ni were 22.50, 26.80, 1.20, 0.95 and 0.89, respectively. Jiang *et al.* (2017) assessed the contamination levels and human health risks of toxic heavy metals in street dust in industrial city of Northwest China and found MPI ranges for Pb (0.358 – 2.590), Cd (0.33 – 2.15), Cu (1.38 – 6.21) and Zn (0.56 – 1.83). These results compare favourably with those obtained in this work for automechanic site.

The contamination factors (CF) of the selected PTMs for soils under different land uses and their respective classification are presented in Table 3. It shows that Cd, Pb, Ni, Zn and Cu have CF of 3.33×10^0 , 4.87×10^0 , 8.13×10^{-1} , 1.08×10^0 and 1.15×10^0 , respectively in the soil sample from auto-mechanic site. Cd slightly contaminated the soil, Pb moderately contaminated the soil; Ni showed no contamination, while Zn and Cu showed suspected contamination. The abattoir CF shows that Cd and Pb moderately contaminated the soil with CF values of 6.00×10^0 and 4.14×10^0 , respectively. Ni severely contaminated the soil with Cf value of 2.20×10^1 while Zn and Cu showed suspected contamination with CF values of 1.87×10^0 and 1.49×10^0 , respectively. Dumpsite CF gave Cd and Zn suspected contamination with values of 1.40×10^0 and 1.06×10^0 , respectively, while Pb, Ni and Cu had no contamination with values of 9.68×10^{-1} , 3.10×10^{-1} and 8.95×10^{-1} , respectively. At the farmland, Cd and Ni had suspected contamination with CF values of 1.70×10^0 and 1.27×10^0 , respectively, while Pb, Zn and Cu showed no contamination of the soil. CF for Cd in the four sites follows the trend: abattoir>auto-mech>farmland>dumpsite. Pb is in the order auto-mech>abattoir>dumpsite>farmland. Ni is in the order abattoir>farmland>auto-mech>dumpsite. Zn follows the trend abattoir>auto-mech>dumpsite>farmland. While the order for Cu is abattoir>auto-mech>dumpsite>farmland. The background values determined the CF value and the classifications for the PTMs. For this study, the world medium pre-industrial values were used as background values for the PTMs. These results varied slightly with CF for Pb (2.15×10^1 – severe contamination), Cu (3.86×10^1 – severe contamination), Zn (2.4×10^0 – slight contamination), Ni (3.1×10^0 – slight contamination) and Cd (1.90×10^0 – suspected contamination) reported by Pam *et al.* (2013) for Apir auto-mechanic site in Makurdi. Ekeocha *et al.* (2017) who worked on soils from major auto-mechanic in Abuja (Kugbo, Zuba and Apo) reported range of CF values for Cd (11.8 – 13.9), Pb (2.0 – 3.92), Ni (3.63 – 6.7), Zn (8.50 – 38.3) and Cu (14.2 – 213). Orji *et al.* (2018) also worked on soil from auto-mechanic workshop in Abuja and reported CF values that were < 1 for Cd, Pb, Ni and Zn and Cu was between 1.17 – 1.64. The results obtained by Edori and Kpee (2017) who worked on three abattoirs (Agip, Iwofe and Mile 3) in Port Harcourt showed CF values corresponding to no contamination of the soil by Cd, Pb, Ni, Zn and Cu as all CF values were < 1. Odukoya (2015) worked on dumpsites in Ojota Lagos and reported varied CF values for Cd (4 – 15.3), Pb (2.24 – 30.32), Ni (0.96), Zn (0.3 – 23.3) and Cu (0.32 – 1.4). It does appear that CF values reported in the different work do not compare. Factors such as the nature of soil, sampling and analytical techniques employed as well as the purity of the analytical reagents used could be responsible for the variation.

The index of geo-accumulation (I-geo) of the selected PTMs for soils under different land uses in Makurdi, Nigeria are

presented in Table 4. At the auto-mechanic site, Cd accumulation is gradually moving from its unpolluted status to moderately polluted level with a value of 5.89×10^{-2} , Pb is at the extremely polluted level with I_{geo} value of 5.01×10^0 , Nickel is at a moderately polluted level with a value of 1.86×10^0 , Zn is still maintaining unpolluted status having a value of -6.07×10^{-2} , while Cu is gradually accumulating towards a moderately polluted level with a value of 9.41×10^{-2} . At the abattoir site, Cd, Zn and Cu have gradually accumulated from unpolluted states towards moderately polluted levels with values of 7.98×10^{-1} , 3.83×10^{-1} and 5.01×10^{-1} , respectively. While Pb and Ni have accumulated to moderately polluted with a value of 1.34×10^0 and extremely polluted with a value of 5.45×10^0 , respectively. The dumpsite soil sample showed that Cd and Cu have not accumulated to a level of pollution as their I_{geo} values are still -1.93×10^{-1} and -1.20×10^{-1} respectively, Pb is moderately polluting the soil with its value of 1.28×10^0 , while Ni and Zn are gradually accumulating towards moderately polluting the soil with values of 4.53×10^{-1} and 1.34×10^{-1} , respectively. The soil sample from farmland showed that all five PTMs have not accumulated beyond unpolluted levels having I_{geo} values of -2.77×10^0 , -1.55×10^0 , -8.64×10^{-1} , -1.69×10^0 and -3.29×10^0 for Cd, Pb, Ni, Zn and Cu respectively. These results show that contamination of the soils due to anthropogenic influence follows the trend: auto-mechanic site – Pb>Ni>Cu>Cd>Zn; abattoir – Ni>Pb>Cd>Cu>Zn; Dumpsite – Pb>Ni>Zn>Cu>Cd and Farmland – Ni>Cu>Zn>Pb>Cd. The trend seen at the auto-mechanic site varied with the Igeo trend reported by Pam *et al.* (2013) and Orji *et al.* (2018) for Apir auto-mechanic site in Makurdi (Cu>Pb>Ni>Zn>Cd) and Abuja (Cu>Zn>Pb>Ni>Cd) respectively. Edori and Kpee (2017) reported Igeo trend for three abattoirs in Port Harcourt thus Agip (Cu>Zn>Pb>Ni>Cd), Iwofe (Cu>Zn>Pb>Ni>Cd) and Mile 3 (Cu>Zn>Pb>Ni>Cd), the values show minimal influence from anthropogenic sources. The results of Odukoya (2015) showed Igeo range of values (unpolluted – extremely polluted) for dumpsite in Ojota Lagos with a trend Cd>Pb>Zn>Cu>Ni. The nature of the soil, the nature and type of waste disposed onto the soil, the environmental management system in place at the various locations as well as the analytical procedures employed could be responsible for the variation in the trend.

In order to have a total assessment of the degree of contamination in the sites, the PLI is used to prove the level of deterioration of the soil condition as a result of accumulation of PTMs. It is a geometric average of MPI (Varol, 2011). The PLI calculated for soils under different land uses in Makurdi, Nigeria and their respective levels of deterioration are presented in Table 5. As indicated in the table, the soils of auto-mechanic site at Apir and that of Wadata abattoir were polluted as a result of human activities in the area having PLI values of 1.75×10^0 and 4.33×10^0 , respectively. The soil at the NASME dumpsite and the farmland sampled in this study were yet to be polluted having PLI values of 8.32×10^{-1} and 5.07×10^{-1} , respectively. Information from the users of the dumpsite indicated that the site was newly created, this could be the reason why the pollution load index was low. The results further confirmed that the Apir auto-mechanic and Wadata abattoir are facing probable environmental pollution as a result of human activities especially with hazardous PTMs such as Pb in the auto-mechanic site and Cd, Pb and Ni in the abattoir. Elsewhere in India, Yadav and Yadav (2018) worked on an agricultural soil irrigated with wastewater and determined the PLI ranging from 48.7 to 74.3 indicating extreme pollution due to Cu, Fe, Zn, Pb and Ni

The EF calculated for soils under different land uses in Makurdi, Nigeria and their respective significance are presented in Table 6. The values for EF speculate that

contaminations originating from anthropogenic sources is increasing from deficiency level to minimal enrichment in the four sites with abattoir having the highest EF value of 8.63×10^{-1} , followed by auto-mechanic with EF value of 6.03×10^{-1} , while the dumpsite and farmland have EF values of 5.69×10^{-1} and 4.57×10^{-1} , respectively. Enrichment factor is the extent of the possible impact of anthropogenic activities on the PTMs concentration in the soil. The content of PTM characterized by low variability of occurrence (LV) is used as a reference to identify the expected impact of anthropogenesis on the PTMs in the soils (Kowalska *et al.*, 2018). A reference element is an element particularly stable in the soil, which is characterized by absence of vertical mobility and/or degradation phenomena (Barbieri, 2016). It also assesses the presence and intensity of anthropogenic contaminant deposition on surface soil (Zinkute *et al.*, 2017). The constituent chosen in this work was Mn whose concentration is generally not anthropogenically altered. Though, the EF in this study may be considered not significant, they are indicators that the PTMs are accumulating, because the value of EF arises from the differences in composition of the various soil and the immobile element (Mn) used in the calculation.

Table 5: Pollution load index (PLI) of toxic metals in soils from the study areas

Sampling sites	PLI	Significance
Auto Mechanic site	1.75×10^0	Polluted
Abattoir	4.33×10^0	Polluted
Dumpsite	8.32×10^{-1}	Not Polluted
Farmland	5.07×10^{-1}	Not polluted

Table 6: EF of toxic metals in soils from the study areas

Sampling sites	EF	Significance
Auto Mechanic site	6.03×10^{-1}	Deficiency to minimal enrichment
Abattoir	8.63×10^{-1}	Deficiency to minimal enrichment
Dumpsite	5.69×10^{-1}	Deficiency to minimal enrichment
Farmland	4.57×10^{-1}	Deficiency to minimal enrichment

Table 7: PERI of toxic metals in soils from the study areas

Sampling sites	PERI	Significance
Auto Mechanic site	3.27×10^2	Considerable ecological risk
Abattoir	4.37×10^2	Considerable ecological risk
Dumpsite	7.64×10^1	Low ecological risk
Farmland	1.45×10^1	Low ecological risk

Table 8: Degree of contamination (Ca) of toxic metals in soils from the study areas

Sampling sites	C _d	Significance
Auto Mechanic site	5.85×10^1	Very high degree of contamination
Abattoir	7.59×10^1	Very high degree of contamination
Dumpsite	1.00×10^1	Moderate degree of contamination
Farmland	2.17×10^0	Low degree of contamination

Table 9: Average of pollution index (PI_{avg}) of toxic metals in soils from the study areas

Sampling sites	PI _{avg}	Significance
Auto Mechanic site	1.17×10^1	Low quality soil due to contamination
Abattoir	1.52×10^1	Low quality soil due to contamination
Dumpsite	2.01×10^0	Low quality soil due to contamination
Farmland	4.35×10^{-1}	High quality soil

Table 10: Nemerow pollution index (PI_{Nemerow}) for toxic metals in soils from the study areas

Sampling sites	PI _{Nemerow}	Significance
Auto Mechanic site	3.52×10^1	Seriously polluted domain
Abattoir	4.75×10^1	Seriously polluted domain
Dumpsite	2.94×10^0	Moderately polluted domain
Farmland	6.60×10^{-1}	Safety domain

The PERI calculated for soils under different land uses in Makurdi, Nigeria are presented in Table 7. It indicated that there is considerable ecological risk at the auto-mechanic and abattoir sites with PERI values of 3.27×10^2 and 4.37×10^2 , respectively, this implies that there is high tendency for the soil to cause harm to the ecosystem in the vicinity of the sites with severe consequences. While the dumpsite and farmland have low ecological risks with PERI values 7.64×10^1 and 6.27×10^1 , respectively. The trend is such that abattoir>auto-mechanic>dumpsite>farmland. The values obtained in this study compares favourably with those of Ekeocha *et al.* (2017) who reported PERI of 2.51×10^2 (Kugbo), 1.67×10^2 (Zuba) and 1.22×10^2 (Apo) in Abuja major mechanic workshops. Orji *et al.* (2018) reported a lower PERI range of values (for $9.92 \times 10^0 - 1.35 \times 10^1$) in Abuja mechanic workshop.

The C_d calculated for soils under different land uses in Makurdi, Nigeria and their respective significance are presented in Table 8. It shows that auto-mechanic and abattoir have very high degree of contamination with C_d values of 5.85×10^1 and 7.59×10^1 respectively, it implies that soil in these two sites are of low quality. While dumpsite and farmland have moderate and low degree of contamination respectively with C_d values of 1.00×10^1 and 2.12×10^0 . C_d values in this study are in the order abattoir>auto-mechanic>dumpsite>farmland. The value for dumpsite in this study is within the range of Cd values ($8.59 \times 10^0 - 8.79 \times 10^1$) reported by Odukoya (2015) for Ojota dumpsite in Lagos. The auto-mechanic result is relatively higher than the value range of values ($2.37 \times 10^0 - 3.80 \times 10^0$) reported by Orji *et al.* (2018) for Abuja workshop, but comparable to the values ($6.88 \times 10^1 -$ Kugbo) and ($5.00 \times 10^1 -$ Zuba) reported by Ekeocha *et al.* (2018), it is however lower than the value ($2.87 \times 10^2 -$ Apo) reported by Ekeocha *et al.* (2018).

The PI_{avg} calculated for soils under different land uses in Makurdi, Nigeria and their respective significance are presented in Table 9. It showed that auto-mechanic, abattoir and dumpsite soil are of low quality because of contamination with PI_{avg} values of 1.17×10^1 , 1.52×10^1 and 2.01×10^0 respectively, while the agric-land indicated high quality soil with PI_{avg} value of 4.35×10^{-1} . As the PI_{avg} increases, an increasingly large percentage of the population is likely to experience increasingly severe adverse health effects.

The Nemerow pollution index allows the assessment of the overall degree of pollution of the soil and includes the contents of all analyzed PTMs. The PI_{Nemerow} calculated for soils under different land uses in Makurdi, Nigeria and their respective classes of soil quality are presented in Table 10. It indicated that on a wider scope of the soil environment, the auto-mechanic and abattoir environment were seriously polluted domain with PI_{Nemerow} values of 3.52×10^1 and 4.75×10^1 , respectively. The dumpsite environment is a moderately polluted domain with PI_{Nemerow} value of 2.94×10^0 while the farmland environment indicated a safety domain with PI_{Nemerow} value of 6.60×10^{-1} . These results compares favourable with those reported by Lawal *et al.* (2015) who reported a PI_{Nemerow} range of values (7.21×10^{-1} to 3.31×10^0) for soils of urban areas in Rivers State, Anani and Olomukoro (2017) who reported PI_{Nemerow} range of values (2.83×10^0 to

4.65 x 10¹) for sediments of Ossiomo River in Rivers State. In China, Jiang *et al.* (2014) reported $PI_{Nemerow}$ of 1.95 x 10⁰ for dumpsite in northeast China.

Human health risks assessment

The hazards quotients and the cancer risks of the selected contaminants for adults and children through the various exposure pathways at the various land use locations are presented in Tables 11 - 15.

Table 11 shows the PTMs and TPH hazard quotients for children and adults ($HQ_{children}$, HQ_{adults}) and the cancer risks for children and adults ($CR_{children}$, CR_{adults}) around the abattoir domain. It shows that ingestion hazards quotient values for Cd, Pb, Ni, Zn, Cu and TPH for children were 2.04 x 10⁻², 2.28 x 10⁻¹, 2.49 x 10⁻¹, 4.95 x 10⁻³, 1.06 x 10⁻² and 3.57 x 10⁻⁴, respectively, decreasing in the order: Ni>Pb>Cd>Cu>Zn>TPH. Ingestion vales for adults were 2.18 x 10⁻³, 2.44 x 10⁻², 2.67 x 10⁻², 5.30 x 10⁻⁴, 1.13 x 10⁻³ and 3.82 x 10⁻⁵ for Cd, Pb, Ni, Zn, Cu and TPH, respectively, decreasing in the order Ni>Pb>Cd>Cu>Zn>TPH. Ingestion cancer risk for children were 6.12 x 10⁻⁶, 6.78 x 10⁻⁶, 8.48 x 10⁻³ and 3.71 x 10⁻⁵ for Cd, Pb, Ni and TPH, respectively, increasing in the order Cd<Pb<TPH<Ni, while ingestion cancer risks for adults were 6.55 x 10⁻⁷, 7.26 x 10⁻⁷, 9.08 x 10⁻⁴ and 3.98 x 10⁻⁶ for Cd, Pb, Ni and TPH, respectively, increasing in the order Cd<Pb<TPH<Ni. There are no evidence of carcinogenicity for Zn and Cu and so slop factors were not provided for Zn and Cu. Inhalation HQ for children were 5.62 x 10⁻⁵, 1.57 x 10⁻⁴, 1.52 x 10⁻³, 1.36 x 10⁻⁷, 2.91 x10⁻⁷ and 9.78 x 10⁻⁹ for Cd, Pb, Ni, Zn, Cu and TPH, respectively, in a decreasing order: Ni>Pb>Cd>Cu>Zn>TPH. Inhalation HQ for adults were 3.21 x 10⁻⁵, 8.97 x 10⁻⁵, 8.73 x 10⁻⁴, 7.80 x 10⁻⁸, 1.66 x 10⁻⁷ and 5.59 x 10⁻⁹ for Cd, Pb, Ni, Zn, Cu and TPH, respectively, in a decreasing order: Ni>Pb>Cd>Cu>Zn>TPH. Inhalation CR for children were 3.96 x 10⁻⁹, 9.23 x 10⁻¹⁰, 1.40 x 10⁻⁷ and 1.02 x 10⁻⁹ for Cd, Pb, Ni and TPH, respectively while inhalation CR for adults were 2.26 x 10⁻⁹, 5.28 x 10⁻¹⁰, 8.01 x 10⁻⁸ and 5.85 x 10⁻¹⁰ for Cd, Pb, Ni and TPH respectively. Dermal HQ for children were 1.14 x 10⁻⁴, 4.25 x 10⁻³, 2.59 x 10⁻³, 6.93 x 10⁻⁵, 4.93 x 10⁻⁵ and 3.58 x 10⁻⁵ for Cd, Pb, Ni, Zn, Cu and TPH, respectively. Dermal HQ for adults were 1.74 x 10⁻⁵, 6.49 x 10⁻⁴, 3.95 x 10⁻⁴, 1.06 x 10⁻⁵, 7.52 x 10⁻⁶ and 5.47 x 10⁻⁶ for Cd, Pb, Ni, Zn, Cu and TPH, respectively. The degree of PTM and TPH contaminations in soil can pose hidden dangers to human health via different ways (e.g., oral ingestion pathway, inhalation pathway and dermal contact pathway) (Zheng *et al.*, 2010; Luo *et al.*, 2012). Studies have shown that toxicity of exposure to these contaminants is influenced by numerous factors, including the route of exposure, absorption, metabolism and distribution in the human body (Morton *et al.*, 2009; Liu *et al.*, 2016). The results in this work imply that there are no adverse non carcinogenic health effects expected due to exposure for the three exposure routes. A person's age is also a significant factor that should be given more consideration. It has been reported that children and infants are more likely to be affected compared with adults, because of their behavioral characteristics (e.g., outdoor activities, mouthing non-food objects, and sucking their hands or fingers) and are at greater risk of exposure to contaminants in soils Yang *et al.*, 2013; Liu *et al.*, 2016). Ingestion cancer risks for children and adults due to exposure to Ni exceeded the acceptable range (10⁻⁶ to 10⁻⁴), with that of children higher than that of adults. Though within acceptable range, ingestion cancer risks for children and adults due to exposure to TPH are of concern values due to chronic effects. This abattoir is surrounded by Wadata market in which women do business with their children. Children are more susceptible to a known dose of contaminants and are likely to inadvertently ingest substantial quantities of mixed contaminants due to their

hand-to-mouth behavior; ingestion is therefore a key contaminants exposure pathway for children.

Table 12 shows the mixed contaminants hazard quotient (HQ) and the cancer risks (CR) for children and adults around the farmland domain. It shows that ingestion hazards quotient values due to Cd, Pb, Ni, Zn, Cu and TPH for children were 5.78 x 10⁻³, 1.04 x 10⁻², 1.44 x 10⁻², 2.16 x 10⁻³, 7.08 x 10⁻³ and 5.83 x 10⁻⁶, respectively. Ingestion values for adults were 6.19 x 10⁻⁴, 1.11 x 10⁻³, 1.54 x 10⁻³, 2.32 x 10⁻⁴, 7.58 x 10⁻⁴ and 6.24 x 10⁻⁷ for Cd, Pb, Ni, Zn, Cu and TPH, respectively. Ingestion cancer risk for children were 1.73 x 10⁻⁶, 3.10 x 10⁻⁷, 4.89 x 10⁻⁴ and 4.47 x 10⁻⁷ for Cd, Pb, Ni and TPH, respectively, while ingestion cancer risks for adults were 1.86 x 10⁻⁷, 3.32 x 10⁻⁸, 5.24 x 10⁻⁵ and 4.79 x 10⁻⁸ for Cd, Pb, Ni and TPH, respectively. There are no evidence of carcinogenicity for Zn and Cu and so slop factors were not provided for Zn and Cu. Inhalation HQ for children were 4.25 x 10⁻⁴, 1.92 x 10⁻⁴, 2.35 x 10⁻³, 1.59 x 10⁻⁶, 5.20 x10⁻⁷ and 3.73 x 10⁻⁹ for Cd, Pb, Ni, Zn, Cu and TPH, respectively. Inhalation HQ for adults were 4.55 x 10⁻⁵, 2.05 x 10⁻⁵, 2.52 x 10⁻⁴, 1.71 x 10⁻⁷, 5.58 x 10⁻⁸ and 4.00 x 10⁻¹⁰ for Cd, Pb, Ni, Zn, Cu and TPH, respectively. Inhalation CR for children were 2.99 x 10⁻⁸, 1.13 x 10⁻⁹, 2.16 x 10⁻⁷ and 3.28 x 10⁻¹⁰ for Cd, Pb, Ni and TPH, respectively while inhalation CR for adults were 3.21 x 10⁻⁹, 1.21 x 10⁻¹⁰, 2.31 x 10⁻⁸ and 3.52 x 10⁻¹¹ for Cd, Pb, Ni and TPH, respectively. Dermal HQ for children were 2.31 x 10⁻⁶, 1.39 x 10⁻⁵, 1.07 x 10⁻⁵, 2.16 x 10⁻⁶, 2.36 x 10⁻⁷ and 4.31 x 10⁻⁷ for Cd, Pb, Ni, Zn, Cu and TPH, respectively. Dermal HQ for adults were 8.66 x 10⁻⁸, 5.21 x 10⁻⁷, 3.99 x 10⁻⁷, 8.11 x 10⁻⁸, 8.85 x 10⁻⁹ and 6.58 x 10⁻⁸ for Cd, Pb, Ni, Zn, Cu and TPH, respectively. These values indicate that adverse non carcinogenic health effects due to ingestion, inhalation and skin contact are not possible. However, cancer risk for children due to ingestion of Ni was higher than the acceptable range. In this farm land, adults' carcinogenic risks due to ingestion of Ni is within tolerable limit.

Table 13 shows the PTMs and TPH hazard quotient (HQ) and the cancer risks (CR) on children and adults around the auto-mechanic domain. It shows that hazards quotient values for TPH, Cd, Pb, Ni, Zn and Cu on children when these contaminants are ingested were 1.21 x 10⁻³, 1.13 x 10⁻², 2.68 x 10⁻¹, 9.20 x 10⁻³, 2.85 x 10⁻³ and 8.14 x 10⁻², respectively. Ingestion vales for adults were 1.30 x 10⁻⁴, 1.21 x 10⁻³, 2.87 x 10⁻², 9.86 x 10⁻⁴, 3.05 x 10⁻⁴ and 8.72 x 10⁻³ for TPH, Cd, Pb, Ni, Zn and Cu, respectively. Ingestion cancer risk for children were 1.17 x 10⁻⁴, 3.40 x 10⁻⁶, 7.98 x 10⁻⁶ and 3.13 x 10⁻⁴ for TPH, Cd, Pb and Ni, respectively, while ingestion cancer risks for adults were 1.25 x 10⁻⁵, 3.64 x 10⁻⁷, 8.54 x 10⁻⁷ and 3.35 x 10⁻⁵ for TPH, Cd, Pb and Ni, respectively. There are no evidence of carcinogenicity for Zn and Cu and so slop factors were not provided for Zn and Cu. Inhalation HQ for children were 8.80 x 10⁻⁷, 8.33 x 10⁻⁴, 4.92 x 10⁻³, 1.50 x 10⁻³, 2.09 x 10⁻⁶ and 5.98 x10⁻⁶ for TPH, Cd, Pb, Ni, Zn and Cu, respectively. Inhalation HQ for adults were 9.43 x 10⁻⁸, 8.92 x 10⁻⁵, 5.28 x 10⁻⁴, 1.61 x 10⁻⁴, 2.24 x 10⁻⁷ and 6.41 x 10⁻⁷ for TPH, Cd, Pb, Ni, Zn and Cu, respectively. Inhalation CR for children were 1.17 x 10⁻⁴, 5.87 x 10⁻⁸, 2.89 x 10⁻⁸, and 1.38 x 10⁻⁷ for TPH, Cd, Pb and Ni, respectively while inhalation CR for adults were 1.25 x 10⁻⁵, 6.29 x 10⁻⁹, 3.10 x 10⁻⁹ and 1.48 x 10⁻⁸ for TPH, Cd, Pb and Ni, respectively. Dermal HQ for children were 1.13 x 10⁻⁴, 4.53 x 10⁻⁶, 3.57 x 10⁻⁴, 6.82 x 10⁻⁶, 2.85 x 10⁻⁶ and 2.71 x 10⁻⁶ for TPH, Cd, Pb, Ni, Zn and Cu, respectively. Dermal HQ for adults were 1.72 x 10⁻⁵, 1.70 x 10⁻⁷, 1.34 x 10⁻⁵, 2.56 x 10⁻⁷, 1.07 x 10⁻⁷ and 1.02 x 10⁻⁷ for TPH, Cd, Pb, Ni, Zn and Cu, respectively. These values indicate that adverse non carcinogenic health effects due to ingestion, inhalation and skin contact are not possible. However, cancer risk for children due to ingestion of Ni and

TPH were higher than the acceptable range. At the auto-mechanic site, adults' carcinogenic risks due to ingestion of Ni and TPH were within tolerable limit. It is however a concern as the exposure man-hour for many of the adults (especially the Mechanics) is higher than 365 days used in these calculations. The results in this study compares favourably with health risks assessment results (Pb- 2.8×10^{-4} – 3.24×10^{-2} ; Cu- 8.0×10^{-6} – 1.57×10^{-3} ; Ni- 1.68×10^{-4} – 1.55×10^{-4} ; Cd- 7.0×10^{-4} – 1.4×10^{-3}) by Inam *et al.* (2015), on a mechanic village in Uyo.

Table 11: Hazard quotients and cancer risks of contaminants in abattoir soil in Makurdi, Nigeria

Entry route	Cont.	HQ _{Children}	HQ _{Adult}	CR _{Children}	CR _{Adult}
Ingestion	Cd	2.04×10^{-2}	2.18×10^{-3}	6.12×10^{-6}	6.55×10^{-7}
	Pb	2.28×10^{-1}	2.44×10^{-2}	6.78×10^{-6}	7.26×10^{-7}
	Ni	2.49×10^{-1}	2.67×10^{-2}	8.48×10^{-3}	9.08×10^{-4}
	Zn	4.95×10^{-3}	5.30×10^{-4}	-	-
	Cu	1.06×10^{-2}	1.13×10^{-3}	-	-
	TPH	3.57×10^{-4}	3.82×10^{-5}	3.71×10^{-5}	3.98×10^{-8}
Inhalation	Cd	5.62×10^{-5}	3.21×10^{-5}	3.96×10^{-9}	2.26×10^{-9}
	Pb	1.57×10^{-4}	8.97×10^{-5}	9.23×10^{-10}	5.28×10^{-10}
	Ni	1.52×10^{-3}	8.73×10^{-4}	1.40×10^{-7}	8.01×10^{-8}
	Zn	2.36×10^{-7}	7.80×10^{-8}	-	-
	Cu	2.91×10^{-7}	1.66×10^{-7}	-	-
	TPH	9.78×10^{-9}	5.59×10^{-9}	1.02×10^{-9}	5.85×10^{-10}
Dermal	Cd	1.14×10^{-4}	1.74×10^{-5}	-	-
	Pb	4.25×10^{-3}	6.49×10^{-4}	-	-
	Ni	2.59×10^{-3}	3.95×10^{-4}	-	-
	Zn	6.93×10^{-5}	1.06×10^{-5}	-	-
	Cu	4.93×10^{-5}	7.52×10^{-6}	-	-
	TPH	3.58×10^{-5}	5.47×10^{-6}	-	-

Cont. = Contaminant

Table 12: Hazards quotients and cancer risks of contaminants in farmland soil in Makurdi, Nigeria

Entry route	Cont.	HQ _{Children}	HQ _{Adult}	CR _{Children}	CR _{Adult}
Ingestion	Cd	5.78×10^{-3}	6.19×10^{-4}	1.73×10^{-6}	1.86×10^{-7}
	Pb	1.04×10^{-2}	1.11×10^{-3}	3.10×10^{-7}	3.32×10^{-8}
	Ni	1.44×10^{-2}	1.54×10^{-3}	4.89×10^{-4}	5.24×10^{-5}
	Zn	2.16×10^{-3}	2.32×10^{-4}	-	-
	Cu	7.08×10^{-3}	7.58×10^{-4}	-	-
	TPH	5.83×10^{-6}	6.24×10^{-7}	4.47×10^{-7}	4.79×10^{-8}
Inhalation	Cd	4.25×10^{-4}	4.55×10^{-5}	2.99×10^{-8}	3.21×10^{-9}
	Pb	1.92×10^{-4}	2.05×10^{-5}	1.13×10^{-9}	1.21×10^{-10}
	Ni	2.35×10^{-3}	2.52×10^{-4}	2.16×10^{-7}	2.31×10^{-8}
	Zn	1.59×10^{-6}	1.71×10^{-7}	-	-
	Cu	5.20×10^{-7}	5.58×10^{-8}	-	-
	TPH	3.73×10^{-9}	4.0×10^{-10}	3.28×10^{-10}	3.52×10^{-11}
Dermal	Cd	2.31×10^{-6}	8.66×10^{-8}	-	-
	Pb	1.39×10^{-5}	5.21×10^{-7}	-	-
	Ni	1.07×10^{-5}	3.99×10^{-7}	-	-
	Zn	2.16×10^{-6}	8.11×10^{-8}	-	-
	Cu	2.36×10^{-7}	8.85×10^{-9}	-	-
	TPH	4.31×10^{-7}	6.58×10^{-8}	-	-

Cont. = Contaminant

Table 13: Hazards quotients and cancer risks of contaminants in apir auto-mechanic site soil in Makurdi, Nigeria

Entry route	Cont.	HQ _{Children}	HQ _{Adult}	CR _{Children}	CR _{Adult}
Ingestion	Cd	1.13×10^{-2}	1.21×10^{-3}	3.40×10^{-6}	3.64×10^{-7}
	Pb	2.68×10^{-1}	2.87×10^{-2}	7.98×10^{-6}	8.54×10^{-7}
	Ni	9.20×10^{-3}	9.86×10^{-4}	3.13×10^{-4}	3.35×10^{-5}
	Zn	2.85×10^{-3}	3.05×10^{-4}	-	-
	Cu	8.14×10^{-2}	8.72×10^{-3}	-	-
	TPH	1.21×10^{-3}	1.30×10^{-4}	1.17×10^{-4}	1.25×10^{-5}
Inhalation	Cd	8.33×10^{-4}	8.92×10^{-5}	5.87×10^{-8}	6.29×10^{-9}
	Pb	4.92×10^{-3}	5.28×10^{-4}	2.89×10^{-8}	3.10×10^{-9}
	Ni	1.50×10^{-3}	1.61×10^{-4}	1.38×10^{-7}	1.48×10^{-8}
	Zn	2.09×10^{-6}	2.24×10^{-7}	-	-
	Cu	5.98×10^{-6}	6.41×10^{-7}	-	-
	TPH	8.80×10^{-7}	9.43×10^{-8}	8.57×10^{-8}	9.18×10^{-9}
Dermal	Cd	4.53×10^{-6}	1.70×10^{-7}	-	-
	Pb	3.57×10^{-4}	1.34×10^{-5}	-	-
	Ni	6.82×10^{-6}	2.56×10^{-7}	-	-
	Zn	2.85×10^{-6}	1.07×10^{-7}	-	-
	Cu	2.71×10^{-6}	1.02×10^{-7}	-	-
	TPH	1.13×10^{-4}	1.72×10^{-5}	-	-

Cont. = Contaminant

Table 14: Hazards quotients and cancer risks of contaminants in dumpsite soil at NASME, Makurdi, Nigeria

Entry route	Cont.	HQ _{Children}	HQ _{Adult}	CR _{Children}	CR _{Adult}
Ingestion	Cd	4.76×10^{-3}	5.10×10^{-4}	1.43×10^{-6}	1.53×10^{-7}
	Pb	5.32×10^{-2}	5.70×10^{-3}	1.58×10^{-6}	1.70×10^{-7}
	Ni	3.51×10^{-3}	3.76×10^{-4}	1.12×10^{-4}	1.28×10^{-5}
	Zn	2.80×10^{-3}	3.00×10^{-4}	-	-
	Cu	6.33×10^{-2}	6.79×10^{-3}	-	-
	TPH	2.02×10^{-5}	2.17×10^{-6}	1.85×10^{-6}	1.98×10^{-7}
Inhalation	Cd	3.50×10^{-4}	3.75×10^{-5}	2.47×10^{-8}	2.64×10^{-9}
	Pb	9.78×10^{-4}	1.05×10^{-4}	5.75×10^{-9}	6.16×10^{-10}
	Ni	5.74×10^{-4}	6.15×10^{-5}	5.27×10^{-8}	5.64×10^{-9}
	Zn	2.06×10^{-6}	2.21×10^{-7}	-	-
	Cu	4.66×10^{-6}	4.99×10^{-7}	-	-
	TPH	1.38×10^{-8}	1.48×10^{-9}	1.36×10^{-9}	1.45×10^{-10}
Dermal	Cd	1.90×10^{-6}	7.13×10^{-8}	-	-
	Pb	7.10×10^{-5}	2.66×10^{-6}	-	-
	Ni	2.60×10^{-6}	9.75×10^{-8}	-	-
	Zn	2.80×10^{-6}	1.05×10^{-7}	-	-
	Cu	2.11×10^{-6}	7.92×10^{-8}	-	-
	TPH	1.78×10^{-6}	2.72×10^{-7}	-	-

Cont. = Contaminant

Table 15: Hazards index (HI) and total cancer risks (TCR) of contaminants in soils from the study areas

Land Use	Cont.	HI _{Children}	HI _{Adult}	TCR _{Children}	TCR _{Adult}
Abattoir	Cd	2.06×10^{-2}	2.23×10^{-3}	6.12×10^{-6}	6.57×10^{-7}
	Pb	2.32×10^{-1}	2.51×10^{-2}	6.78×10^{-6}	7.27×10^{-7}
	Ni	2.53×10^{-1}	2.80×10^{-2}	8.48×10^{-3}	9.08×10^{-4}
	Zn	5.02×10^{-3}	5.41×10^{-4}	-	-
	Cu	1.06×10^{-2}	1.14×10^{-3}	-	-
	TPH	3.93×10^{-7}	4.37×10^{-8}	3.71×10^{-8}	3.98×10^{-9}
Farmland	Cd	6.20×10^{-3}	6.64×10^{-4}	1.76×10^{-6}	1.89×10^{-7}
	Pb	1.06×10^{-2}	1.14×10^{-3}	3.11×10^{-7}	3.33×10^{-8}
	Ni	1.67×10^{-2}	1.79×10^{-3}	4.89×10^{-4}	5.24×10^{-5}
	Zn	2.17×10^{-3}	2.32×10^{-4}	-	-
	Cu	7.08×10^{-3}	7.58×10^{-4}	-	-
	TPH	6.26×10^{-9}	6.91×10^{-10}	4.67×10^{-10}	4.79×10^{-11}
Dumpsite	Cd	5.11×10^{-3}	5.47×10^{-4}	1.45×10^{-6}	1.56×10^{-7}
	Pb	5.43×10^{-2}	5.81×10^{-3}	1.59×10^{-6}	1.70×10^{-7}
	Ni	4.09×10^{-3}	4.38×10^{-4}	1.19×10^{-4}	1.28×10^{-5}
	Zn	2.80×10^{-3}	3.00×10^{-4}	-	-
	Cu	6.33×10^{-2}	6.79×10^{-3}	-	-
	TPH	2.20×10^{-8}	2.44×10^{-9}	1.85×10^{-9}	1.98×10^{-10}

Cont. = Contaminant

Table 14 shows the PTMs and TPH hazard quotients (HQ) and the cancer risks (CR) on children and adults around the dumpsite domain. It shows that hazard quotient values for TPH, Cd, Pb, Ni, Zn and Cu on children when these contaminants are ingested were 2.02×10^{-5} , 4.76×10^{-3} , 5.32×10^{-2} , 3.51×10^{-3} , 2.80×10^{-3} and 6.33×10^{-2} , respectively. Ingestion vales for adults were 2.17×10^{-6} , 5.10×10^{-4} , 5.70×10^{-3} , 3.76×10^{-4} , 3.00×10^{-4} and 6.79×10^{-3} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. Ingestion cancer risk for children were 1.85×10^{-6} , 1.43×10^{-6} , 1.58×10^{-6} and 1.12×10^{-4} for TPH, Cd, Pb and Ni, respectively, while ingestion cancer risks for adults were 1.98×10^{-7} , 1.53×10^{-7} , 1.70×10^{-7} and 1.28×10^{-5} for TPH, Cd, Pb and Ni, respectively. There are no evidence of carcinogenicity for Zn and Cu and therefore, slop factors were not provided for Zn and Cu. Inhalation HQ for children were 1.38×10^{-8} , 3.50×10^{-4} , 9.78×10^{-4} , 5.74×10^{-4} , 2.06×10^{-6} and 4.66×10^{-6} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. Inhalation HQ for adults were 1.48×10^{-9} , 3.75×10^{-5} , 1.05×10^{-4} , 6.15×10^{-5} , 2.21×10^{-7} and 4.99×10^{-7} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. Inhalation CR for children were 1.36×10^{-9} , 2.47×10^{-8} , 5.75×10^{-9} , and 5.27×10^{-8} for TPH, Cd, Pb and Ni, respectively while inhalation CR for adults were 1.45×10^{-10} , 2.64×10^{-9} , 6.16×10^{-10} and 5.64×10^{-9} for TPH, Cd, Pb and Ni, respectively. Dermal HQ for children were 1.78×10^{-6} , 1.90×10^{-6} , 7.10×10^{-5} , 2.60×10^{-6} , 2.80×10^{-6} and 2.11×10^{-6} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. Dermal HQ for adults were 2.72×10^{-7} , 7.13×10^{-8} , 2.66×10^{-6} , 9.75×10^{-8} , 1.05×10^{-7} and 7.92×10^{-8} for TPH, Cd, Pb, Ni, Zn and Cu respectively. These values indicate that adverse non carcinogenic health effects due to ingestion, inhalation and skin contact are not possible. However, cancer risk for children due to ingestion of Ni was higher than the acceptable range. At the solid waste dumpsite located around NASME, adults' carcinogenic risks due to ingestion of Ni is within tolerable limit. It is therefore advisable to prevent children exposure at the dumpsite. Adults should also limit man-hour in their activities at the dumpsite. Though the results of mixed contaminants interactions might be synergistic, it can be assumed that all the contaminants risks are additive (Luo *et al.*, 2012). Therefore, the cumulative noncarcinogenic hazard expressed as hazard index (HI) and carcinogenic risk expressed as total cancer risks (TCR) can be calculated. The HI and TCR of the selected PTMs and TPH calculated for the soils under different land uses in Makurdi, Nigeria on children and adults are presented in Table 15. The probability that long-term hazards effects will be experienced increases with increasing values of HI (Wang *et al.*, 2012; Ogunkunle *et al.*, 2013). Table 16 shows children and adult hazard index (HI) and total cancer risks (TCR) for the four sampling sites. At the abattoir, children HI were 3.93×10^{-7} , 2.06×10^{-2} , 2.32×10^{-1} , 2.53×10^{-1} , 5.02×10^{-3} and 1.06×10^{-2} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. HI for adults were 4.37×10^{-8} , 2.23×10^{-3} , 2.51×10^{-2} , 2.80×10^{-2} , 5.41×10^{-4} and 1.14×10^{-3} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. TCR for children were 3.71×10^{-8} , 6.12×10^{-6} , 6.78×10^{-6} and 8.48×10^{-3} for TPH, Cd, Pb and Ni, respectively while TCR for adult were 3.98×10^{-9} , 6.57×10^{-7} , 7.27×10^{-7} and 9.08×10^{-4} for TPH, Cd, Pb and Ni, respectively. At the farmland, HI for children were 6.26×10^{-9} , 6.20×10^{-3} , 1.06×10^{-2} , 1.67×10^{-2} , 2.17×10^{-3} and 7.08×10^{-3} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. HI for adults were 6.91×10^{-10} , 6.64×10^{-4} , 1.14×10^{-3} , 1.79×10^{-3} , 2.32×10^{-4} and 7.58×10^{-4} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. TCR for children were 4.47×10^{-10} , 1.76×10^{-6} , 3.11×10^{-7} and 4.89×10^{-4} for TPH, Cd, Pb and Ni respectively while TCR for adults were 4.79×10^{-11} , 1.89×10^{-7} , 3.33×10^{-8} and 5.24×10^{-5} for TPH, Cd, Pb and Ni, respectively. At the auto-mechanic site, HI for children were 1.32×10^{-6} , 1.22×10^{-2} , 2.73×10^{-1} , 1.07×10^{-2} , 2.85×10^{-3}

and 8.14×10^{-2} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. HI for adults were 1.47×10^{-7} , 1.30×10^{-3} , 2.92×10^{-2} , 1.15×10^{-3} , 3.06×10^{-4} and 8.72×10^{-3} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. TCR for children were 1.17×10^{-7} , 3.46×10^{-6} , 8.00×10^{-6} and 3.13×10^{-4} for TPH, Cd, Pb and Ni, respectively, while TCR for adults were 1.25×10^{-8} , 3.70×10^{-7} , 8.57×10^{-7} and 3.35×10^{-5} for TPH, Cd, Pb and Ni, respectively. At the dumpsite, HI for children were 2.20×10^{-8} , 5.11×10^{-3} , 5.43×10^{-2} , 4.09×10^{-3} , 2.80×10^{-3} and 6.33×10^{-2} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. HI for adults were 2.44×10^{-9} , 5.47×10^{-4} , 5.81×10^{-3} , 4.38×10^{-4} , 3.00×10^{-4} and 6.79×10^{-3} for TPH, Cd, Pb, Ni, Zn and Cu, respectively. $HI_{children}$ and HI_{adults} decrease in the order: $Cu > Pb > Cd > Ni > Zn > TPH$. This order slightly deviated from the order $(Cd > Cu > Pb > Fe > Zn)$ observed by Ogunbanjo *et al.* (2016) in their work on a dumpsite in Sagamu Ogun State, however, the trend that Cu, Pb and Cd are higher up is still discernible. TCR for children were 1.85×10^{-9} , 1.45×10^{-6} , 1.59×10^{-6} and 1.19×10^{-4} for TPH, Cd, Pb and Ni, respectively, while TCR for adults were 1.98×10^{-10} , 1.56×10^{-7} , 1.70×10^{-7} and 1.28×10^{-5} for TPH, Cd, Pb and Ni, respectively. These HI values were less than 1 which indicates that the hazards are considered low at all the four locations. The total cancer risks TCR for adults due to exposure to Cd and Pb in the four locations were also low, but the TCR for adults due to exposure to Ni at the abattoir was high. The TCR for children due to exposure to Cd, Pb and Ni in the four locations were within acceptable limits except in abattoir where the TCR was higher than the limit. In all cases of the PTMs, the risks increased in the order: dermal < inhalation < ingestion. This trend compares favourably with the trend: $HQ_{ing} > HQ_{inh} > HQ_{derm}$, observed by Xiao *et al.* (2017), when they conducted a health risk assessment of heavy metals in soils from partial areas of Daye city in China. Xiao *et al.* (2017) also showed that $HI_{children}$ was higher than that HI_{adults} . In a similar manner, Aluko *et al.* (2018), worked on human health risks assessment of iron mines in Itakpe and Agbaja in Kogi state and observed that $HI_{children}$ (Pb - 1.11; Cd-0.57; Zn-0.0038; Cu-4.63) was greater than HI_{adults} (Pb-0.12; Cd-0.06; Zn-0.00054; Cu-0.57). It does showed that children are more vulnerable to PTMs contaminations than adults which agrees with the inference drawn by Ihedioha *et al.* (2017) in their work on a municipal waste dumpsite in Uyo.

Conclusion

Ecological assessment of the soil samples showed that except for the farmland, the soil from the auto-mechanic site, abattoir, and dumpsite were of low quality. Human risk assessment showed ingestion pathway is the highest contributor to non-carcinogenic and carcinogenic risks. The results also showed that children are more susceptible to both non-carcinogenic and cancer risks. The HI values were less than 1 which indicates that the hazards are considered low at all the four locations. The TCR for adults due to exposure to Ni at the abattoir was high but low for Cd and Pb. The TCR for children due to exposure to Cd, Pb and Ni in the four locations were within acceptable limits except in abattoir where the TCR was higher than the limit.

It is recommended that adequate measures be put in place to control the source of contaminants into the soils especially at the auto-mechanic sites and abattoir and to control human exposure. It is also recommended that other researchers should assess these sites and other related sites for other contaminants with a view to assessing their ecological and human health risks.

Conflict of Interest

Authors declare that there is no conflict of interest reported on this work.

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