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# Research Article
# Spatial Assessment of Heavy Metal Contamination in Agricultural Soils Developed on Basaltic and Sandstone Parent Materials

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## Abstract

**Background and Objective:** Delineating pollution levels and the ecological risk of heavy metals in agricultural soils are prerequisites for decreasing their pollution load. This study assesses the concentration, pollution loads and ecological risk of heavy metal on soils developed on basaltic and sandstone parent materials in Ikom. **Materials and Methods:** Soil samples were collected at a depth of 0-20 cm from soil developed on basaltic and sandstone parent materials, air-dried and sieved through a 2 mm mesh sieve for Physico-chemical and heavy metals analysis. **Results:** The result indicated that basaltic soil has greater potential for crop cultivation as shown by its fertility indices, pH (5.7), exchangeable Mg (1.94 mg $kg^{-1}$) and base saturation (82%) when compared with its counterpart sandstone soil, but it was constrained by Pb, Cd and Al contamination. Soil developed on both parent materials except those at Atimaka (14.183) and FGC Ikom (19.201) which had a considerable degree of contamination, other sites were heavily contaminated with Cd. The soil was moderate to extremely severe enriched with Pb at Atimaka (7.869) and Nde (4.984) and moderately to extremely severe enriched with Cd at all locations. The Cd had a very high potential ecological risk in soil developed on both parent materials. **Conclusion:** From the foregoing, it can be inferred that the studied soils are not currently in a safe state for the cultivation of edible crops and consumption of crops from the soil in these areas over a long time could pose health issues related to Cd and Pb contamination to humans.

Key words: Ecological risk, heavy metals, inverse distance weighting, parent material, spatial variation

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Parent materials from which the soil is developed plays a significant role in soil nutrient supply, especially in the supply of basic cations including but not limited to Ca, Mg and K. Despite the contribution of parent materials to soil nutrients supply, weathering of metal-bearing geological formations can be an important source of heavy metal contamination in the soil[1-4]. Previous studies on soil contaminated with heavy metals were usually conducted in soils close to sediment and industrial areas in view of receiving compensation from industries that release contaminants beyond the maximum permissible limit[5], neglecting the fact that heavy metals in soils can also be introduced from the parent materials or added to the soil through weathering and pedogenic processes (clay migration, gley formation, podzolization, etc.)[6].

To date, many scientific studies on geogenic heavy metal pollution are mainly focused on soil developed on argillaceous sedimentary rocks, such as shales, slates and mudstones[1,7], ultramafic rocks[8], black shale[9] and limestone[10]. Studies on heavy metal pollution of agricultural soil developed on basalt and sandstone are very limited despite their distribution globally[6,11-13]. Soils developed on basaltic parent materials are found in almost all continents of the world. According to Bryan and Ferrari[14], basaltic soils on the global scale are mainly distributed in North America (Columbia River basalt, high arctic large igneous province), Asia (Siberian traps, Deccan traps, Emeishan traps), South America (Central Atlantic magmatic province and Parana traps) and Africa (Etendeka traps and Karoo-Ferrar province) and in Nigeria, they are mostly found in Jos Plateau State[15] and Cross River State[16]. Similarly, sandstone-derived soils constitute about 18% of the land surface of Nigeria and occur in all the major ecological zones[17] and are also common in Southern California[18].

Research in Nigeria[16,19] and elsewhere in the world[20,21] have compared the potential of soils developed on basaltic and sandstone parent materials for agricultural productivity. In general, basaltic soils are widely cultivated and a large number of staple food crops are predominantly planted on them.

Few conducted studies on the extent of contamination of soil developed on basalt and sandstone parent materials had mixed results. For instance[11], reported basaltic soil to contains significantly higher concentrations of heavy metals (e.g., Cr and Ni) than sandstone soil. Nevertheless, an important reservoir of heavy metal in terrestrial environments is through chemical weathering of parent materials to release toxic metals and these metals can enrich the soil and then enter human body through the food chain, posing health risk to those who consume crops planted on it. According to Aki and Isong[22], heavy metals can be introduced into the soil following several pathways including industrial activities, irrigation, fertilization, atmospheric deposition and point source where metals are produced as a result of refining and refinishing products. The problem of agricultural land contamination by heavy metals in Nigeria and elsewhere around the globe has raised serious concerns for the soils in Cross River State utilized for crop cultivation especially in places where the parent materials from which the soil is developed are suspected to be heavy metal-laden.

However, to the best of our knowledge, there is a lack of public enlightenment concerning the extent of heavy metal pollution, distribution and ecological risk of soils, especially those utilized for agricultural cultivation in Cross River State. Nevertheless, where such information concerning soil pollution by heavy metals and other pollutants is available, they are only accessible by researchers, leaving the consumers (i.e., the populace) and growers of crops produce from the soil incognizant.

In view of ensuring healthy crops and feed for human and animal consumption, information on spatial distribution and contamination of agricultural soils and/or crops by heavy metals most especially highly hazardous metals such Pb, Hg, Cd, Cr, As, etc. should be given priority and made available to the public due to their potential effects on human health. Thus, the present research is significant primarily in alerting the public and scientific world at large about areas vulnerable to metal contamination. This study was designed to assess the fertility status, current pollution loads and ecological risk of heavy metals in soil developed on sandstone and basalt in Ikom LGA, Cross River State, Nigeria.

## MATERIALS AND METHODS

**Study area:** The study was conducted in Ikom Local Government Areas of Cross River State, Nigeria between June, 2019 to January, 2020. The study area lies between Latitudes 5°50' and 6°20' N and Longitudes 8°30' and 8°50' E with elevation ranging from 21-277 m and analytical hill-shading ranging from 20.51-75.21 (Fig. 1). The study area is found within a humid tropical climate characterized by two distinct rainfall peaks. The first rainy period starts from March, reaches a peak in June/July slows down in August and reaches another peak in September/October before it recedes into the dry season from November to early March. The mean annual rainfall of the area exceeds 2500 mm with mean annual air temperatures and relative humidity of 27°C and 87%, respectively. The area is used predominantly for crop

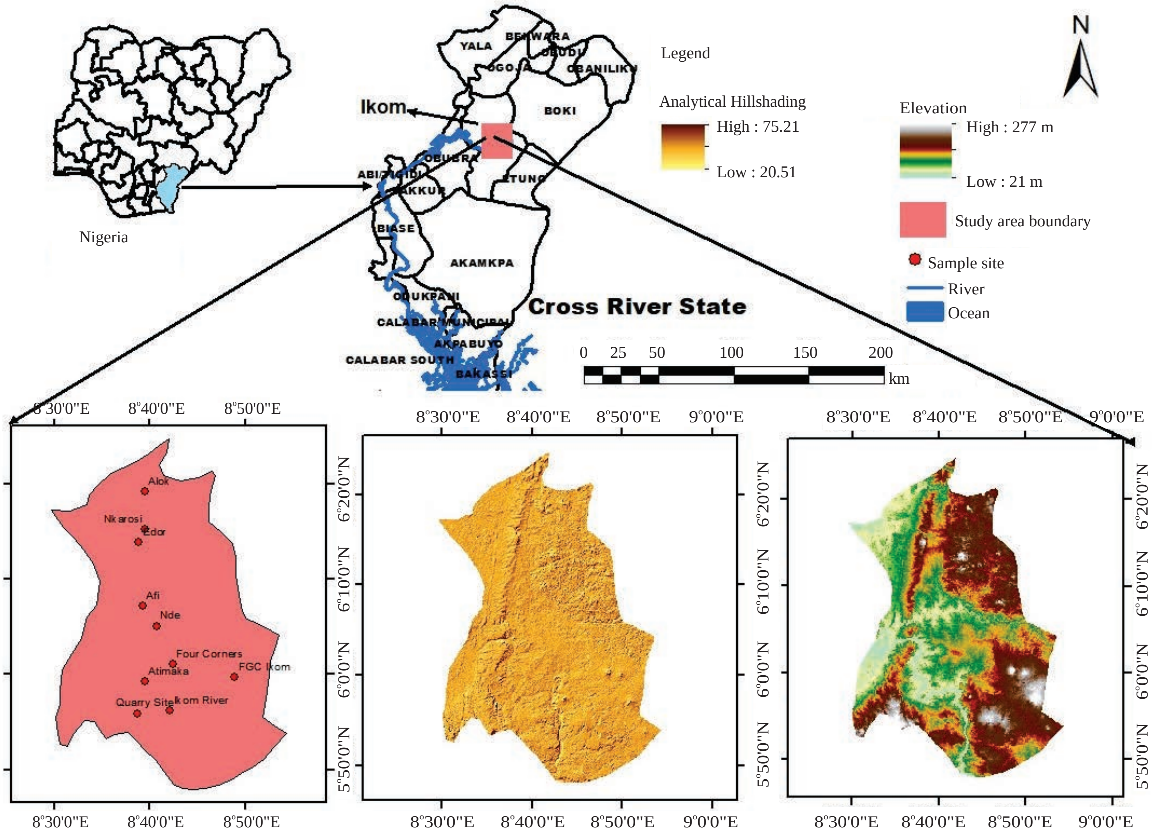


Fig. 1: Location map of the study area

cultivation where crops like fluted pumpkin, cassava, maize, pepper, watermelon and yam are cultivated including woody plants, shrubs, coconut and oil palm trees.

**Sampling collection and preparation:** A soil auger was used in collecting composite samples from five different points within each sampling site (Fig. 1) at a depth of 0-20 cm and placed in labelled bags and transported to the laboratory. Each soil sample was air-dried at room temperature for 2 weeks. The dried soil samples were crushed to powder using a porcelain mortar and pestle and later sieved vigorously to produce homogeneity, through a 2 mm mesh sieve, bagged and labelled for routine and heavy metals analysis.

**Digestion of sample:** The digestion of samples was done by dissolving 1 g of the dried soil samples in a clean 200 mL flask. This was followed by the addition of 0.2 mL of concentrated HCl in small portions, 1 mL of concentrated $HNO_3$ and 5 mL of perchloric acid. The mixture was covered with watch glasses and heated to near boiling for 3 hrs on a hotplate. After cooling, 1 g of ammonium chloride and 20 mL of 0.5 N HCl were added. Samples were reheated for 1 h and evaporated to approximately 10 mL. After cooling, the extracts were filtered into a 100 mL volumetric flask and stored in a high-density plastic bottle for heavy metal analysis.

**Quality assurance:** For the accuracy and precision of the analytical results, the recovery study method was used for the validation of the digestion method. This was achieved by determining metal concentrations in triplicate samples of un-spiked and spiked soil samples. Spiking was performed by adding 1 mL of various concentrations of the metal standard solution to 0.5 g of the soil sample, which was later subjected to the digestion procedure. The formula for calculating the percent recoveries according to Javed *et al.*[1] can be expressed as:

$$\text{Recovery (\%)} = \frac{S-Y}{Z} \times 100 \quad (1)$$

Where:

S = Concentration of metal in the spiked sample
Y = Concentration of metal in the un-spiked sample
Z = Spiking concentration

The percentage recoveries for the soil sample for all metals analyzed were within the range of 94.6-98.20%.

**Laboratory analysis:** Particle size distribution was determined by Bouyoucos hydrometer method[23]. Soil pH was measured potentiometrically in a soil: water suspension (mixed at a ratio of 1:2.5 soil: water) using glass electrode pH meter following the procedure described by Estefan *et al.*[24] Organic carbon was determined by the dichromate wet oxidation method of Walkley and Black as outline in Nelson and Sommers[25]. Total nitrogen was determined by the micro-Kjeldahl digestion method as described by Bremner[26]. Available phosphorous was determined by the Bray-1 method according to the procedure outlined in Estefan *et al.*[24]. Exchangeable bases ($Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$) were extracted by saturating the soil with neutral 1M NH4OAc[27] and Ca and Mg in the extract were determined using Atomic Absorption Spectrophotometer (AAS) while K and Na were determined by flame photometry. Exchangeable acidity was determined by extracting the soil with 0.1 N KCl solution and titrating the aliquot of the extract with 1 N NaOH following the procedure outline by Estefan *et al.*[24]. Effective cation exchange capacity (ECEC) was determined by summing up exchangeable bases ($Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$) and exchangeable acidity ($H^+$ and $Al^{3+}$). Base saturation was calculated as the sum of total exchangeable bases divided by ECEC and expressed as a percentage. Percentage aluminium saturation was computed using the formula below:

$$\text{Al saturation} = \frac{\text{Exchangeable aluminium}}{\text{Effective cation exchange capacity}} \times 100 \quad (2)$$

The concentration of Pb, Cd, Cr and As were determined by atomic absorption spectrophotometer.

**Statistical analysis:** The data collected were subjected to statistical analysis (mean, pollution indices and t-test) using SPSS software (version 25) and Microsoft Excel 2013 and Interpolation was done using inverse distance weighting utilizing ArcGIS 10.7. Various indices to assess the current pollution status were calculated following the models stated in Table 1 and 2.

The interpolation of selected soil pollution indices was done using the deterministic methods of Inverse Distance Weighting (IDW). According to Burrough and McDonnell[28] "IDW is based on the assumption that the value of an attribute in an unsampled area is that of the weighted average of the known data points within a local neighbourhood surrounding

Table 1: Single metal pollution and contamination indices

| Pollution indices | Equation | Class/values | Soil risk grade | References |
|---|---|---|---|---|
| Contamination factor (Cf) | $C_f = C_f \frac{C_{metal}}{C_{background}}$ | CF<1 | Low contamination factor | Hakanson[42] |
| | | $1\leq$CF<3 | Moderate contamination factor | |
| | | $3\leq$CF<6 | Considerable contamination factor | |
| | | CF$\geq$ 6 | Very high contamination factor | |
| Geo-accumulation index ($I_{geo}$) | $I_{geo} = \log_2\left(\frac{C_n}{1.5 * B_n}\right)$ | Class 0 = Igeo <0 | Practically uncontaminated | Muller[57] |
| | | Class 1= 0 <$I_{geo}$ < 1 | Uncontaminated to moderately contaminated | |
| | | Class 2 = 1 <$I_{geo}$ < 2 | Moderately contaminated | |
| | | Class 3 = 2 <$_{Igeo}$ < 3 | Moderately to heavily contaminated | |
| | | Class 4 = 3 <$I_{geo}$ < 4 | Heavily contaminated | |
| | | Class 5 = 4 <$I_{geo}$ < 5 | Heavily to extremely contaminated | |
| | | Class 6 = $I_{geo}$>5 | Extremely contaminated | |
| Enrichment factor (EF) | $EF = \frac{\left(C_M/C_{Al}\right)_{sample}}{\left(C_M/C_{Al}\right)_{earth\ crust}}$ | EF < 1 | Indicates no enrichment | Giri *et al.*[54] |
| | | EF = 1-3 | Minor enrichment | |
| | | EF = 3-5 | Moderate enrichment | |
| | | EF = 5-10 | Moderately severe enrichment | |
| | | EF = 10-25 | Severe enrichment | |
| | | EF = 25 -50 | Very severe enrichment | |
| | | EF>50 | Extremely severe enrichment | |
| Ecological risk factor (Er) | $E_r = T_r \times \frac{C_{metal}}{C_{background}}$ | $E_r$ < 40 | Low potential ecological risk | Hakanson[42] |
| | | 40 $\leq E_r$ <80 | Moderate potential ecological risk | |
| | | 80 $\leq E_r$<160 | Considerable potential ecological risk | |
| | | 160 $\leq E_r$<320 | High potential ecological risk | |
| | | $E_r \geq$320 | Very high potential ecological risk | |

$C_{metal}$: Measured concentration of the examined metal (n) in soil, $C_{background}$: Concentration of the examined metal (n) in the reference environment, Bn: The background concentration of the metal (n) in reference environment, Factor 1.5: The background matrix correction factor due to lithogenic effects, $(C_M/C_{Al})_{sample}$: The ratio of metal concentration (mg kg$^{-1}$) concerning Al (mg kg$^{-1}$) in soil samples, $(C_M/C_{Al})_{earth\ crust}$: The ratio of metal concentration (mg kg$^{-1}$) about Al (mg kg$^{-1}$) in the earth crust, $T_r$: Metal toxic response factor for metals (Cr = 2, Pb = 5, Cd = 30, As =10) and Al does not have value for Tr

Table 2: Integrated metal pollution and contamination indices

| Pollution indices | Equation | Class | Soil risk grade | References |
|---|---|---|---|---|
| Degree of contamination (Cd) | $C_d = \sum_{i=1}^{n} C_f$ | Cd<7 | Low degree of contamination | Hakanson[42] |
| | | 7≤Cd<14 | Moderate degree of contamination | |
| | | 14≤Cd<28 | Considerable degree of contamination | |
| | | Cd≥28 | Very high degree of contamination | |
| Pollution load index (PLI) | $PLI = (CF_1 \times CF_2 \times F_3 \times ... \times F_n)^{1/n}$ | PLI<1 | No metal pollution | Tomlinson *et al.*[49] |
| | | PLI = 1 | Baseline levels of pollutants | |
| | | PLI >1 | Indicates a polluted condition | |
| Ecological risk of environment | $RI = \sum_{i=1}^{n} E_r$ | RI<150<300 | Low risk | Hakanson[42] |
| | | 150≤RI | Moderate risk | |
| | | 300≤ RI <600 | Considerable risk | |
| | | RI≥600 | Very high risk | |

Cf: Contamination factor, RI: Ecological risk of environment, Er: Ecological risk factor

the unsampled location". Estimated values were interpolated based on the data from surrounding locations using the formula:

$$Z(xo) = \sum_{i-1}^{n} wiZ(xi) \quad (3)$$

where, Z(x0) is the estimated value, wi is the weight assigned to the value at each location Z (χi), n is the number of close neighbouring sampled data points used for estimation.

The weights were estimated using:

$$wi = \frac{\frac{1}{d_i^p}}{\sum_{i=1}^{n} \frac{1}{d_i^p}} \quad (4)$$

where, di is the distance between the estimated point and the sample point, p is an exponent parameter.

## RESULTS

**Physicochemical properties of sandstone and basaltic soils:** The texture of soil developed on basalt and sandstone was clay loam and sandy loam, respectively. The silt and clay contents of soil developed on basalt were significantly ($p<0.01$) higher than those obtained on soil developed on sandstone, whereas, the reverse was the case for sand content (Table 3). The soil pH developed on sandstone was strongly acid (5.27) while basaltic soil was moderately acid (5.7). The organic carbon content of the soil was low and sandstone soil was significantly lower than that of basaltic soil ($t = -3.35$, $p<0.01$). Available phosphorus in both soils was low and the content was higher in sandstone soil than basaltic soil. Total nitrogen, exchangeable Ca, K and Na were all low in both soils and were significantly ($p<0.05$) lower in sandstone soil than basaltic soil. Exchangeable Mg was moderate in basaltic soil and low in sandstone soils and the difference was highly significant ($t = -2.47$, $p<0.05$). Similarly, the ECEC and BS were lower in sandstone soil than basaltic soil. Exchangeable aluminium ($Al^{+++}$) was higher in sandstone soil than basaltic soil and the differences were statistically significant ($t = 3.81$, $p<0.05$), while exchangeable acidity ($H^+$) was lower in sandstone soil than basaltic soil.

**Heavy metal concentration of sandstone and basaltic soils:** The concentration lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As) and aluminium (Al) at studied locations is given in Table 4. From the results, Pb, Cd, Cr as and Al were observed to be higher in soil developed on sandstone than soil developed on basalt. However, only Cd and As showed significant differences in concentration between sandstone and basaltic soils as depicted by the t-test values ($t = 4.18$, $p<0.05$) and ($t = 3.65$, $p<0.05$) for Cd and As, respectively.

In basaltic soil, the highest and lowest values for Pb were 41.68 and 20.88 mg $kg^{-1}$, whereas, in sandstone soil, the highest and lowest values were 57.04 and 24.56 mg $kg^{-1}$, respectively. The mean concentration of Cd in sandstone and basaltic soils were 11.97 and 49.92 mg $kg^{-1}$, respectively. The mean values of Cr reported for soils developed on basalt and sandstone were 0.72 and 0.87 mg $kg^{-1}$, respectively. The mean arsenic (As) concentration was 0.043 mg $kg^{-1}$ in soil developed on basalt and 0.05 mg $kg^{-1}$ in soil developed on sandstone in the present research. Aluminium concentration was 66903.85 and 180250.40 mg $kg^{-1}$ for soil developed on basalt and sandstone parent material.

**Pollution loads of sandstone and basaltic soil:** Pollution loads vary from metal to metal and place to place including differences in parent materials.

**Contamination factor (Cf):** The results of this research showed that the studied soils were contaminated with Pb, Cd

Table 3: Differences between selected physicochemical properties and heavy metals in sandstone and basaltic soils in Ikom

| | Mean±SD | | | | |
|---|---|---|---|---|---|
| Soil properties | Sandstone soil | Basaltic soil | Mean difference | t-test | Sig. (2-tail) |
| Sand (g kg$^{-1}$) | 696±52.32 | 368±96.71 | 328.0 | 10.88 | 0.000*** |
| Silt (g kg$^{-1}$) | 172±21.49 | 321.0±71.25 | -149.0 | -7.70 | 0.000*** |
| Clay (g kg$^{-1}$) | 132±48.25 | 315±137.7 | -183.0 | -4.11 | 0.003*** |
| pH | 5.27±0.34 | 5.7±0.16 | -0.46 | -3.61 | 0.006*** |
| Org. C (g kg$^{-1}$) | 7.8±2.39 | 12.45±4.68 | -4.65 | -3.35 | 0.009*** |
| Total N (g kg$^{-1}$) | 0.63±0.23 | 1.06±0.41 | -0.43 | -3.60 | 0.006*** |
| Avail. P (mg kg$^{-1}$) | 7.93±5.71 | 5.21±7.19 | 2.72 | 0.76 | 0.467 |
| Ca (cmol kg$^{-1}$) | 2.18±0.44 | 4.14±0.71 | -1.96 | -9.41 | 0.000*** |
| Mg (cmol kg$^{-1}$) | 1.18±0.24 | 1.94±0.88 | -0.76 | -2.47 | 0.036** |
| K (cmol kg$^{-1}$) | 0.087±0.009 | 0.098±0.010 | -0.011 | -2.40 | 0.040** |
| $Na^+$ | 0.069±0.009 | 0.075±0.0085 | -0.0060 | -1.50 | 0.168 |
| $Al^{+++}$ (cmol kg$^{-1}$) | 1.64±0.65 | 0.73±0.49 | 0.90 | 3.81 | 0.004*** |
| $H^+$ (cmol kg$^{-1}$) | 0.43±0.32 | 0.49±0.119 | -0.064 | -6.2 | 0.552 |
| ECEC (cmol kg$^{-1}$) | 5.58±0.89 | 7.57±1.33 | -1.99 | -3.94 | 0.003*** |
| BS (%) | 63.4±7.41 | 82±6.93 | -186.0 | -6.09 | 0.000*** |
| Pb (mg kg$^{-1}$) | 43.34±11.90 | 30.52±7.41 | 12.78 | 1.49 | 0.211 |
| Cd (mg kg$^{-1}$) | 49.92±12.04 | 11.97±9.37 | 37.95 | 4.18 | 0.014** |
| Cr (mg kg$^{-1}$) | 0.86±0.15 | 0.72±0.11 | 1.49 | 2.05 | 0.11 |
| As (mg kg$^{-1}$) | 0.50±0.0071 | 0.04±0.0041 | 0.0067 | 3.65 | 0.022** |

***Significant at 1%, **Significant at 5%, SD: Standard deviation

Table 4: Field codes, GPS coordinate and heavy metal concentration in the studied sites

| | | | Coordinates | | Heavy metals | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample codes | Parent materials | Sites | Longitude | Latitude | Pb | Cd | Cr | As | Al |
| | | | | | mg kg$^{-1}$ | | | | |
| $B_1$ | Basaltic | Atimaka | 8.65706 | 5.98738 | 29.04 | 3.76 | 0.88 | 0.04 | 8709.76 |
| $B_2$ | Basaltic | FGC Ikom | 8.814675 | 5.994773 | 41.68 | 4.92 | 0.56 | 0.04 | 33412.89 |
| $B_3$ | Basaltic | Four Corners | 8.706329 | 6.018025 | 20.88 | 27.28 | 0.72 | 0.05 | 88435.37 |
| $B_4$ | Basaltic | Quarry site | 8.644381 | 5.931801 | 30.5 | 11.91 | 0.72 | 0.043 | 36697.25 |
| $B_5$ | Basaltic | Ikom River | 8.701983 | 5.935814 | 30.53 | 11.98 | 0.72 | 0.043 | 167264 |
| Mean | | | | | 30.53 | 11.97 | 0.72 | 0.043 | 66903.85 |
| $S_1$ | Sandstone | Alok | 8.657056 | 6.319886 | 48.48 | 68.42 | 1.04 | 0.04 | 223776.2 |
| $S_2$ | Sandstone | Afi | 8.653992 | 6.119072 | 24.56 | 46.48 | 0.94 | 0.05 | 193159 |
| $S_3$ | Sandstone | Nkarasi | 8.657056 | 6.25322 | 57.04 | 34.88 | 0.64 | 0.06 | 337500 |
| $S_4$ | Sandstone | Edor | 8.647081 | 6.231106 | 43.36 | 49.92 | 0.87 | 0.05 | 126315.8 |
| $S_5$ | Sandstone | Nde | 8.678919 | 6.084689 | 43.3 | 49.91 | 0.85 | 0.05 | 20501 |
| Mean | | | | | 43.35 | 49.92 | 0.87 | 0.05 | 180250.40 |
| [a]ASV | | | | | 20 | 0.3 | 90 | 13 | 47,200 |

ASV: World average shale value used as background values, Source: [a]Turekian and Wedenphol[32]

Table 5: Contamination factor, degree of contamination and pollution index of heavy metals in soil developed on sandstone and basaltic soils in Ikom

| Sample code | Parent materials | Sites | Cf-Pb | Cf-Cd | Cf-Cr | Cf-As | Cf-Al | $C_d$ | PLI |
|---|---|---|---|---|---|---|---|---|---|
| $B_1$ | Basaltic | Atimaka | 1.452 | 12.533 | 0.0098 | 0.0031 | 0.185 | 14.183 | 0.159 |
| $B_2$ | Basaltic | FGC Ikom | 2.084 | 16.400 | 0.0062 | 0.0031 | 0.708 | 19.201 | 0.215 |
| $B_3$ | Basaltic | Four Corners | 1.044 | 90.933 | 0.0080 | 0.0038 | 1.873 | 93.863 | 0.352 |
| $B_4$ | Basaltic | Quarry site | 1.525 | 39.700 | 0.0080 | 0.0033 | 0.777 | 42.014 | 0.262 |
| $B_5$ | Basaltic | Ikom river | 1.527 | 39.933 | 0.0080 | 0.0033 | 3.543 | 45.015 | 0.356 |
| Mean | | | 1.526 | 39.900 | 0.008 | 0.0033 | 1.417 | 42.855 | 0.269 |
| $S_1$ | Sandstone | Alok | 2.424 | 228.067 | 0.0116 | 0.0031 | 4.741 | 235.246 | 0.622 |
| $S_2$ | Sandstone | Afi | 1.228 | 154.933 | 0.0104 | 0.0038 | 4.092 | 160.268 | 0.500 |
| $S_3$ | Sandstone | Nkarasi | 2.852 | 116.267 | 0.0071 | 0.0046 | 7.150 | 126.280 | 0.600 |
| $S_4$ | Sandstone | Edor | 2.168 | 166.400 | 0.0097 | 0.0038 | 2.676 | 171.258 | 0.514 |
| $S_5$ | Sandstone | Nde | 2.165 | 166.367 | 0.0094 | 0.0038 | 0.434 | 168.979 | 0.336 |
| Mean | | | 2.167 | 166.407 | 0.0096 | 0.0038 | 3.819 | 172.406 | 0.518 |

Cf: Contamination factor, $C_d$: Degree of contamination, PLI: pollution load index, Pb: Lead, Cd: Cadmium, As: Arsenic, Al: Aluminium and Al while Cr and As showed no contamination (Table 5). Generally, lead (Pb) in both basaltic and sandstone soils were moderately contaminated. Cadmium (Cd) showed very high contamination in both soils. The contamination factor for aluminium varies, soil developed on basalt within Atimaka (0.185), FGC Ikom (0.708) and Quarry site (0.777) showed low contamination with Al, whereas soil located within Nde (0.434) developed on sandstone showed low contamination with Al. The Edor area showed moderate contamination, Alok and Afi showed considerable contamination whereas, Nkarasi showed very high contamination with Al. The result obtained is evidence that soil developed on sandstone tends to be more contaminated than basaltic soil.

**Degree of contamination (Cd):** The result for the degree of contamination as presented in Table 5 indicated that soils developed on sandstone showed a very high degree of contamination, whereas the degree of contamination in soil developed on basalt ranged from a considerable degree of contamination ($14\leq Cd<28$) to a very high degree of contamination ($Cd \geq 28$). Only soil at Atimaka (14.183) and FGC Ikom (19.201) showed a considerable degree of contamination in basaltic soils, others showed a very high degree of contamination.

**Pollution load index (PLI):** The results of the Pollution Load Index (PLI) calculated for both soils are presented in Table 5 and the results showed that the values recorded for all the soils in both parent materials were below 1, indicating an unpolluted condition for the assessed heavy metals. The results of the present evaluation revealed that the soil in Ikom is unpolluted by heavy metals even though there are high contamination factor and a high degree of contamination.

**Geo-accumulation index ($I_{geo}$):** The results of the Geo-accumulation index (Igeo) obtained for this study showed that Pb ranged from practically uncontaminated conditions as observed in Atimaka, Four Corners and Afi to moderately contamination in other locations (Table 6). Soils developed on basalt were heavily contaminated to extremely contaminated with Cd, whereas soil developed on sandstone were all extremely contaminated with Cd. The result also showed that the Igeo values for As and Cr fell in class '0', indicating practically uncontaminated conditions. Al ranged from uncontaminated to heavily contaminated (Nkarasi).

**Enrichment Factor (EF):** The results of the enrichment factor is presented in Table 6. Soil developed on basalt at Four Corners (0.557) and Ikom River (0.431) indicates no enrichment with Pb while those at FGC Ikom and Quarry site were minor enriched, Atimaka (7.869) areas were moderately severe enriched with Pb. However, in sandstone soil, except at Nde, all other sites showed no enrichment, indicating that pollution was mainly from natural sources. Soil developed on basalt except those at Ikom River which was very severely enriched, all other sites showed extremely severe enrichment with Cd. Similarly, the soil at Nkarasi (0.825) developed on sandstone indicated no enrichment, Afi (19.597) severe enrichment, Alok (41.699) very severe enrichment, Edor (78.359) and Nde (63.083) extremely severe enrichment with Cd.

Consequently, soil developed on both parent materials showed no enrichment with Cr. Conversely, soil developed on basalt at Atimaka (5.911) showed moderately severe enrichment, FGC Ikom (1.127) and Quarry site (1.399) were minor enrichment, Four Corners (0.459) and Ikom River (0.402) showed no enrichment with As, whereas in soil developed on sandstone except those at Nde showed no enrichment with As.

**Ecological risk of the study area:** The ecological risk index is employed to evaluate the adverse effects of the contaminants

Table 6: Geo-accumulation index and enrichment factor in soil developed on sandstone and basaltic soils in Ikom

| Sample code | Sample site | $I_{geo}$-Pb | $I_{geo}$-Cd | $I_{geo}$-Cr | $I_{geo}$-As | $I_{geo}$-Al | EF-Pb | EF-Cd | EF-Cr | EF-As |
|---|---|---|---|---|---|---|---|---|---|---|
| $B_1$ | Atimaka | -0.047 | 3.063 | -7.261 | -8.929 | -3.023 | 7.869 | 886.944 | 0.615 | 5.911 |
| $B_2$ | FGC Ikom | 0.474 | 3.451 | -7.913 | -8.929 | -1.083 | 2.943 | 340.867 | 0.328 | 1.127 |
| $B_3$ | Four Corners | -0.523 | 5.922 | -7.550 | -8.607 | 0.321 | 0.557 | 104.325 | 0.060 | 0.459 |
| $B_4$ | Quarry site | 0.024 | 4.726 | -7.550 | -8.824 | -0.948 | 1.961 | 336.084 | 0.128 | 1.399 |
| $B_5$ | Ikom River | 0.025 | 4.735 | -7.550 | -8.824 | 1.240 | 0.431 | 32.047 | 0.036 | 0.402 |
| Mean | | -0.009 | 4.379 | -7.565 | -8.823 | -0.698 | 2.752 | 340.053 | 0.234 | 1.859 |
| $S_1$ | Alok | 0.692 | 7.248 | -7.020 | -8.929 | 1.660 | 0.511 | 41.699 | 0.042 | 0.137 |
| $S_2$ | Afi | -0.289 | 6.690 | -7.166 | -8.607 | 1.448 | 0.300 | 19.597 | 0.025 | 0.687 |
| $S_3$ | Nkarasi | 0.927 | 6.276 | -7.720 | -8.343 | 2.253 | 0.399 | 0.8251 | 0.010 | 0.142 |
| $S_4$ | Edor | 0.531 | 6.793 | -7.277 | -8.607 | 0.835 | 0.810 | 78.359 | 0.044 | 0.423 |
| $S_5$ | Nde | 0.529 | 6.793 | -7.311 | -8.607 | -1.788 | 4.984 | 63.083 | 0.530 | 3.321 |
| Mean | | 0.344 | 6.131 | -7.373 | -8.678 | 0.707 | 1.455 | 82.238 | 0.132 | 0.996 |

$_{geo}$: Geo-accumulation Index, EF: Enrichment factor, Pb: Lead, Cd: Cadmium, As: Arsenic, Al: Aluminium

Table 7: Ecological risk factor of heavy metal in soil developed on sandstone and basaltic soils in Ikom

| Sample code | Parent material | Sites | Er-Pb | Er-Cd | Er-Cr | Er-As | RI |
|---|---|---|---|---|---|---|---|
| $B_1$ | Basaltic | Atimaka | 7.26 | 376 | 0.019 | 0.031 | 383.31 |
| $B_2$ | Basaltic | FGC Ikom | 10.42 | 492 | 0.012 | 0.031 | 502.46 |
| $B_3$ | Basaltic | Four Corners | 5.22 | 2728 | 0.016 | 0.038 | 2733.27 |
| $B_4$ | Basaltic | Quarry_site | 7.625 | 1191 | 0.016 | 0.033 | 1198.67 |
| $B_5$ | Basaltic | Ikom River | 7.6325 | 1198 | 0.016 | 0.033 | 1205.68 |
| Mean | | | 7.632 | 1197 | 0.016 | 0.0033 | 1204.68 |
| $S_1$ | Sandstone | Alok | 12.12 | 6842 | 0.023 | 0.031 | 6854.17 |
| $S_2$ | Sandstone | Afi | 6.14 | 4648 | 0.021 | 0.038 | 4654.19 |
| $S_3$ | Sandstone | Nkarasi | 14.26 | 3488 | 0.014 | 0.046 | 3502.32 |
| $S_4$ | Sandstone | Edor | 10.84 | 4992 | 0.019 | 0.0384 | 5002.89 |
| $S_5$ | Sandstone | Nde | 10.825 | 4991 | 0.019 | 0.038 | 5001.88 |
| Mean | | | 9.921 | 3908 | 0.018 | 0.037 | 3917.98 |

Er: Ecological risk factor, RI: Ecological risk of environment, Pb: Lead, Cd: Cadmium, As: Arsenic, Al: Aluminium, Ecological risk factor reflects possible risks caused by heavy metals to the soil and biological communities

on the environment and reflects the sensitivity of various biological communities and possible risks caused by heavy metals. In this study, the ecological risk factor of individual heavy metals (Pb, Cd, Cr and As) considered showed only Cd to have very high potential ecological risk in the studied soils and soil developed on sandstone tend to show higher risk values than basaltic soil. The calculated potential ecological risk (Table 7) indicates that all the studied sites have a high ecological risk concerning Cd. Similarly, the integrated ecological risk index of the environment classified the soil of the area as having a very high-risk potential ecological risk. This risk comes mainly from soil polluted with Cd.

**Spatial assessment of pollution loads and ecological risk:** In the present study, the spatial variability results for the studied heavy metals in soil developed on basalt and sandstone parent materials are presented in Fig. 2. The inverse distance weighting interpolation method was only employed on pollution indices that showed contamination and ecological risks. Spatial variability results of Pb for contamination factor (Cf) (Fig. 2a) showed that Pb was accumulated more in the Northern regions (i.e., Edor, Alok and Nkarasi) compared to Southern and Eastern regions of the studied area. Hence, similar management practices to ameliorate Pb can be imposed on areas with similarities. Spatial variability results of Cd for Cf (Fig. 2b) showed that it accumulated more in Northern and Central regions (i.e., soil developed on sandstone) as compared to Southern regions of the studied area. Spatial variability results of Al for Cf (Fig. 2c) showed that it accumulated more in Northern regions as compared to Southern, Western and Eastern regions of the studied area. Spatial variability results of degree of contamination ($C_d$) (Fig. 2d) showed that it accumulated more in Northern and Central regions (i.e., soil developed on sandstone) as compared to Southern and Eastern regions of the studied area.

Further results showed that spatial variability of the geo-accumulation index (Igeo) for Cd (Fig. 2e) showed that it accumulated more in Northern and Central regions (i.e., Alok, Edok, Afi, Nkarasi and Nde), while those observed in the Southern part from the vicinity of Ikom river, Quarry site and Four corners had moderate values, Atimaka and FGC from the West and Eastern part had low values. Similarly, spatial variability results of the geo-accumulation index (Igeo) for Al (Fig. 2f) showed that higher values are concentrated in the Northern and Southern part within the vicinity of Alok, Nkasori, Edok, Afi, Ikom river and Four corners).

The spatial variability map of Pb for Enrichment Factor (EF) (Fig. 2g) showed that Pb was moderately severe enriched in the West and Central regions (Atimaka and Nde) and no enrichment to minor enrichment was observed in the Northern and Southern regions. Spatial analysis map of enrichment factor for Cd (Fig. 2h) showed that soils in the west and east direction were within the same range of enrichment, while those in the north and part of the south had the same range of enrichment. Spatial analysis map of enrichment factor for As (Fig. 2i) showed that soils in the west direction were minor to moderately enriched, while those in the northward and South-East direction had no enrichment to minor enrichment. Spatial variability results of ecological risk of the study area for Cd (Fig. 2j) and potential ecological risk of the environment (Fig. 2 k) showed that the soil of the area had considerably to very high ecological risk and soil in the northward direction have the same range of ecological risk. Similarly, soils in the South-East direction were also within the same range of ecological risk.


Fig. 2(a-l): Spatial distribution of contamination factor a (Pb), b (Cd), c (Al), d (degree of contamination), e (geo-accumulation index Cd), f (geo-accumulation index Al), g (enrichment factor Pb), h (enrichment factor Cd), i (enrichment factor As), j (potential ecological risk Cd) and K (integrated ecological risk)

## DISCUSSION

The observed texture of soil developed on basaltic and sandstone parent materials was clay loam and sandy loam, respectively. The high clay content in basaltic soil than sandstone soil was in line with the studies of Donatus *et al.*[19] who reported that basalt-derived soils have a higher content of clay than sandstone soil. This result implies that basaltic soil can hold an appreciable quantity of exchangeable cations for plant growth compared to sandstone soil. The soil pH recorded for basaltic soil was within the tolerant range of 5.5-6.5 for the growth and performance of arable crops[29]. The pH values obtained in this study were higher than those reported for similar sandstone and basaltic soil in Southeastern Nigeria[29] but comparable to those reported by Abam and Orji[16] in Cross River State. The low values of available phosphorus may be a result of fixation in the acidic soil medium[30]. The low level of potassium contents could be attributed to several factors including parent materials, fixation and leaching losses[31]. The nutrient values obtained in this study showed that the soils will require the addition of NPK fertilizer and organic matter incorporation into the soil as an option to increase nutrient contents.

The concentration of lead (Pb) obtained in this study were all above baseline Pb value (20 mg $kg^{-1}$) for surface soil on the global scale estimate[32]. The abundance of Pb in the continental crust is around 14.8 mg $kg^{-1}$ and among the common sedimentary rocks, shales have a higher Pb abundance (22 mg $kg^{-1}$) than sandstones (10 mg $kg^{-1}$)[33]. Judging from the world average shale value of 20 mg $kg^{-1}$ for Pb[32], it can be inferred that the soil of the area is polluted with Pb. Basaltic soils were reported by Althaus *et al.*[3] to have a Cd value (0.59 mg $kg^{-1}$) higher than sandstone soils (0.39 mg $kg^{-1}$) in the Rio Grande do Sul (Brazil). However, this report is contrary to our present investigation where Cd concentration was higher in sandstone soil compared with basaltic soil. A report by Adamu and Nganje[34] showed sandstone soil to have moderate levels of cadmium 2.0 mg $kg^{-1}$ in middle Benue trough, Nigeria. Nikova *et al.*[2] reported that Cd levels in igneous and metamorphic rocks widely vary but rarely exceed 0.5 mg $kg^{-1}$, in sedimentary rocks, carbonate and in sandstone it occurs in the lowest values (0.035 mg $kg^{-1}$) but in the present study, the values observed in soil developed on both basalt and sandstone far exceeded this stipulated values and the lithogenic threshold of 0.3 mg $kg^{-1}$ [32], average world soil 0.5[35] and 0.01-0.7 mg $kg^{-1}$ value established for mineral soil environment[36]. The result of the present study showed that all the soils in the area were contaminated with Cd and also suggests that Cd did not only originate from natural sources, but anthropogenic sources also have a great contribution to the enrichment of these metals. The global mean of Cr for shale has been estimated to be 90 mg $kg^{-1}$ [32] and any higher values for the studied soils may reflect anthropogenic influences. The average values obtained from basaltic (0.72 mg $kg^{-1}$) and sandstone (0.87 mg $kg^{-1}$) soils in the present investigation were far lower than the average value of shale and those reported in Fuxin City, China (51.08 mg $kg^{-1}$)[37] and Ijebu-Ode, Nigeria (8.02 mg $kg^{-1}$)[38]. According to Kabata-Pendias and Pendias[1], "the concentration of chromium (Cr) in soils may vary considerably according to the natural composition of rocks and sediments that compose them, being higher in mafic (170-200 mg $kg^{-1}$) and ultramafic (1600-3400 mg $kg^{-1}$) and lower in igneous and sedimentary rocks (5-120 mg $kg^{-1}$)". A certain study showed basaltic soils in the Rio Grande do Sul (Brazil) to have 94 mg $kg^{-1}$ of Cr whereas, soils developed on sandstone had 28 mg $kg^{-1}$ [34]. In Nigeria, soils of sandstone origin in Middle Benue through, had a value of 0.40 mg $kg^{-1}$ of Cr[34]. Proshad *et al.*[39] reported 6.73 mg $kg^{-1}$ of Cr in the Tangail district industrial area, Bangladesh.

All the concentrations of As found in this study were far below the lithogenic threshold of 13 mg $kg^{-1}$ [32], world soil As content (5 mg $kg^{-1}$)[35] and 1-50 mg $kg^{-1}$ value established for mineral soil environment[36]. The result showed that the soil of the study area is unpolluted with As and suggest that it only originated from natural sources.

Except in Atimaka and Nde, the Al concentrations obtained for the study were far above the background level of 47,200 mg $kg^{-1}$ [32]. Comparing the average concentrations of Al in soil developed on both parent materials, it was observed that the average Al concentration was higher than those obtained for other metals (As, Cd, Cr and Pb), indicating that this metal is naturally high in the soil. According to Mandeng *et al.*[40], aluminium is the third most abundant element in the earth's crust, it is naturally present in our environment (sediment, soil and water). The range of aluminium in the present study is far higher than those reported by Silveira *et al.*[41] in sediments from Piabanha watershed in Brasil and Mandeng *et al*[40] in sediments from Abiete-Toko watershed in Southern Cameroon, but was at variant with the reported values of Aki and Isong[22] and Ephraim and Ayaji[5].

Following Hakanson[42] classification criteria for contamination factor, the results of this study showed that the studied soils were contaminated with Pb, Cd and Al while Cr and As showed no contamination (Table 5). The result obtained in this study was in line with the report of Mandeng *et al.*[40], who indicated sediments of Abiete-Toko watersheds, Cameroon to have been moderately contaminated with Pb. The contamination of agricultural soil with lead has been a major problem globally. The result obtained for this investigation corroborates with the reports of several scholars[39,43-45], who all recorded low Cf for Cr in Agricultural Soils in Katsina State (North-Western Nigeria), Mkpuma Ekwoku (South-eastern Nigeria), El Obour (Egypt) and Tarutia (Bangladesh), but was contrary to the studies of Omran[46] who had both moderate contamination and considerable contamination for Cr in soils of Bahr El Baqar, Egypt. The result obtained by Salman *et al.*[45] showed As to have very high contamination in the soil, which was contrary to the present study.

Cadmium (Cd) showed very high contamination in both basaltic and sandstone soil in the present investigation. Chukwu and Oji[44] and Proshad *et al.*[39] also had very high contamination for Cd in their studies. Soils contaminated with Cd can cause serious ecological risks and negatively impact human health as Cd being a highly toxic heavy metal can enter the food chain through soil-plant interaction[43]. Cadmium has no essential biological function. It is toxic to humans, causing lung damage and may cause cancer from long-term exposure[47], thus, caution should be taken in utilizing these soils for crop cultivation.

In the result obtained from this study, it is evident that soil developed on sandstone tends to be more contaminated than basaltic soil. The value obtained for Al is in strong agreement with the result of Aki and Isong[22] in which the soil along coastal marine sediment was contaminated with Al, but contrary to the report of Mandeng *et al.*[40] in sediments of Abiete-Toko watersheds, Cameroon whose result indicated no contamination for Al.

The result for the degree of contamination as presented in Table 4 indicated that soils developed on sandstone showed a very high degree of contamination compared with basaltic soil. This finding was consistent with the study of Salman *et al.*[45] and Omran[46], who also obtained values that corresponded to a very high degree of contamination. Abou El-Anwar[48] had a moderate degree of contamination for all studied samples in cultivated soil in Egypt. Further, $C_d$ values of heavy metals for agricultural soils in a tropical Sudan savannah area, Katsina State[45] were lower than those reported for this study.

The results of the Pollution Load Index (PLI) calculated following the method of Tomlinson *et al.*[49] indicated an unpolluted condition for the assessed heavy metals. The result of the present study is comparable with those of Addis and Abebaw[50], who reported that the soil cultivated with garlic in East Gojjam Zone, Amhara Region, Ethiopia is unpolluted by heavy metals and but differs from those of Barakat *et al.*[51] in Day River, Morocco whose values lies between 1.57-2.20 and Salman *et al.*[45], who had 1.25-2.40, indicating that the concentration levels of the studied metals in most of the stations exceeded the background values. Rabee *et al.*[52] in Tigris River Sediment in Baghdad Region also obtained a very low pollution load index ranging between 0.301-0.970. However, the low PLI obtained for the present study are not static, there is a tendency for an increase as a result of increased human input and activities and hence there is a need for regular check.

The result obtained for geo-accumulation index ($I_{geo}$) showed that Pb as and Cr values all fell in class '0', indicating practically uncontaminated conditions. The values of Igeo of the present study for Cr were also comparable with those reported in previous studies[45,46] but contrary to the report of Chukwu and Oji[44] and Salman *et al.*[45], whose Igeo for As higher than those reported in this study. However, soil developed on both parent materials were contaminated with Cd and Al. The result of Igeo reported for Cd was consistent with the reported values of 3.97-4.61 by Salman *et al.*[45] and Omran[46] also reported high values corresponding to class 6 (extremely contaminated) in his study. The result obtained is also in line with those reported by Ephraim and Ajayi[5].

The enrichment factor is widely used to estimate the actual degree of contribution from anthropogenic sources of soil[53]. The soil under investigation was enriched with Pb, Cd and As. The result of this study corroborates with the findings of Mandeng *et al.*[40] and Salman *et al.*[45], where the EF for Pb corresponds to minor enrichment to moderately severe enrichment following the rating of Giri *et al.*[54]. Previous studies Salman *et al.*[45] and Proshad[39] also showed soil to be enriched with As. However, the values obtained in this study were lower than these reports.

The study showed only Cd to have very high potential ecological risk in the studied soils and soil developed on sandstone tend to show higher risk values than basaltic soil. Several reports showed that cadmium injures the kidney and causes symptoms of chronic toxicity including impaired kidney function, poor productive capacity, hypertension and tumour[39,47]. Similarly, the integrated ecological risk index of the environment classified the soil of the area as having a very high-risk potential ecological risk. This risk comes mainly from soil pollution with Cd. Studies by Abou El-Anwar[48] also indicated Cd to be the primary contributor to integrated ecological risk. This metal can harm both plants and human health, hence, caution should be given to the consumption of food coming from these areas. Our present investigation is in line with the several studies[39,45,46] on agricultural soils that also observed a very high ecological risk of soil caused by Cd.

As reported by Adimalla[55], "spatial distribution maps play a vital role in identifying the safe and unsafe zones and for providing baseline information necessary to prevent and control further contamination of soils". This study employed inverse distance weighting to assess pollution loads and the ecological risk of the area. The studied metals exhibited high spatial variability in the study area as shown in Fig. 2. In the result obtained from this study, it is evident that soil developed on sandstone tends to be more contaminated with heavy metals than basaltic soil. The mapping showed that the soil developed on sandstone were at higher risk of contamination than basaltic soils. Ataysese *et al.*[56], Adimalla[55] and Muller[57] pointed out that increasing levels of soil contamination with heavy metals can result in its transformation and transportation into plant tissues and from plants passes into animals and humans.

## CONCLUSION

The result of this study indicated that basaltic soil has greater potential for crop cultivation as shown by its fertility indices compared with its counterpart sandstone soil but was constrained alongside sandstone soil by Pb, Cd and Al contamination. Soils developed on sandstone showed a very high degree of contamination, whereas the degree of contamination in soil developed on basalt ranged from a considerable degree of contamination to a very high degree of contamination. The pollution load index of the area showed an unpolluted condition for the assessed heavy metals. Soil developed on both parent materials except those at Atimaka and FGC Ikom which had a considerable degree of contamination, other sites were heavily contaminated with Cd. Similarly, Cd showed heavily to extremely contamination by Geo-accumulation index (Igeo) at all locations. The soils were also moderately to extremely severe enriched with Pb at Atimaka and Nde and moderately to extremely severe enriched with Cd at all locations. Cd had a very high potential ecological risk in soil developed on both parent materials. Cd was also the primary contributor to integrated ecological risk.

## SIGNIFICANCE STATEMENT

This research study has indicated that basaltic soil has greater potential for crop cultivation as shown by its high fertility indicators including pH, exchangeable Mg and base saturation when compared with its counterpart sandstone soil. However, basaltic soil including sandstone soil in the study area is constrained by Pb, Cd and Al contamination. Soils developed on both parent materials showed a very high degree of contamination. The pollution load index of the area showed an unpolluted condition. Soil developed on both parent materials except those at Atimaka and Federal Girls College, Ikom which had a considerable degree of contamination, other sites is heavily contaminated with Cd. The result of this study will be beneficial to environmental scientists, agronomists and growers in knowing cropping areas laden with heavy metal. It will also serve as a pointer to the government in providing remediation options to provide good conditions for crop cultivation.

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